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Addendum

TENTH INTERNATIONAL SYMPOSIUM ON ALCOHOL FUELS

THE ROAD TO COMMERCIALIZATION

November 7-10, 1993

THE BROADMOOR HOTEL
COLORADO SPRINGS, COLORADO

NOTICE

ISAF X
Colorado Springs, Colorado
November 1993

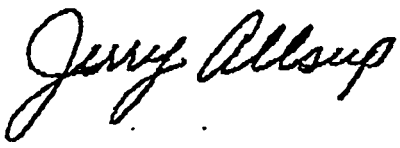
This is the second time the United States has hosted the International Symposium on Alcohol Fuels (ISAF). The first symposium held in the United States, which was the third in the series, was held at Asilomar, California. For those of us fortunate enough to attend, it appears in retrospect to have been a watershed event. At that symposium, researchers first considered the potential benefits of using alcohol fuels in compression ignition engines—a seemingly illogical combination. But a participant observed that such an alliance could be the only way for diesel engines to break the apparent technological barrier of the trade-off between particulate and NO_x emissions without using exhaust aftertreatment.

At the fifth symposium in New Zealand, the discussion of the lack of refueling infrastructure resulted in the idea that the problem could possibly be internalized to the developing microprocessor engine control technology. The disparate optical and/or dielectric properties of alcohols relative to gasoline could be used to feed the microprocessor controls.

In 1993, we have maturing technology that has been successfully built on both these ideas. Alcohol fuel-powered diesel engines are among the handful of compression ignition engines certified to meet the Environmental Protection Agency's NO_x and particulate standards for heavy duty truck applications without the use of particulate traps. Similarly, alcohol-fuel-capable automobiles that use an input from fuel quality sensors to determine alcohol concentration and maintain air/fuel stoichiometry are available from almost every automobile manufacturer. These accomplishments demonstrate the progress that has been made in the last decade and have led us to set the theme for ISAF X—"The Road to Commercialization."

These are only two examples of the significant contributions that have arisen out of each ISAF conference. The hallmark of this symposium series is that scientists, engineers, and practitioners gather to discuss the technology, to share their ideas, and to consider solutions to the challenges that lie ahead. Historically, the participants have been of the highest technical caliber and have unselfishly shared the results of their work. We hope that through our combined efforts, ISAF X will continue in this tradition.

Please join me in expressing your appreciation to the members of the Scientific Committee, the National Organizing Committee, and the International Organizing Committee. We hope that we have put together a stimulating program in an environment conducive to collaborating with your colleagues to move alcohol fuels forward to full commercialization.



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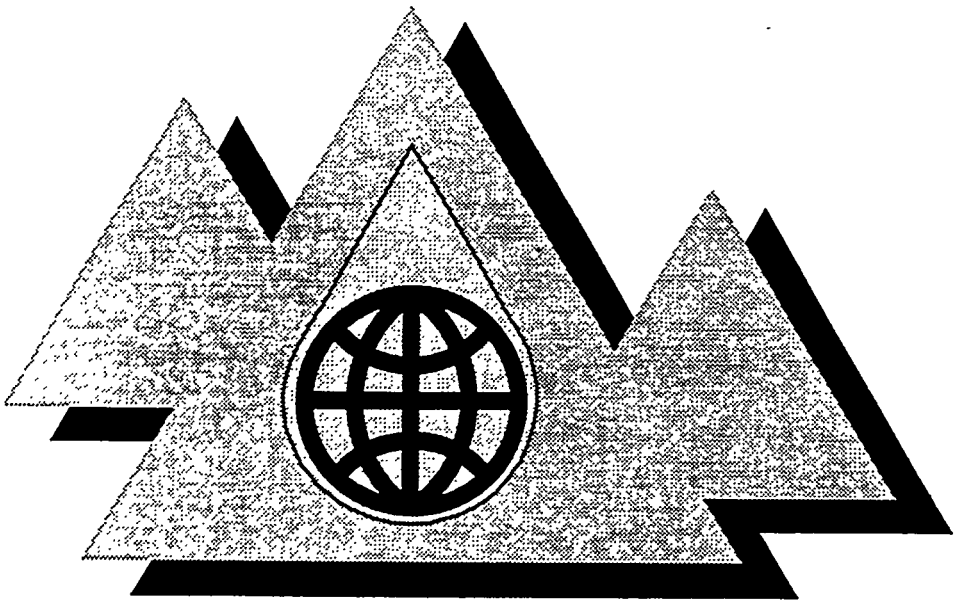

Light Duty Vehicle Technology and Trials

932773

Methanol Vehicle Emissions Round Robin Test Program

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ABSTRACT

A vehicle emissions round robin test program was conducted using a methanol-fueled vehicle operating on M85. Each of 16 participants conducted two to six Federal Test Procedure (FTP) emissions tests. All participants measured emission rates of hydrocarbon (HC), CO, NO_x, methanol, formaldehyde, and acetaldehyde. One participant, designated as a reference lab, conducted emissions testing at the beginning, the end, and two intermediate times during the round robin. Results of the reference lab demonstrated that no significant drift in emissions levels occurred during the 2-year program.

Relative lab-to-lab variability for FTP-composite emissions was lowest for NO_x, with a coefficient of variation (C.V.) of 12%. CO variability was 16%, HC variabilities (by GC and bench FID) were 17 and 35%, respectively. Methanol, formaldehyde, and acetaldehyde were found to have variabilities of 34, 17, and 63%, respectively. The large difference between formaldehyde and acetaldehyde variability is probably a consequence of their different concentrations--formaldehyde's emission rate was approximately 40 times that of acetaldehyde. This is consistent with an expected increase in variability at emission levels near detection limits. Emission rates of three HC species were also determined: methane, benzene, and toluene. They showed variabilities ranging from 20-30%, only slightly higher than for the criteria emissions.

INTRODUCTION

In 1990, the CAPI-8 Project Group of the Coordinating Research Council Air Pollution Research Advisory Committee (CRC-APRAC) organized a round robin test program to measure emissions from a methanol-fueled automobile. The purpose of the program was threefold:

1. Provide a "benchmark" for laboratories which are just beginning to measure emissions from methanol-fueled vehicles.

2. Establish interlaboratory variability of emissions measurements.

3. Improve the credibility of emissions results from all laboratories.

A single methanol-fueled vehicle was used in the test program. It was transported (not driven) from one laboratory to the next throughout the course of about 2 years. The 16 organizations listed in Table I participated in the test program. One of the 16 acted as a reference lab, and conducted emissions tests at four different times throughout the program. One other lab received and tested the vehicle twice. Since each receipt of the vehicle was considered a separate testing event, there were a total of 20 participants in the round robin program.

All the participants measured emission rates of HC, CO, NO_x, methanol, formaldehyde, and acetaldehyde. In addition, several labs measured individual HC species including methane, benzene, and toluene. These emissions components include the regulated emissions (HC, CO, NO_x), toxic compounds (formaldehyde, acetaldehyde, and benzene), and fuel-related emissions (methanol and toluene). When the round robin program was planned, some of these measurements were required for certification (HC, CO, NO_x, methanol, and formaldehyde) and some were under consideration for future requirements (i.e., acetaldehyde by California Air Resources Board).

Table I. Participants in Round Robin Program

Organization	Representative
1. Amoco	Les Asher
2. Automotive Testing Laboratories	Gary Smith
3. AutoResearch Laboratories	John Baudino
4. BP Oil	Wendy Clark
5. California Air Resources Board	Jim Shikiya
6. Chevron Research and Technology Company	S. Kent Hoekman
7. Chrysler-Chelsea	Richard Middleton
8. Chrysler-Highland Park	Arnold Weibel
9. EPA - Ann Arbor	John Shelton
10. EPA - Research Triangle Park	John Sigsby
11. Ford Motor Company	Ted Jensen
12. General Motors	Daniel Sougstad
13. Mobil Research & Development Company	Diane Sansone
14. National Institute for Petroleum and Energy Research	Bill Marshall
15. Shell Development Company	Tim Sprik
16. Southwest Research Institute	Lawrence Smith

In this study, results of the testing at each participant location are reported for the three phases (bags) of the FTP and the calculated composite average. The relative lab-to-lab variability was determined by comparing average results from each laboratory.

EXPERIMENTAL

VEHICLE - The vehicle used in the test program was a 1987 Ford Crown Victoria flexible fuel vehicle (FFV). A complete description of this vehicle is given in Table II. The vehicle was loaned to CRC-APRAC by Ford Motor Company. It had previously been used in the Auto/Oil Air Quality Improvement Research Program, where it was identified as Vehicle 06M.[1,2]

Table II. Description of Round Robin Test Vehicle

Vehicle Type:	Ford Crown Victoria FFV
Model Year:	1987
Catalyst Type:	Three-Way Catalyst and Oxidation Catalyst
Engine:	5.0 Liter V-8
Fuel System:	Sequential Fuel Injection
Odometer:	Approximately 30,000 Miles
Transmission:	Automatic
Inertia Weight:	4250 Lb
Road Load Horsepower:	13.2

This vehicle is not representative of marketable FFV technology. It was selected for use in the round robin program because of its availability, its relatively high mileage (approximately 30,000 miles), and its history of stable emissions levels.

FUEL - A single batch of M85 test fuel was blended and distributed by BP Oil Company. This fuel consisted of 85 vol % methanol and 15 vol % Indolene, and is different from the Auto/Oil Fuels Z and Z1. Measured properties of the fuel are summarized in Table III.

Table III. Round Robin Test Fuel

Fuel Composition: Methanol - 85 Vol %
Indolene - 15 Vol %

Fuel Properties:

Test	Result
RVP, psi	8.15
D 86 Distillation, °F	
IBP	108
T_{10}	141
T_{50}	146
T_{90}	147
EP	150
Carbon, Wt %	43.83
Hydrogen, Wt %	12.64
Oxygen, Wt %	44.18
Water, ppm	447
Heating Value, Btu/Lb	9840
Octane, (R+M)/2	95.5
Density, g/mL	0.7888

VEHICLE PRECONDITIONING - Vehicle preconditioning procedures were stipulated to provide an equivalent starting point for testing in each laboratory. This is particularly important in a test program such as this one where lengthy delays in testing can occur between one lab and the next.

All vehicle preconditioning was conducted in the laboratory. An important component of preconditioning involved purging of the canister. All participants were asked to follow the purging procedure summarized in Table IV.

Table IV. Procedure for Vehicle Canister Purge

Purge Gas:	Clean Air
Purge Rate:	48 Ft^3/Hour
Purge Time:	20 Minutes
Temperature:	70-78°F
Humidity:	50 ± 10 Grains Water/Lb Dry Air

Following the canister purge, the fuel tank was drained and refilled to 40% of full with the M85 test fuel. Two LA-4 test cycles were then done to complete the preconditioning.

Target emissions values were not given to the testing laboratories, but some acceptance criteria were provided. If the FTP results exceeded 6.5 g/mile for CO and 0.9 g/mile for methanol, the testing laboratory representative was asked to contact the program coordinator to receive instructions. In a few cases, initial testing at a laboratory required consultation with the program coordinator. In these instances, the problems were resolved and all labs were able to obtain acceptable results.

EMISSIONS TESTS - All emissions tests were conducted according to the Federal Test Procedure (FTP). Only exhaust emissions were measured; hence, the fuel tank heating portion of the FTP was omitted. Each participant conducted a minimum of two emissions tests; several conducted more than two. Along with the FTP-composite test results, individual bag results were reported for each phase of the FTP.

MEASUREMENT PROCEDURES - All participants were required to measure the three criteria pollutants (HC, CO, and NO_x), methanol, formaldehyde, and acetaldehyde. In addition, participants were encouraged to measure as many other species as possible. Standard FTP methodologies were specified for measurement of the criteria pollutants. All other species were to be measured using procedures of the participants' choice.

To aid in calibration of oxygenated hydrocarbons, a common set of standards was prepared and distributed by the U.S. Environmental Protection Agency (EPA). These materials included a sample of neat methanol and an acetonitrile solution which contained 2,4-dinitrophenylhydrazine (DNPH) derivatives of aldehydes and ketones. In addition, each participant was provided (and encouraged to use) a set of DNPH-coated silica cartridges for sampling aldehyde emissions. These cartridges were obtained from a preproduction batch that was manufactured during the evaluation phase of the product. The DNPH cartridges, configured in the Sep-Pak Plus® style, contain 0.35 g chromatographic-grade silica (55-105 μm) coated with 1.0 mg purified 2,4-dinitrophenylhydrazine. These cartridges are available from Millipore Corporation, Waters Chromatography Division, Milford, Massachusetts (Part No. 37500).

Most participants used impingers for collection of aldehyde emissions--only 7 of the 20 participants used cartridges. All participants used high performance liquid chromatography (HPLC) to quantify the aldehyde emissions. Although there were slight differences among the laboratories, most employed HPLC procedures similar to those used in the Auto/Oil Program.[3,4]

Methanol emissions were collected in water-filled impingers and analyzed by gas chromatography (GC). Auto/Oil procedures were employed by most participants.[3,4] Similarly, Auto/Oil GC procedures were used by most participants to measure emission rates of individual HC compounds.[4,5]

Total HC emissions were determined in several ways. The first involved an unadjusted value from the standard bench-FID analyzer measurement. That is, the measurement was conducted as if a gasoline vehicle were being tested. This measurement assumes an exhaust gas composition of $C_{1.00}H_{1.85}$ and a density of 16.33 g/ft^3. For a methanol vehicle, these assumptions are obviously incorrect. Nevertheless, this methodology provides a convenient basis for comparison among the participants.

A second HC value, called adjusted-FID HC, is more meaningful for methanol-fueled vehicles. To calculate adjusted-FID HC, the bench-FID measurement was used, but the portion of the detector response due to the presence of methanol was subtracted. This adjustment requires two additional pieces of information: (1) an independent measure of the methanol emission rate, and (2) the FID response factor for methanol. The equation for calculating adjusted-FID HC is given below:

$$\text{Adjusted-FID } HC_{g/Mile} = \frac{[HC_{ppm} - (DF \times FID\ BKGRD\ HC_{ppm}) - (MeOH_{ppm} \times MeOH\ RF)] \times 16.33 \times CVS\ Vol_{ft^3}}{Miles\ Traveled \times 10^6}$$

where:

DF = Dilution Factor. In EPA's Federal Register description of emission rate calculations, this parameter is referred to as "1/(1-DF)".

RF = FID response factor for methanol (on a per-carbon basis). Each lab determined its own value of RF--most were in the range of 0.7-0.8 (relative to a propane value of 1.0).

A third measurement of HC was based upon GC analyses. Total HC was determined by summing all individual HC species measured by GC--including methane, but excluding methanol. In theory, total HC

results determined by GC should be in close agreement with the adjusted-FID HC results. To compare these two results, a variable called "GC versus FID" was created. This variable is defined below:

$$\text{GC Versus FID} = \frac{\text{(GC Result - Adjusted-FID Result)}}{\text{(Adjusted-FID Result)}}$$

By this definition, the adjusted-FID result is used as the reference point, and the GC result is expressed as a difference from the reference. (This approach was selected due to the importance of the FID-determined value in regulatory applications.) If the two results are equivalent, the variable GC versus FID will equal zero. Positive values for this variable indicate the GC result was higher than the adjusted-FID result; negative values indicate the GC result was lower.

TESTING SCHEDULE

The testing schedule for the Round Robin Program is summarized in Table V. The first emissions tests were conducted by the Reference Lab in January 1991; the last ones were conducted in October 1992. In all, the Reference Lab conducted emissions testing at four separate occasions. This lab is identified in Table V as Lab No. 1, 6, 12, and 20.

In addition to the testing dates, Table V shows the number of FTP tests conducted at each lab, indicates the measurement technique for methane and the sampling technique for aldehydes, and identifies which labs conducted GC speciation.

DATA ANALYSIS

All participants were asked to use a standardized form in reporting the results from each phase of the FTP test (Bags 1, 2, and 3), as well as the FTP-composite values. All results were compiled into a single data base. Each participant was then sent a copy of his own results, and was asked to review them for accuracy. The participants also received a set of summary statistics from the total program results. Comparison of individual lab results to the average of all labs allowed each participant to validate his own data, independent of the other participants' data.

A number of obvious individual mistakes were corrected by this process (missing values, typographical errors, etc.). In addition, two entire sets of FTP results were eliminated: one of the five FTP tests by Lab No. 4, and one of the six tests by Lab No. 16.

As shown in Table V, not all participants conducted the same number of FTP tests. To provide equal weighting to the results from each participant, all data analysis was performed using the average results from each lab. Also, since only a single vehicle was used, data analysis was done using normal emission rate units of g/mi (or mg/mi) rather than logarithms of the emission rates. Outlier results were identified using Grubbs' tests. Data from each FTP bag and from the FTP-composite values were assessed separately. (An outlier for a single bag result does not necessarily cause an outlier for the FTP-composite value.) Outlier results are included in the data tables shown in this report, but were excluded for purposes of statistical analysis.

Relative lab-to-lab variability--expressed as the coefficient of variation (C.V.)--was determined by comparing average results from each laboratory. This overall variability arises from several sources, including emissions testing procedures, analytical methodologies, and the vehicle itself.

Table V. Round Robin Test Schedule

Lab No.	Testing Date	No. Tests Conducted	Methane Technique[b]	Aldehyde Technique[c]	GC Speciation
1[a]	Jan-Feb 1991	6	B	I, C	Yes
2	Mar 1991	2	B	C	No
3	Apr 1991	2	B, GC	I	Yes
4	May 1991	5	GC	C	Yes
5	Jun 1991	3	GC	I	Yes
6[a]	Aug 1991	2	B	I	Yes
7	Aug 1991	3	B	I	Yes
8	Sep 1991	3	B	I	Yes
9	Oct 1991	3	B, GC	I	Yes
10	Oct 1991	4	GC	I, C	Yes
11	Nov 1991	3	B	C	No
12[a]	Nov 1991	2	B	I	Yes
13	Dec 1991	2	GC	C	Yes
14	Feb 1992	2	GC	I	Yes
15	Apr 1992	2	GC	I	Yes
16	May 1992	6	B	I	Yes
17	May 1992	5	GC	I, C	Yes
18	Jul 1992	2	GC	I	Yes
19	Jul 1992	3	B	I	No
20[a]	Oct 1992	2	B	I	Yes

[a]Reference Lab.
[b]Methane measured by bench analyzer (B) or by GC (GC).
[c]Aldehydes collected by impinger (I) or cartridges (C).

RESULTS AND DISCUSSION

FTP-composite results from each round robin participant are summarized in Table VI; results for each phase of the FTP test are included in Appendices I-III. In these data tables, the average results from each lab are listed, along with the mean, standard deviation, and coefficient of variation (C.V.) of these average results. Outlier points, identified by parentheses, are shown in the data tables, but were not included when generating the statistical summaries.

The FTP-composite results are further illustrated in Figures 1-15. These figures show results of individual FTP tests, as well as the average results from each lab. The zig-zag lines which connect the average results have no physical meaning, but are helpful in visually identifying lab-to-lab differences.

Results from the reference lab are highlighted (as filled circles) in these figures and show that no large shifts in emission levels were apparent during the 2-year duration of the round robin program. The horizontal lines in each figure represent the program average from all labs (solid line) with ±1 standard deviation (dashed lines). The shaded bars represent the average of the Reference Lab results ±1 standard deviation. Each emission category is briefly discussed below.

1. Fuel Economy

While not a direct emissions parameter, fuel economy is calculated from emissions measurements. Furthermore, fuel economy can serve as a useful diagnostic when comparing other results among labs. [In general, fuel consumption (gal./mile) is a measured quantity and therefore an intrinsic variable, while the inverse, fuel economy (mile/gal.), is not. Since fuel economy is the more commonly used form of this variable, it will also be used here.]

Accurate determination of fuel economy from methanol-fueled vehicles is not trivial. Several different calculational approaches have been used in the past. In this round robin program, a relatively simple carbon balance calculation was used. Although not consistent with the most recent EPA guidelines,[6] the round robin calculation (shown below) is simple, and provides a consistent basis for comparison among all participants. This calculation of volumetric fuel economy is very similar to that recently used in the Auto/Oil Air Quality Improvement Research Program.[7]

$$\text{Fuel Economy}_{(mpg)} = \frac{\text{FFC} \times \text{Fuel Density} \times 3785.4\ \text{mL/Gal.}}{(\text{HCFC} \times \text{HC}) + (0.429 \times \text{CO}) + (0.273 \times \text{CO}_2)}$$

where:

FFC = Fuel fraction carbon (0.4383 for this test fuel).

Fuel Density = 0.7888 g/mL

HCFC = HC exhaust fraction carbon (by definition, this is equivalent to FFC).

HC, CO, and CO_2 are all emission rates (in g/mile). HC refers to the unadjusted-FID measurement.

As shown in Table VI, the variability in fuel economy was lower than for any other emissions category (C.V. of 6.8%). This is expected, since fuel economy is primarily a function of CO_2 levels, which are high, relatively constant, and easy to measure. Nevertheless, Figure 1 shows that some significant differences were measured among the participants. For instance, all four determinations by Lab No. 10 are clustered around 9.5 mpg, while the five determinations by Lab No. 17 are clustered around 10.6 mpg. Differences of this magnitude suggest that some systematic measurement biases may exist among the labs.

A possible source of fuel economy variability is driver inexperience with the test vehicle. Other important factors may include dynamometer type, dynamometer calibration, and soak conditions. Difficulties in cold starting can result in reduced fuel economy and increased emission levels. (Cold start instructions were placed within the test vehicle, and were available to the drivers at all testing locations.) As shown in Figure 1, most of the non-reference labs reported lower fuel economy than the Reference Lab. Also, many (but not all) of these non-reference labs reported higher than average methanol emissions (see Figure 8) which is indicative of cold start problems. The generally higher fuel economy (and lower variability) measured by the Reference Lab may be due to this lab's greater experience with the test vehicle.

2. Unadjusted-FID HC

Figure 2 shows that the unadjusted-FID HC results from all labs were considerably less constant than results from the Reference Lab (C.V. of 27% versus 13%). Lab No. 2 reported the extreme low result, while Labs 15 and 18 reported the highest results. Only the result from Lab No. 18 was identified as an outlier.

The high result from Lab No. 18 may be attributable to vehicle malfunctioning problems. When the test vehicle reached Lab No. 19, a burned spark plug wire fault was discovered and the wire was replaced. Also, an EGR fault was found and corrected. If these problems also existed during testing at Lab No. 18, high emission rates would be expected in several categories. As shown in Table VI, this situation was observed, with

Table VI. Average FTP-Composite Emissions Results From Methanol Vehicle Round Robin Test Program

• Outliers are shown in parentheses.

Lab No.	Fuel Econ., mpg	Unadjusted FID-HC, g/Mile	Adjusted FID-HC, g/Mile	GC-HC, g/Mile	Comparison of HC, GC Vs. FID	CO, g/Mile	NO_x, g/Mile	Methanol, g/Mile	Formald. Impinger, mg/Mile	Formal. Cartridge, mg/Mile	Acetald. Impinger, mg/Mile	Acetald. Cartridge, mg/Mile	Methane, mg/Mile	Benzene, mg/Mile	Toluene, mg/Mile
1	10.39	0.436	0.210	0.207	-0.012	5.614	0.481	0.584	42.7	40.0	0.77	1.05	64.5	6.97	27.0
2	10.62	0.279	0.049			5.185	0.422	0.715		45.0		1.00	54.0		
3		0.379	0.195	0.211	0.097	4.817	0.543	0.540	54.0		1.00		91.0		
4	10.05	0.463	0.278	0.294	0.052	6.650	0.510	0.568		50.5		1.05	92.0	6.75	51.5
5	9.95	0.625	0.330	0.233	-0.247	6.550	0.417	0.803	37.9		1.13		82.7	8.67	34.2
6	10.19	0.534	0.251	0.237	-0.053	6.527	0.393	0.762	43.5		0.60		67.5	8.40	35.0
7	10.27	0.345	0.110	0.285	1.656	6.263	0.407	0.771	42.9		(9.07)		62.0	7.20	33.4
8	10.46	0.389	0.253	0.310	0.271	4.637	0.449	0.476	34.2		2.02		68.9	6.60	23.0
9	9.15	0.620	0.151	0.232	0.518	5.627	0.449	1.412	57.1		3.20		89.7	9.53	24.5
10	9.55	0.412	0.314	0.329	0.050	5.251	0.465	0.441	44.5	25.5	0.83	0.11	96.3	(17.75)	22.0
11	8.70	0.458	0.275			5.080	0.420	0.562		55.7		2.17	66.0		
12	10.98	0.463	0.198	0.227	0.139	4.147	0.405	0.711	46.5		0.50		64.5	6.15	30.0
13	9.15	0.674	0.313	0.293	-0.062	7.037	0.398	1.161		20.5		0.45	89.0	10.15	38.9
14	9.45	0.560	0.110	0.286	1.961	5.978	0.467	1.226	30.1		1.50		62.9	8.00	32.9
15	9.81	0.850	0.197	0.321	0.683	6.428	0.420	0.715	43.0		0.65		97.5	7.90	36.5
16	9.72	0.590	0.191	0.337	1.807	6.681	0.351	0.920	57.8		1.17		112.8	10.23	44.6
17	10.62	0.546	0.282	0.287	0.022	4.832	0.330	0.806	50.6	50.1	1.35	2.13	101.1	6.28	23.4
18	8.80	(0.988)	(0.621)	0.350	-0.459	(10.209)	0.436	1.087	(76.3)		1.20		126.4	11.30	27.7
19	8.85	0.526	0.204			5.167	0.349	1.062	52.3		0.33		78.7		
20	9.82	0.390	0.188	0.219	0.177	4.176	0.394	0.587	44.5		0.80		69.0	6.00	14.5
Mean	9.82	0.502	0.216	0.274	0.388	5.613	0.425	0.795	45.4	41.0	1.14	1.14	81.8	8.01	31.2
Std Dev	0.67	0.135	0.076	0.047	0.727	0.894	0.053	0.269	7.9	13.3	0.72	0.78	19.2	1.67	9.2
CV, %	6.8	26.9	35.2	17.3	187	15.9	12.4	33.9	17.5	32.5	63.0	68.2	23.5	20.9	29.6

Lab No. 18 reporting high results in many categories--including HC, CO, formaldehyde, and methane.

3. Adjusted-FID HC

FID response is fairly constant (on a per-carbon basis) across a wide range of C_2 and larger HC species, but varies substantially for oxygenated species. When significant levels of oxygenates are present in exhaust mixtures--such as from methanol-fueled vehicles--it is necessary to correct the FID result.

The results in Table VI indicate that, on average, HC emission rates determined by the adjusted-FID method are only about one-half as great as those determined by the unadjusted-FID method. Comparison of Figures 2 and 3 shows many similarities. For instance, Lab No. 2 reported the lowest results in both cases, and Lab No. 18 the highest (perhaps due to vehicle malfunctioning as described above). However, some differences are also apparent. For example, Lab No. 9 reported higher than average unadjusted-FID HC, but lower than average adjusted-FID HC. This is because the methanol result from Lab No. 9 was much higher than average; thus, the calculation of adjusted-FID HC (see equation above) involved a large subtraction. In contrast, the opposite situation occurred with Lab No. 10, due to a smaller than average methanol subtraction.

4. GC-HC

GC offers a direct measurement of HC--no adjustment is necessary for methanol or other oxygenated species. Seventeen of the twenty testing locations reported GC-HC results. As shown in Table VI, the average of these results is 27% higher than the adjusted-FID HC result (25% higher if Lab No. 18 is excluded), while variability is much lower.

The results from Lab No. 18 deserve comment. Although this lab showed by far the highest results for both unadjusted-FID HC and adjusted-FID HC, its results for GC-measured HCs were not greatly different from the other labs. The explanation for this discrepancy is not known.

5. GC Versus FID

Comparison of GC-HC and adjusted-FID HC results from each test was done by calculating the variable called GC versus FID. Table VI lists the average of the GC versus FID results from each lab. (Note that these values are not the same as would be calculated using the mean GC-HC and the mean adjusted-FID HC results.) The overall average of GC versus FID from all labs is 0.39, indicating a 39% higher emission rate of HC measured by GC as compared to the adjusted-FID method.

Inspection of Figure 5 shows that most labs reported GC values within 50% of the adjusted-FID result. Although no average FTP-composite results were identified as Grubbs' Test outliers, it is clear that some individual test results from Labs 7, 14, and 16 were very high. It should be emphasized that large values for the variable GC versus FID (either positive or negative) merely indicate a significant discrepancy between the two measurement techniques, but do not identify the cause of the discrepancy.

In the case of Lab No. 7, the extremely high data points shown in Figure 5 correspond to the low values for adjusted-FID HC shown in Figure 3. Conversely, the extremely low values of GC versus FID from Labs 5 and 18 correspond to the very high values of adjusted-FID HC. At least in these cases, the large deviations from zero for the variable GC versus FID seem to be caused more by anomalous adjusted-FID results than by poor GC results. Reasons for the large deviations in results from Labs 14 and 16 are not as apparent.

6. CO

The variability in measured CO emission rates was quite low, with a C.V. of approximately 16% (excluding Lab No. 18). As shown in Figure 6, the FTP-composite results from Lab No. 18 are higher than from any other lab. The average CO value from Lab No. 18 was determined to be a statistical outlier--not only the FTP-composite result, but also the results from each FTP Bag (see Appendices I-III). This is the clearest indication that the vehicle may have been performing poorly, as discussed earlier, during testing at Lab No. 18.

7. NO_x

The NO_x results showed lower variability than any other criteria emission--C.V. of approximately 12%. No outlier points were identified for individual bag results or FTP-composite results.

8. Methanol

The FTP-composite methanol results shown in Figure 8 vary in magnitude by a factor of 3, and have an overall C.V. of 34%. This is similar to the variability found for adjusted-FID HC, and is substantially higher than the variability for GC-HC, CO, and NO_x. As shown in Appendix II, the methanol variability was particularly high for Bag 2 results, where two labs reported values in excess of 100 mg/mile, and three labs reported values at or near zero. The overall C.V. for the Bag 2 methanol results was approximately 100%. This suggests that at low emission rates, there may be significant measurement problems for methanol. This may become

a more serious issue when testing modern, low-emitting vehicles.

9. Formaldehyde

Sixteen laboratories collected aldehyde emissions using impingers, while seven labs used cartridges. Only three participants (Labs 1, 10, and 17) used both collection techniques. Of these three, only Lab 1 used the two techniques simultaneously (and only for two of their six FTP tests). Labs 10 and 17 used impinger collection for some FTP tests and cartridges for other tests. Thus, this round robin program did not generate sufficient information to verify that the two sampling techniques provide equivalent results. However, sampling comparability has been demonstrated in other studies.[3]

The mean FTP-composite emission rates measured for formaldehyde are 45.4 mg/mile by impinger (excluding Lab No. 18) and 41.0 mg/mile by cartridge. There is no statistically significant difference between these two results. The overall variability for the impinger results was quite low (C.V. of 18%), similar to that determined for CO and GC-HC. Even at the lower emission rates of Bag 2 samples (mean emission rate of 23 mg/mile) the lab-to-lab variability is quite acceptable (C.V. of 33%). At lower formaldehyde emission rates, as required by California's Low Emission Vehicle Standards,[8] somewhat higher variability might be expected.

10. Acetaldehyde

The mean FTP-composite acetaldehyde emission rates measured by impinger and cartridge techniques are identical at 1.14 mg/mile. This rate is considerably lower than was found for formaldehyde. The acetaldehyde variability was much greater than the formaldehyde variability--even when excluding the outlier results of Lab No. 7. Interestingly, the Lab 7 acetaldehyde results were identified as outliers for every FTP bag, while none of the formaldehyde results from this lab were outliers.

While the formaldehyde emission levels from this vehicle were quite high (several times the allowable standard), the acetaldehyde levels may be considered indicative of carbonyl emissions from modern vehicles. In this study, the acetaldehyde variability was approximately twice as high as the formaldehyde variability (for FTP-composite results). This difference in variability is related to a difference in concentration. As emission levels decrease, variability increases. This is illustrated in Figure 16, where the variabilities of both formaldehyde and acetaldehyde results are plotted versus emission rate. (The four data points for each aldehyde refer to the three FTP bag results and the FTP-composite result.) It is reasonable to expect that at equivalent emission levels, formaldehyde and acetaldehyde would show similar variabilities.

11. Methane

Not all participants used the same measurement technique for methane. As shown in Table V, 12 participants used a bench analyzer, 10 participants used a GC speciation technique, and 2 used both techniques. When suitable calibration procedures are used, these two techniques are expected to provide comparable results. This expectation was confirmed by the two participants who used both techniques.

The methane results shown in the data tables and in Figure 13 include both bench analyzer and GC-determined values. For labs which used both techniques, only the bench analyzer results are included. The FTP-composite results gave a mean of 82 mg/mile and a C.V. of approximately 24%. This variability is comparable to that observed for measurement of unadjusted-FID HC.

12. Benzene

As one of the EPA-designated air toxics, benzene is of particular interest. Figure 14 shows that, excluding Lab. No. 10, the variability in FTP-composite benzene levels was quite low (C.V. of 21%). Appendix II shows that the outlier results for Lab No. 10 were caused primarily by exceptionally high values for Bag 2 samples. In general, variability was much higher for Bag 2 emissions than for the other FTP bags. This is expected since the emission rates were lowest for Bag 2. The participants were not asked to report their detection limits, but it is likely that the average Bag 2 benzene level of 1.5 mg/mile approached the detection limit for some labs.

13. Toluene

Toluene emission rates are illustrated in Figure 15. Although not a statistical outlier on an FTP-composite basis, the average result for Lab No. 4 was an outlier in Bag 2 (see Appendix II). If the Lab 4 results are excluded, the average FTP-composite emission rate drops from 31.2 to 29.8 mg/mile, and the C.V. drops from 30% to 26%.

If benzene and toluene are considered representative of all HC species, these results suggest that individual HC emission rates can be measured among the participating laboratories with a C.V. of 20-30%. Higher variabilities may be expected when lower emission levels are measured.

SUMMARY

A FFV methanol vehicle round robin emissions test program has been completed where HC, CO, NO_x, methanol, formaldehyde, acetaldehyde, methane, benzene, and toluene were measured at 16 laboratories around the country. Most participants measured all compounds. The vehicle was stable through the 2-year program, as shown by results of the Reference Lab testing at four times during the round robin, and low variability in fuel economy determinations from all labs (C.V. = 7%).

Of the criteria emissions, variability was lowest for NO_x, with a C.V. of 12% for the FTP-composite results. The variability for CO emissions was only slightly higher, with a C.V. of 16% (excluding one outlier). The variability of HC emissions depended upon the analytical method used. Measurement of total HC by GC provided relatively low variability (C.V. of 17%). When measured by bench-FID, the HC variability was approximately twice as large.

It is of interest to compare these variability results with repeatability results that are available from the Auto/Oil Air Quality Improvement Research Program. In the Auto/Oil Program, a fleet of 20, 1989 model-year vehicles was tested using a wide variety of gasoline fuels. Since all vehicle/fuel combinations were tested more than once, an assessment of repeatability could be made in each case. The overall emission repeatabilities for the entire fleet (average of C.V. for each case) were 8.0%, 16.7%, and 8.7% for NO_x, CO, and HC, respectively.[7] Given this context, the lab-to-lab variabilities observed in this single-vehicle round robin study do not seem excessive.

The average FTP emission rate of methanol in the round robin program was approximately three times the average emission rate of HC. Variability of the FTP-composite methanol results was somewhat high (C.V. of 34%). Formaldehyde variability was substantially lower (C.V. of 17%) while acetaldehyde variability was much higher (C.V. of 63%). For all these oxygenated species, measurement variability is expected to increase as the emission levels decrease. Results from the individual FTP bags confirms this phenomenon. The large difference in variability between formaldehyde and acetaldehyde is probably a consequence of their different emission rates--formaldehyde's emission rate was approximately 40 times that of acetaldehyde.

Emission rates of three HC species were determined: methane, benzene, and toluene. The FTP-composite results showed variabilities ranging from 20-30%. As with the oxygenates, higher variabilities were found at lower emission rates, i.e., in FTP Bag 2 samples. At the emission levels produced by this vehicle, the measurement variability for individual HC species was only slightly higher than the variabilities for criteria emissions.

Emissions measurement variability may arise from several significant sources, namely: vehicle variability (from both normal and poor operation), test cell and procedural variability, and analytical measurement variability. The total observed variability results from a combination of these sources. This study was not designed to assess the independent contribution of each source.

The results of this round robin demonstrate that a vehicle can be shipped to numerous locations for emissions testing without major changes in the vehicle's performance. In this study, a large number of laboratories made measurements of FFV exhaust emissions with acceptable variability in the data. The data set which was generated also provides a useful measure of the relative lab-to-lab variability which existed at the time of the study.

This was the first time a round robin emissions program was attempted using a methanol-fueled vehicle. Several of the participating laboratories had just begun doing emissions measurements of some reported species. It is believed that this study represented a learning experience for all the laboratories. An expected result is that the participants' capabilities to measure the species reported here have been improved.

ACKNOWLEDGMENTS

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APPENDIX I

AVERAGE FTP BAG 1 EMISSIONS RESULTS FROM METHANOL VEHICLE ROUND ROBIN TEST PROGRAM

- Outliers are shown in parentheses.

Lab No.	Fuel Econ., mpg	Unadjusted FID-HC, g/Mile	Adjusted FID-HC, g/Mile	GC-HC, g/Mile	Comparison of HC, GC Vs. FID	CO, g/Mile	NO_x, g/Mile	Methanol, g/Mile	Formald. Impinger, mg/Mile	Formal. Cartridge, mg/Mile	Acetald. Impinger, mg/Mile	Acetald. Cartridge, mg/Mile	Methane, mg/Mile	Benzene, mg/Mile	Toluene, mg/Mile
1	9.46	1.590	0.636	0.596	-0.029	23.057	0.528	2.709	92.0	76.3	1.90	2.40	119.7	27.00	101.5
2	9.57	1.069	0.000			23.630	0.446	3.320		133.0		2.00	121.0		
3		1.213	0.398	0.471	0.214	19.189	0.604	2.662	133.0		2.00		146.5		
4	9.11	1.573	0.730	0.646	-0.096	24.245	0.648	2.570		136.0		2.37	153.5	16.70	126.1
5	9.13	2.093	0.740	0.640	-0.036	25.150	0.520	3.683	114.1		2.67		139.8	30.93	125.8
6	9.40	2.080	0.769	0.735	-0.042	27.714	0.407	3.526	132.0		1.25		135.0	34.00	139.0
7	9.53	1.184	0.066			24.493	0.460	3.541	132.3		(11.77)		143.5	30.50	133.2
8	9.64	1.382	0.766	1.051	0.454	20.223	0.495	2.159	88.7		3.22		118.3	23.30	82.3
9	8.26	2.393	0.195	0.642	2.571	23.333	0.602	6.714	145.5		5.73		166.7	32.27	95.9
10	8.71	1.418	0.946	0.729	-0.188	23.042	0.620	2.142	119.0	63.5	1.51	0.24	147.8	36.75	84.0
11	8.07	1.731	0.875			21.698	0.477	2.627		150.0		3.73	128.0		
12	10.23	1.758	0.544	0.693	0.307	18.123	0.482	3.262	130.5		1.55		120.5	25.00	114.0
13	8.50	2.535	1.036	0.835	-0.190	27.130	0.493	4.806		40.6		0.70	169.0	38.15	155.1
14	8.68	2.189	0.214	0.921	(4.531)	26.305	0.550	5.380	123.7		3.20		148.3	33.10	136.5
15	8.96	3.750	0.835	0.912	0.099	25.601	0.701	3.244	115.0		1.50		182.0	31.90	158.5
16	8.91	2.212	0.458	0.885	-0.282	25.399	0.424	4.154	151.7				178.0	38.30	169.3
17	10.01	1.978	0.756	0.742	-0.015	18.969	0.420	3.730	148.1	135.7	2.60	3.33	158.2	23.96	95.8
18	8.10	3.621	(1.907)	0.889	-0.574	(34.487)	0.565	5.074	(208.7)		2.55		220.7	41.00	102.0
19	8.07	1.990	0.527			22.294	0.457	4.826	151.5		1.67		169.0		
20	9.20	1.301	0.410	0.507	0.289	17.796	0.463	2.585	122.5		1.85		109.0	21.50	62.0
Mean	9.03	1.953	0.574	0.743	0.165	23.020	0.518	3.636	126.6	105.0	2.37	2.11	148.7	30.27	117.6
Std Dev	0.65	0.728	0.299	0.161	0.714	3.011	0.082	1.204	19.3	43.6	1.16	1.28	27.2	6.83	30.4
CV, %	7.2	37.2	52.1	21.7	432	13.1	15.9	33.1	15.2	41.5	48.9	60.6	18.3	22.6	25.9

APPENDIX II

AVERAGE FTP BAG 2 EMISSIONS RESULTS FROM METHANOL VEHICLE ROUND ROBIN TEST PROGRAM

• Outliers are shown in parentheses.

Lab No.	Fuel Econ., mpg	Unadjusted FID-HC, g/Mile	Adjusted FID-HC, g/Mile	GC-HC, g/Mile	Comparison of HC, GC Vs. FID	CO, g/Mile	NO_x, g/Mile	Methanol, g/Mile	Formald. Impinger, mg/Mile	Formal. Cartridge, mg/Mile	Acetald. Impinger, mg/Mile	Acetald. Cartridge, mg/Mile	Methane, mg/Mile	Benzene, mg/Mile	Toluene, mg/Mile
1	10.12	0.129	0.120	0.119	-0.028	0.279	0.410	22.3	29.3	30.8	0.67	0.65	57.5	0.60	5.93
2	10.19	0.063	0.058			0.130	0.365	16.5		19.0		0.00	41.5		
3		0.168	0.159	0.157	-0.010	0.811	0.459	28.0	30.5		1.00		91.5		
4	9.83	0.158	0.148	0.220	0.574	0.838	0.395	17.5		26.3		0.73	85.3	4.50	(38.48)
5	9.68	0.240	0.230	0.140	-0.345	1.115	0.317	26.7	14.1		0.67		80.4	2.47	9.03
6	9.81	0.127	0.119	0.111	-0.066	0.443	0.308	21.5	18.0		0.00		55.0	0.90	6.90
7	9.93	0.112	0.116			0.577	0.343	21.3	18.0		(7.10)		39.6	0.70	4.90
8	10.18	0.129	0.124	0.118	-0.046	0.327	0.375	19.0	21.3		1.35		65.3	1.80	6.80
9	9.03	0.116	0.104	0.107	-0.083	0.343	0.328	2.5	30.8		3.17		70.0	2.50	3.83
10	9.22	0.157	0.157	0.234	0.676	0.570	0.348	0.0	22.0	14.5	0.69	0.09	100.5	(14.25)	6.00
11	8.37	0.113	0.113			0.436	0.347	0.0		30.0		1.57	55.3		
12	10.60	0.126	0.115	0.111	-0.084	0.464	0.296	27.5	21.5		0.30		57.5	1.50	7.75
13	8.80	0.179	0.111	0.155	0.401	1.240	0.312	(219.0)		18.2		0.50	82.1	1.65	4.95
14	9.02	0.125	0.085	0.113	0.501	0.564	0.364	110.0	8.6		0.90		38.8	0.85	3.95
15	9.49	0.000	0.000	0.161		0.754	0.271	11.9	20.7		0.45		88.3	0.00	0.00
16	9.51	0.156	0.139	0.206	0.549	0.828	0.277	17.7	31.5				109.0	1.73	9.73
17	10.10	0.175	0.170	0.177	0.054	0.903	0.283	15.0	22.8	23.4	1.05	1.70	103.0	1.02	2.96
18	8.45	0.239	0.225	0.179	-0.144	(2.029)	0.360	40.1	37.9		0.85		93.2	1.30	3.10
19	8.65	0.121	0.116			0.126	0.245	19.9	18.0		0.00		50.0		
20	9.37	0.141	0.132	0.142	0.075	0.457	0.307	25.5	19.0		0.50		65.5	1.00	0.00
Mean	9.49	0.139	0.127	0.153	0.135	0.690	0.335	23.3	22.8	23.1	0.83	0.75	71.5	1.50	5.06
Std Dev	0.64	0.053	0.051	0.041	0.316	0.309	0.052	23.2	7.5	6.2	0.77	0.66	22.0	1.07	2.87
CV, %	6.8	38.1	39.9	26.7	234	52.5	15.5	99.7	32.9	26.8	93.6	89.0	30.8	71.4	56.7

APPENDIX III

AVERAGE FTP BAG 3 EMISSIONS RESULTS FROM METHANOL VEHICLE ROUND ROBIN TEST PROGRAM

• Outliers are shown in parentheses.

Lab No.	Fuel Econ., mpg	Unadjusted FID-HC, g/Mile	Adjusted FID-HC, g/Mile	GC-HC, g/Mile	Comparison of HC, GC Vs. FID	CO, g/Mile	NO_x, g/Mile	Methanol, g/Mile	Formald. Impinger, mg/Mile	Formal. Cartridge, mg/Mile	Acetald. Impinger, mg/Mile	Acetald. Cartridge, mg/Mile	Methane, mg/Mile	Benzene, mg/Mile	Toluene, mg/Mile
1	11.83	0.143	0.109	0.095	-0.105	2.545	0.577	0.096	30.0	30.0	0.00	0.75	36.2	3.93	10.15
2	12.14	0.090	0.068			0.830	0.512	0.068		27.0		1.00	26.0		
3		0.145	0.110	0.118	0.074	1.508	0.652	0.089	38.5		1.00		48.0		
4	11.47	0.213	0.185	0.170	-0.081	4.480	0.623	0.100		32.1		0.73	58.2	3.68	20.10
5	11.38	0.240	0.203	0.107	-0.483	2.760	0.527	0.103	25.5		0.77		43.7	3.57	12.47
6	11.78	0.138	0.109	0.100	-0.082	2.055	0.544	0.079	24.5		0.00		40.0	3.30	9.55
7	11.83	0.152	0.130			3.247	0.483	0.095	22.7		(10.73)		42.6	1.80	12.00
8	12.00	0.132	0.113	0.117	0.069	1.021	0.557	0.069	17.7		2.39		38.2	3.07	9.13
9	10.32	0.229	0.208	0.160	-0.240	2.347	0.563	0.058	39.9		3.20		68.0	5.60	9.60
10	11.13	0.140	0.138	0.208	0.530	0.789	0.575	0.000	30.0	15.5	0.60	0.06	48.3	9.25	5.50
11	10.07	0.153	0.128			1.397	0.524	0.077		40.0		2.03	39.7		
12	12.54	0.125	0.095	0.094	-0.015	0.565	0.552	0.079	31.0		0.20		36.0	1.00	8.20
13	10.50	0.206	0.148	0.143	-0.035	2.825	0.488	0.185		9.8		0.35	41.8	5.20	15.15
14	11.24	0.152	0.080	0.134	0.789	0.853	0.600	0.195	(0.0)		1.30		44.1	2.65	9.55
15	11.37	0.265	0.090	0.179	(1.735)	2.721	0.490	0.139	30.7		0.35		51.0	4.85	13.55
16	10.94	0.185	0.086	0.172	1.072	3.616	0.438	0.185	36.4				71.0	5.33	16.40
17	12.40	0.171	0.139	0.154	0.113	1.610	0.389	0.099	29.8	36.3	1.00	1.87	53.9	3.02	7.46
18	10.30	(0.418)	(0.399)	0.266	-0.318	(7.372)	0.481	0.057	52.2		1.00		(118.4)	8.00	18.20
19	10.05	0.188	0.131			1.775	0.465	0.186	42.1		0.00		64.7		
20	11.15	0.176	0.126	0.148	0.173	0.955	0.509	0.144	34.0		0.65		44.0	3.00	5.50
Mean	11.29	0.171	0.126	0.148	0.097	1.995	0.527	0.105	32.3	27.2	0.89	0.97	47.1	4.20	11.41
Std Dev	0.77	0.044	0.039	0.046	0.412	1.095	0.063	0.052	8.6	11.0	0.92	0.74	11.7	2.14	4.31
CV, %	6.8	26.0	31.0	31.1	423	54.9	12.0	49.3	26.7	40.2	104	76.2	24.8	50.9	37.8

TABLE OF FIGURES

Figure Legends

- Data points represent FTP-composite results from individual tests.
- Closed circles designate Reference Lab.
- Zig-zag lines connect mean results from each lab.
- Shaded bar represents average of Reference Lab results ±1 standard deviation.
- Horizontal solid and dashed lines represent average of all lab means ±1 standard deviation.

Figure Titles

Figure 1

Fuel Economy, mpg

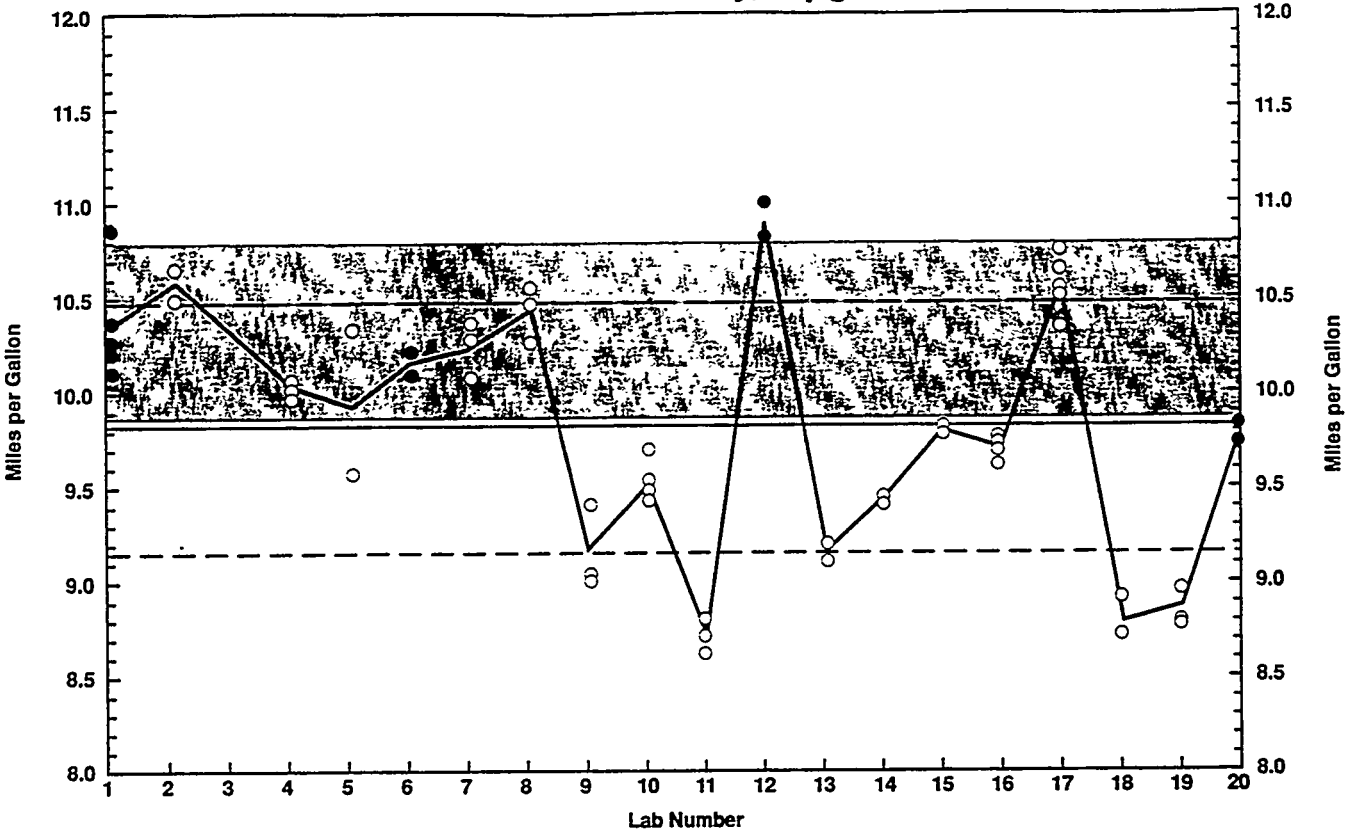
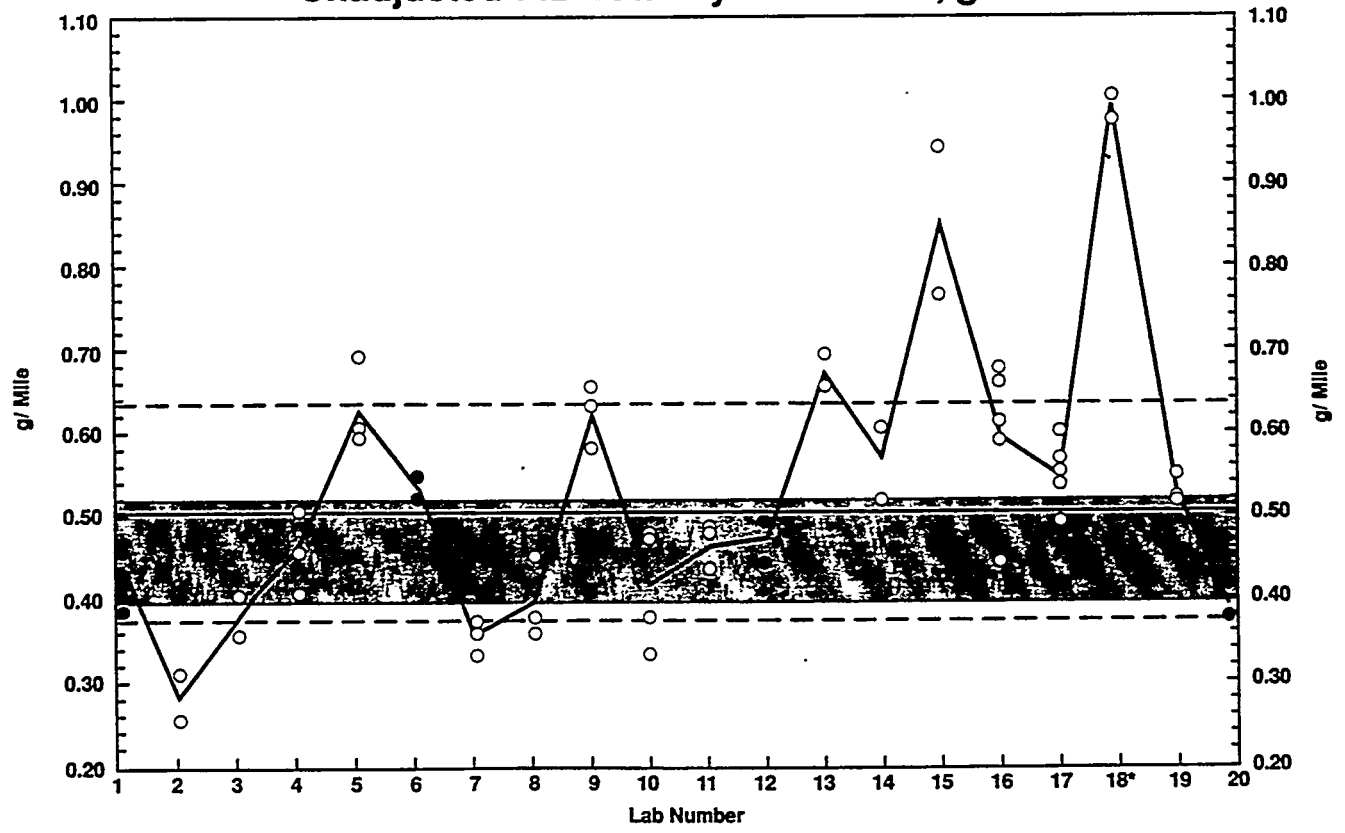


Figure 2

Unadjusted-FID Total Hydrocarbons, g/Mile



*Outlier Point; Not Included in Statistical Analysis

Figure 3

Adjusted-FID Total Hydrocarbons, g/Mile

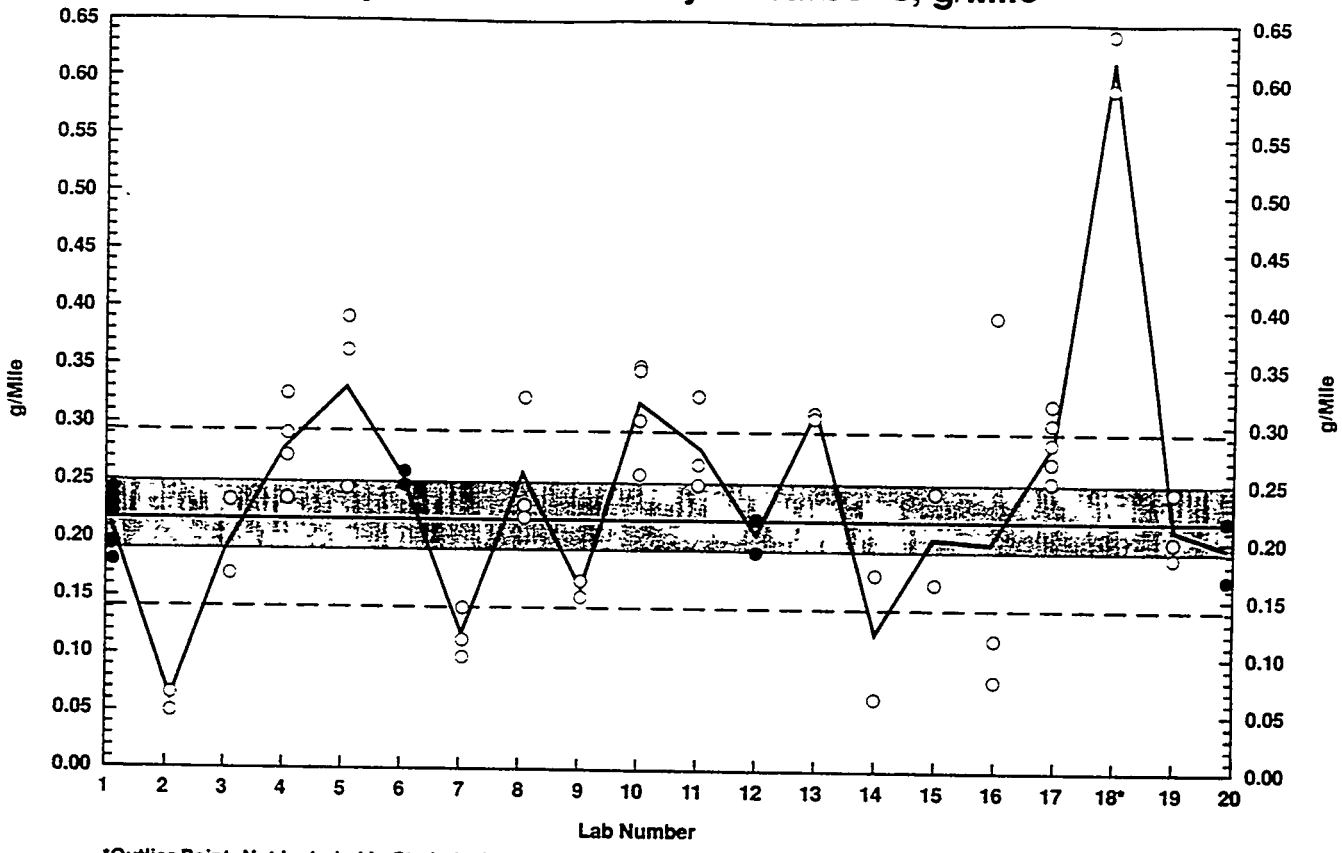


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Figure 4

GC-Measured Total Hydrocarbons, g/Mile

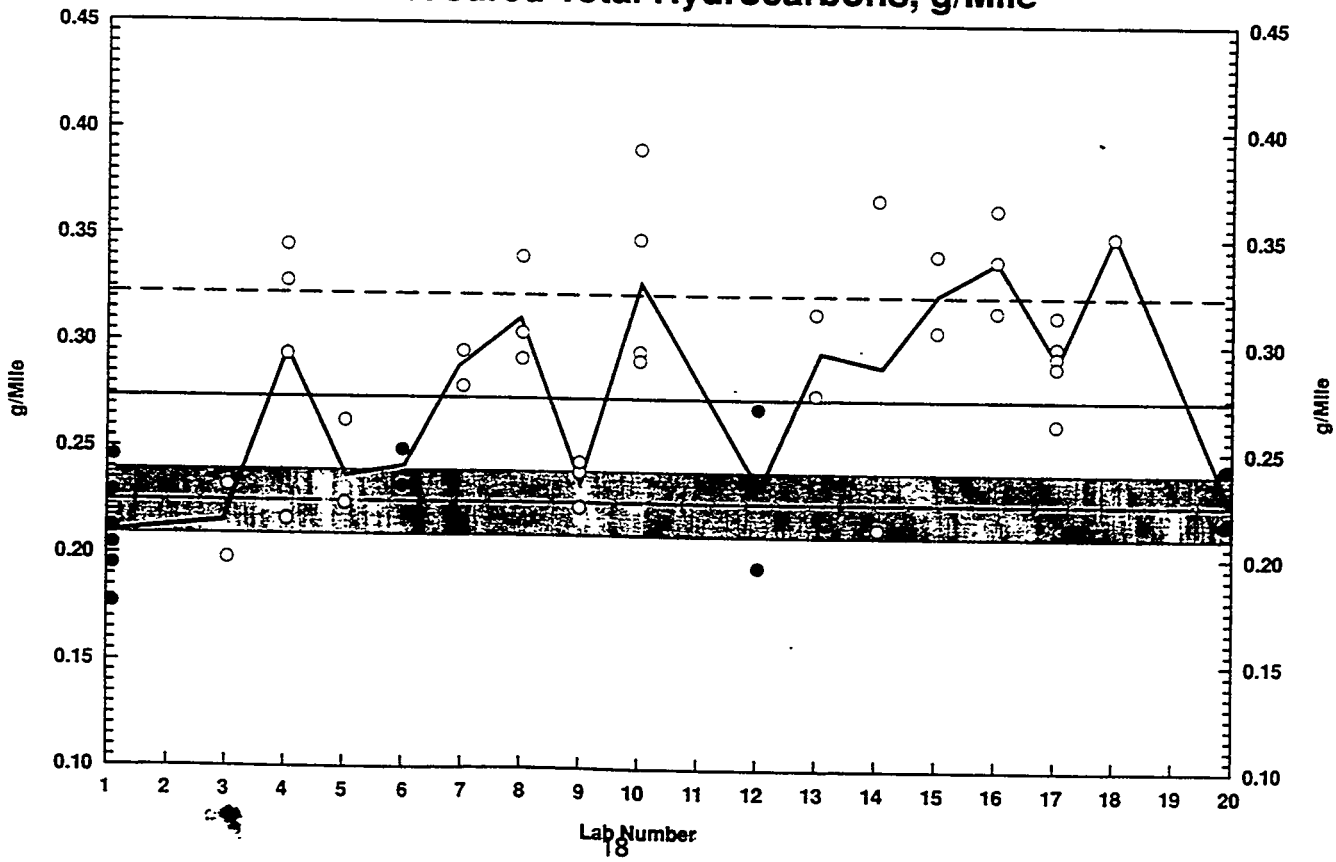


Figure 5

Comparison of HC Results: GC Versus FID

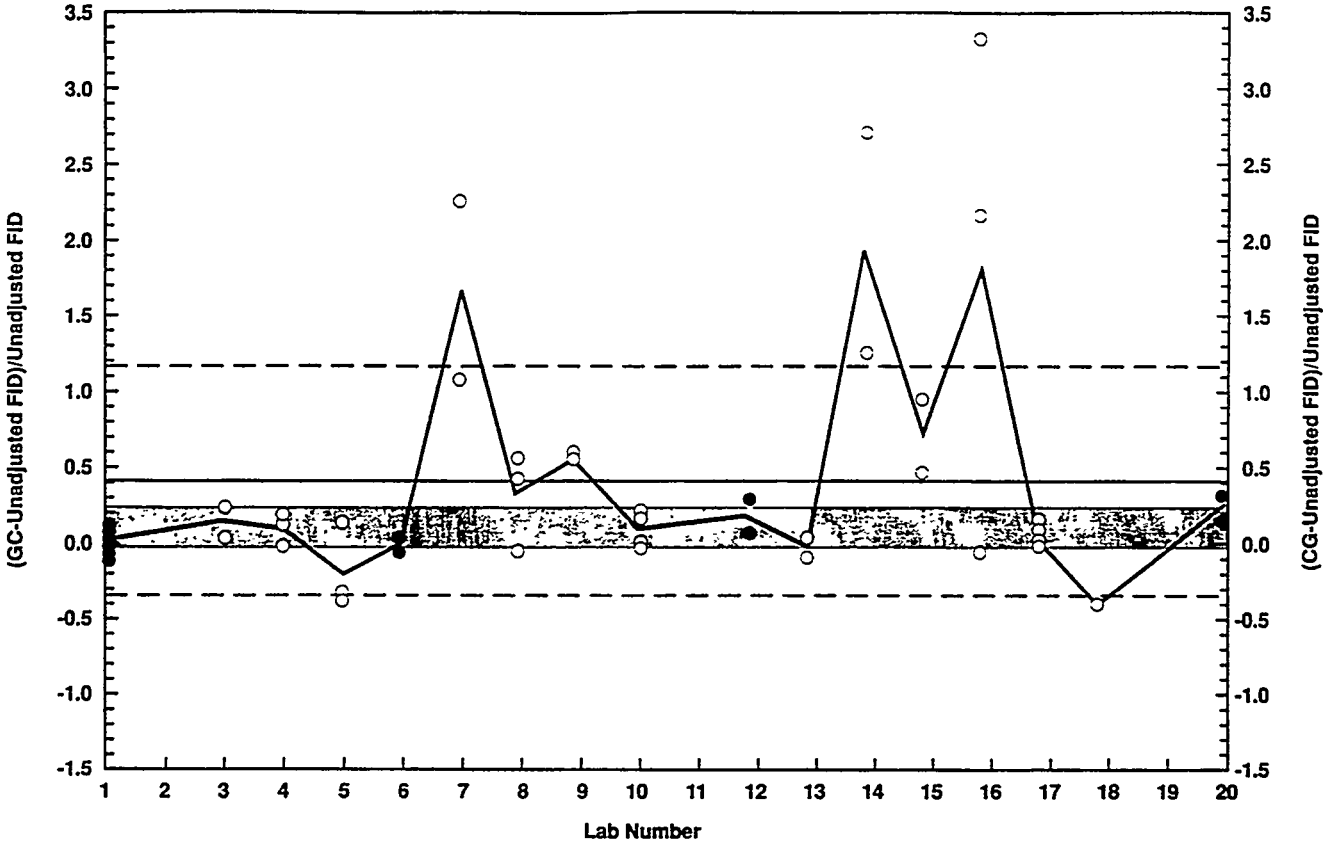
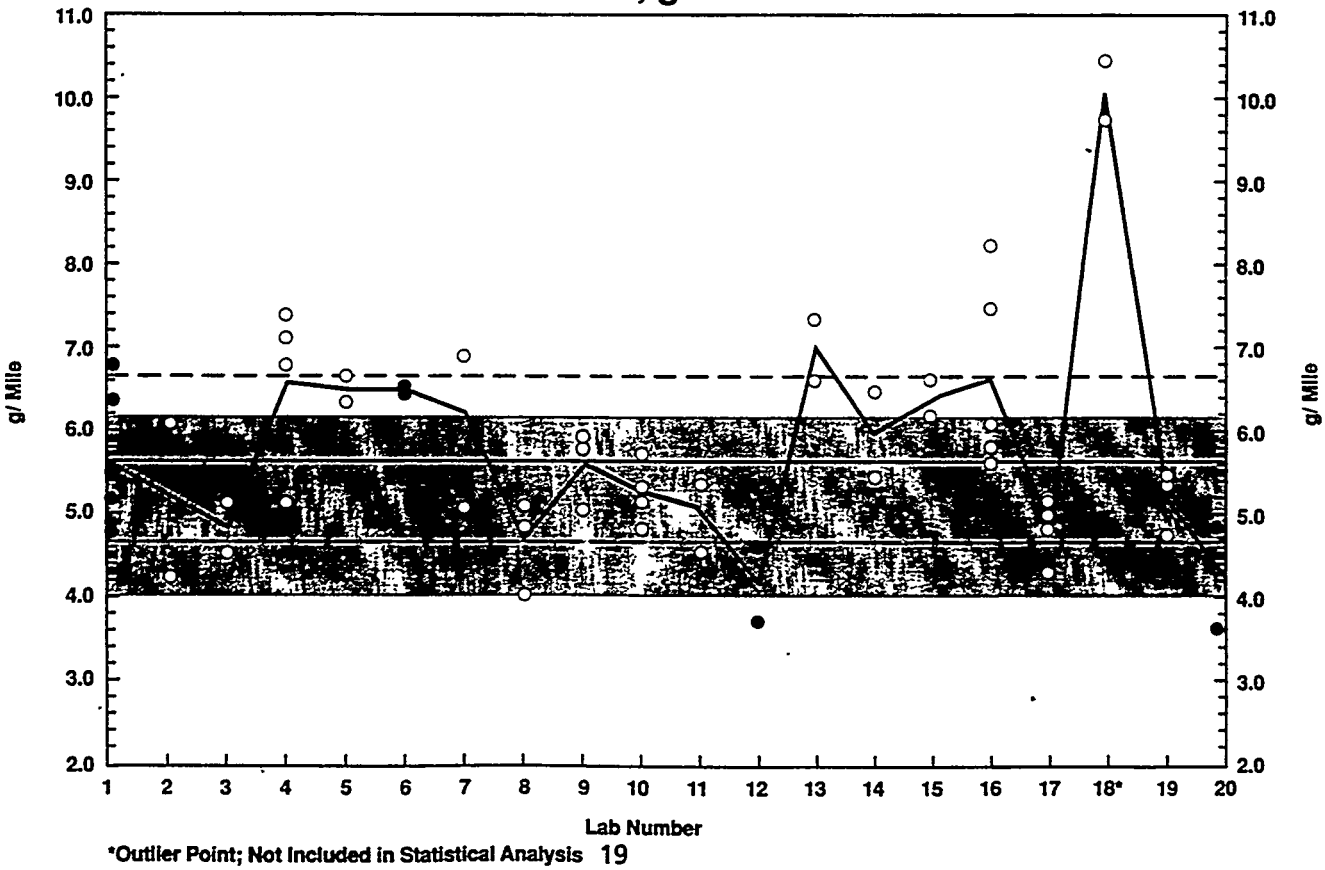


Figure 6

CO, g/Mile



*Outlier Point; Not Included in Statistical Analysis

Figure 7

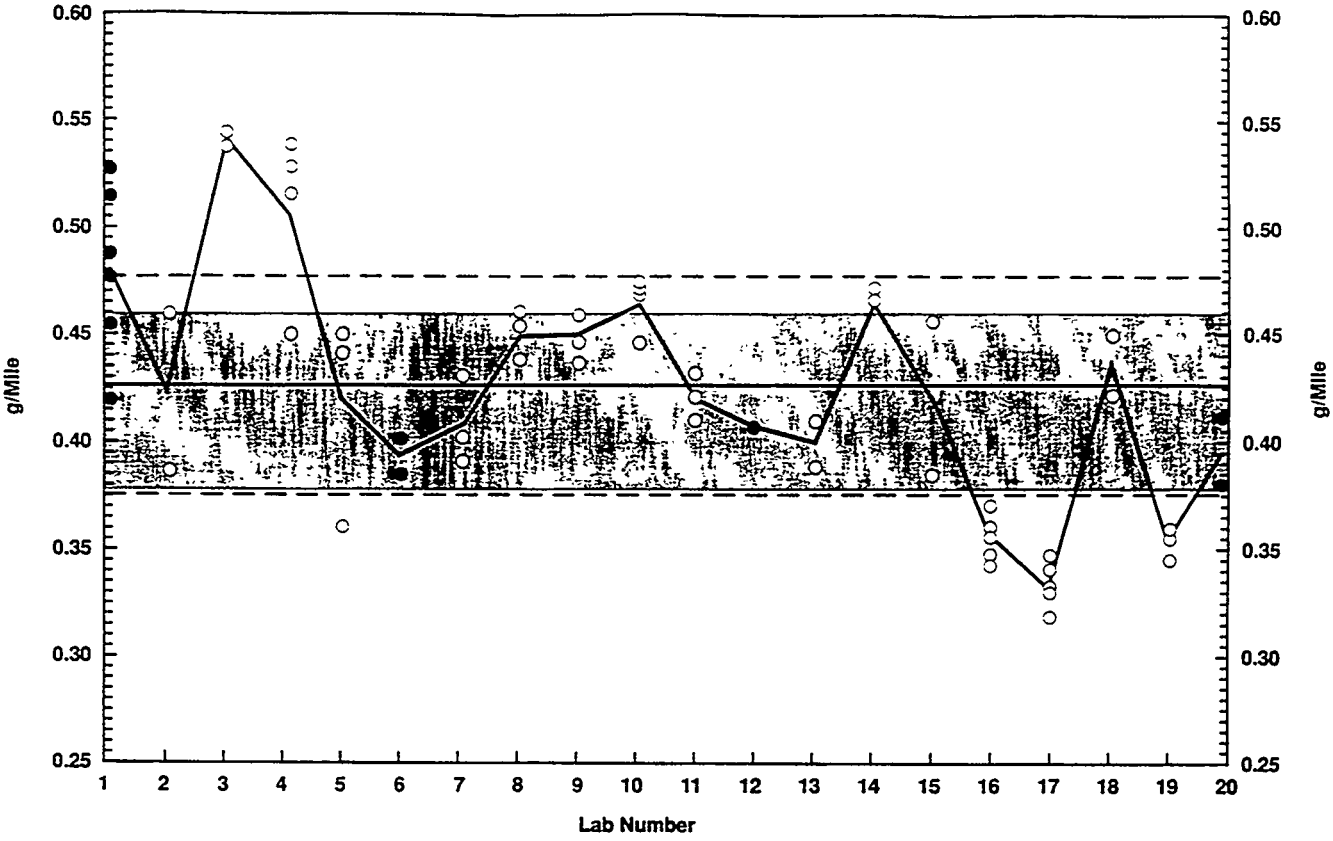


Figure 8

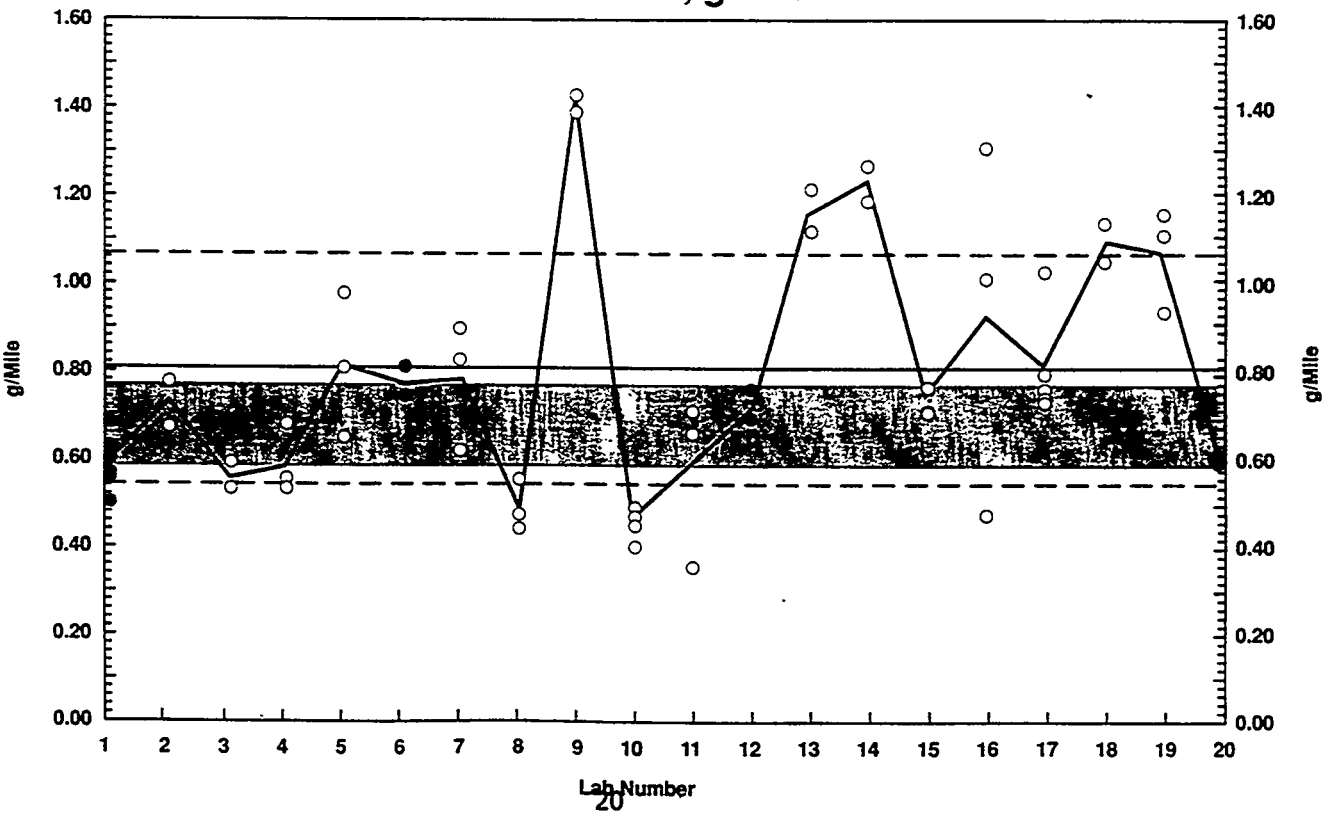
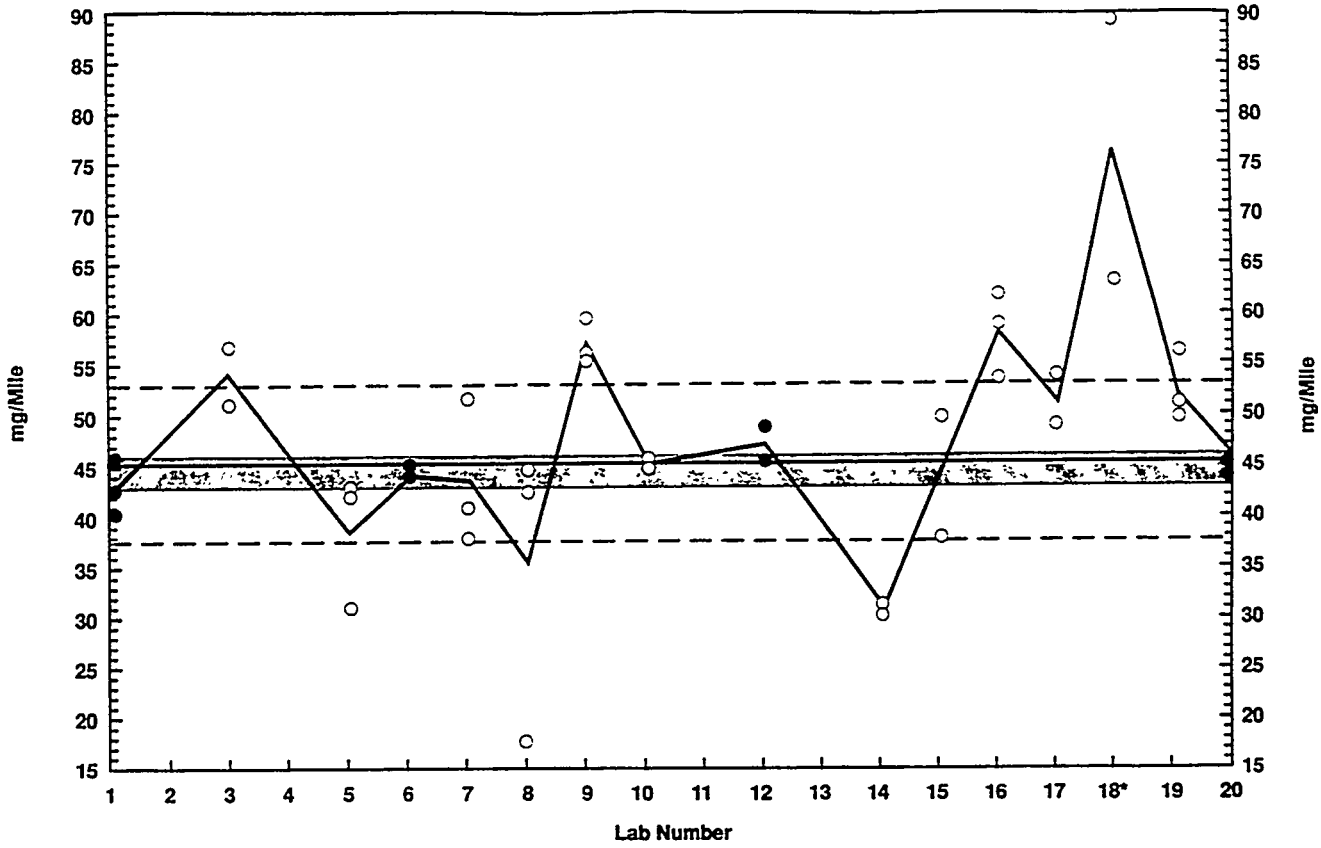


Figure 9

Impinger Formaldehyde, mg/Mile



*Outlier Point; Not Included in Statistical Analysis

Figure 10

Cartridge Formaldehyde, mg/Mile

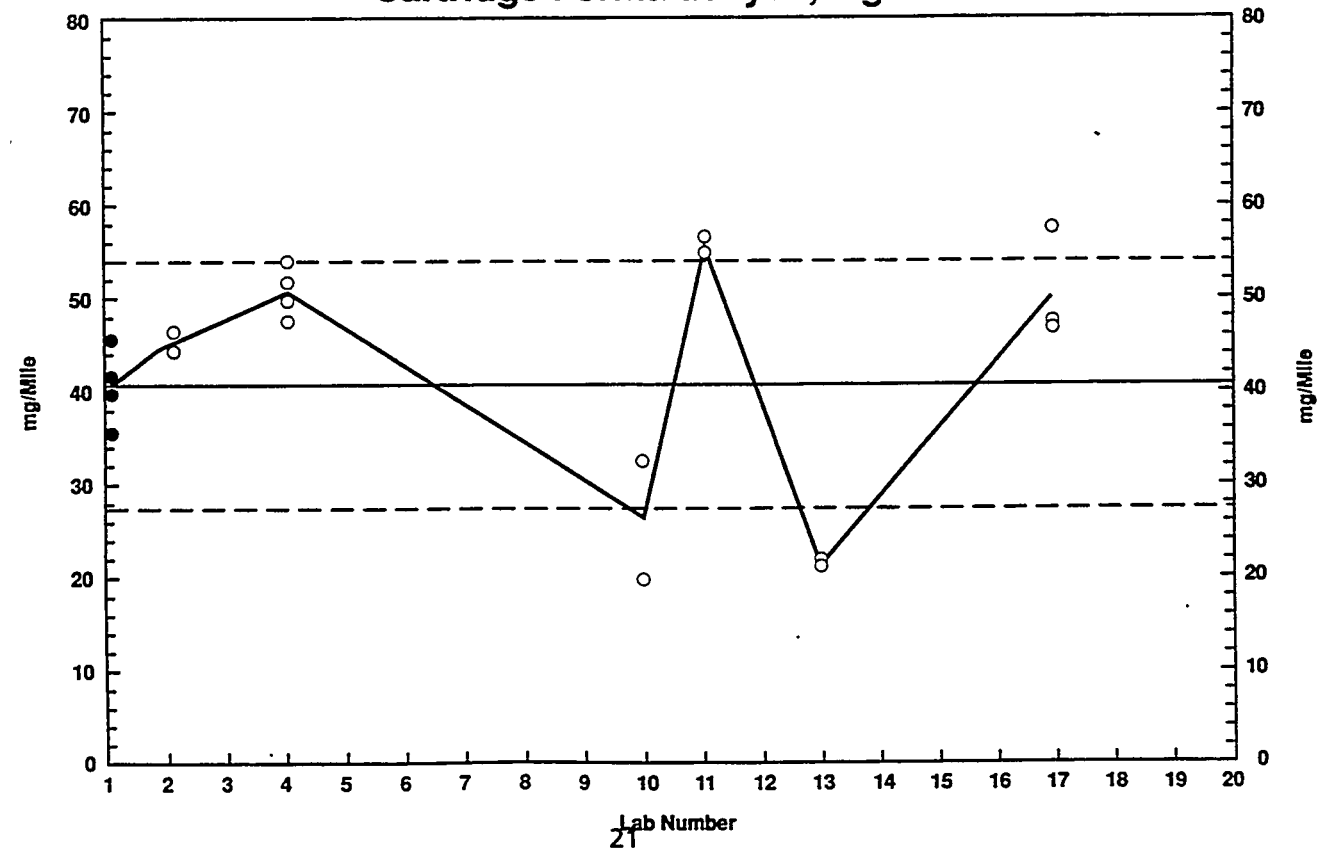
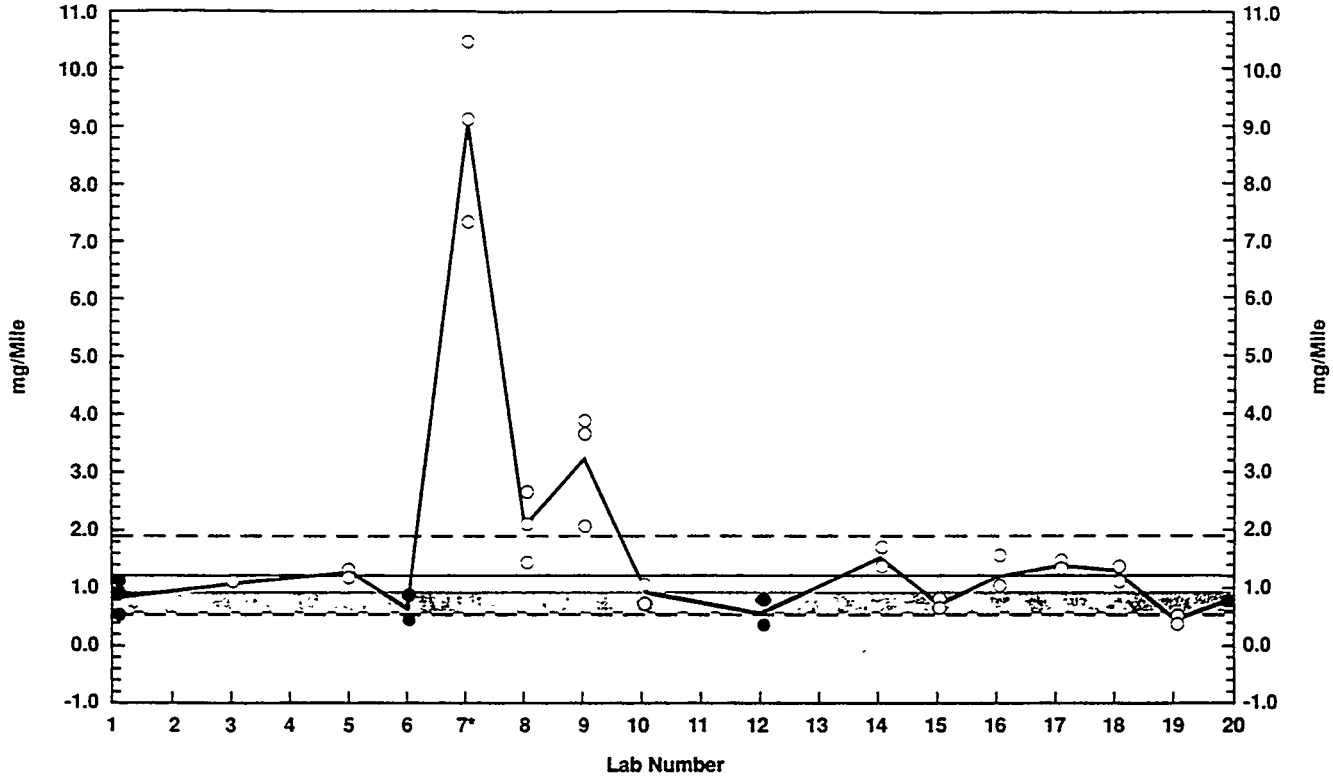


Figure 11

Impinger Acetaldehyde, mg/Mile



*Outlier Point; Not Included in Statistical Analysis

Figure 12

Cartridge Acetaldehyde, mg/Mile

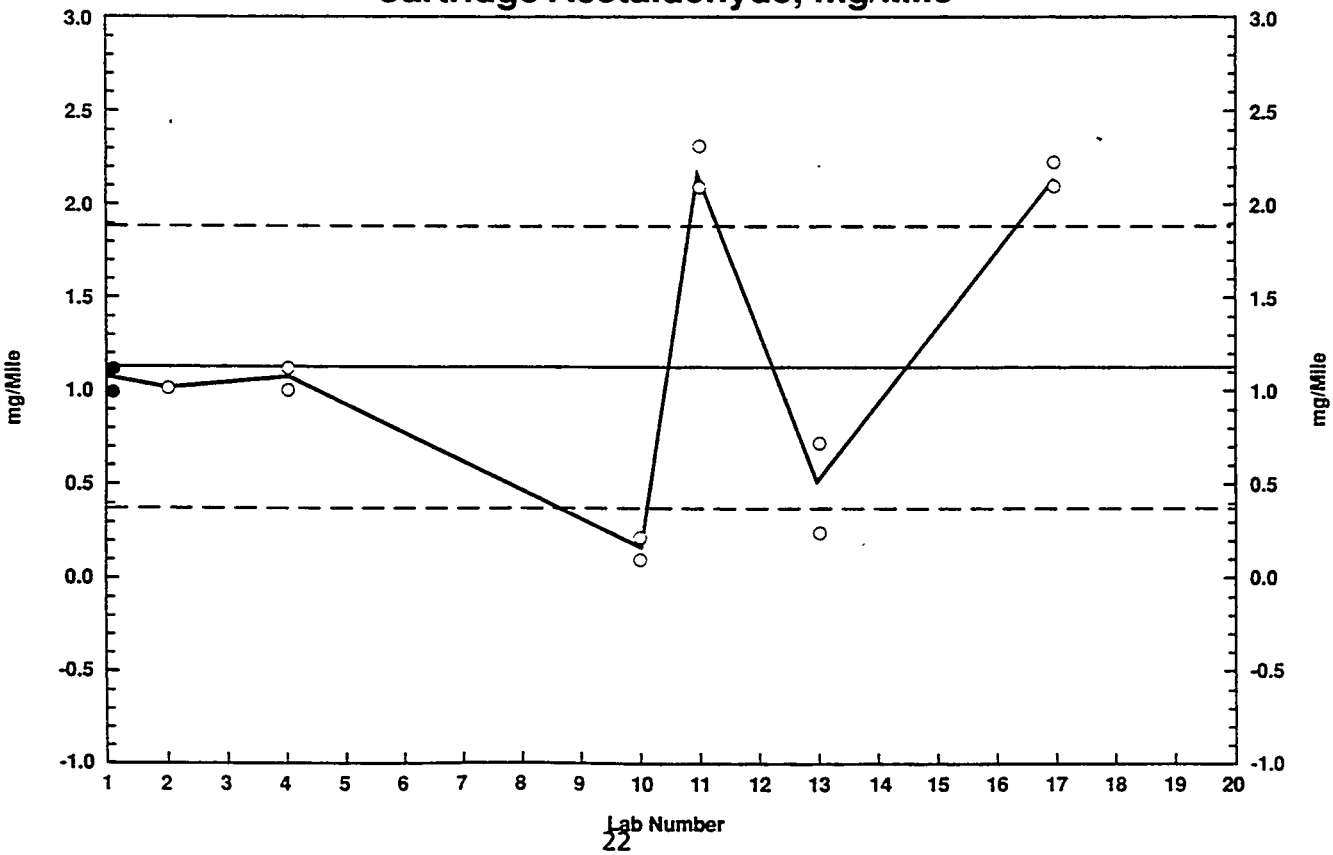


Figure 13

Methane, mg/Mile

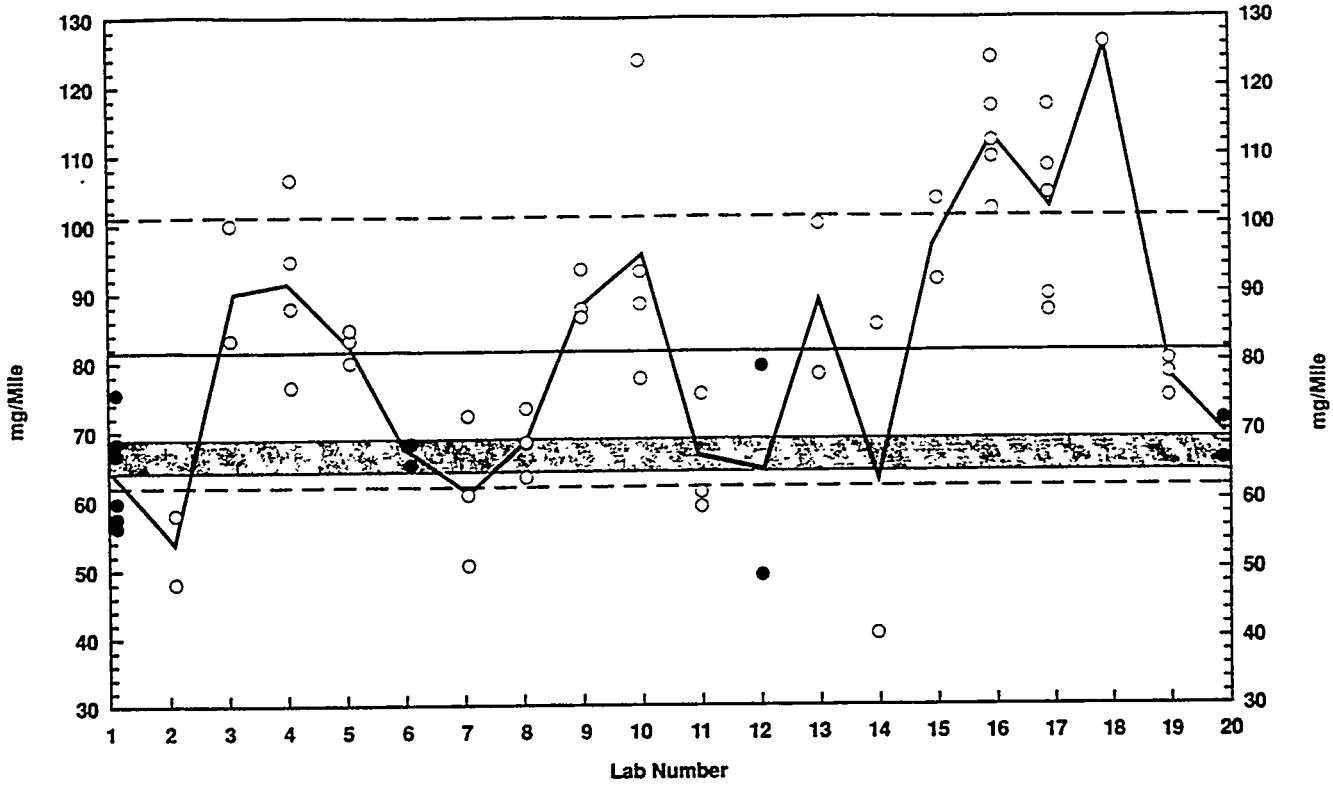
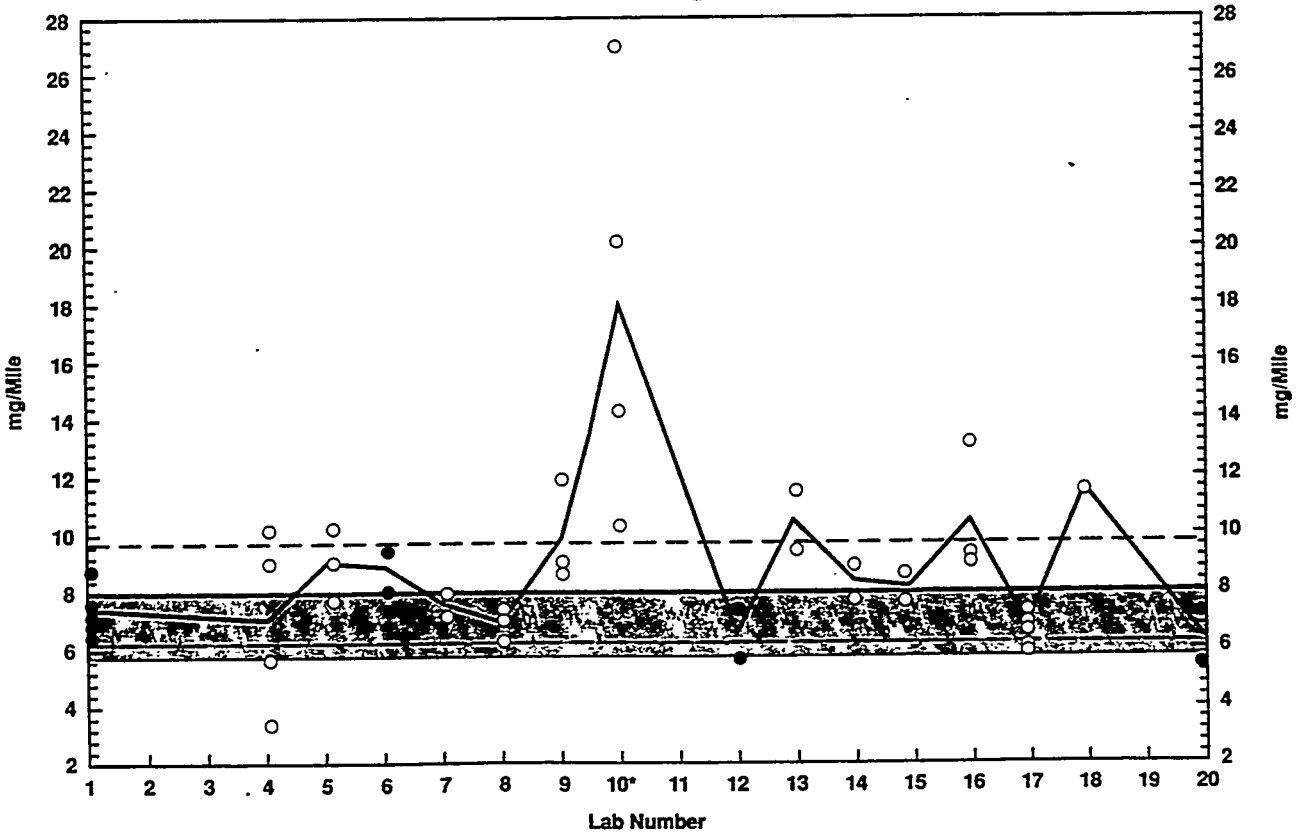


Figure 14

Benzene, mg/Mile



*Outlier Point; Not Included in Statistical Analysis

Figure 15

Toluene, mg/Mile

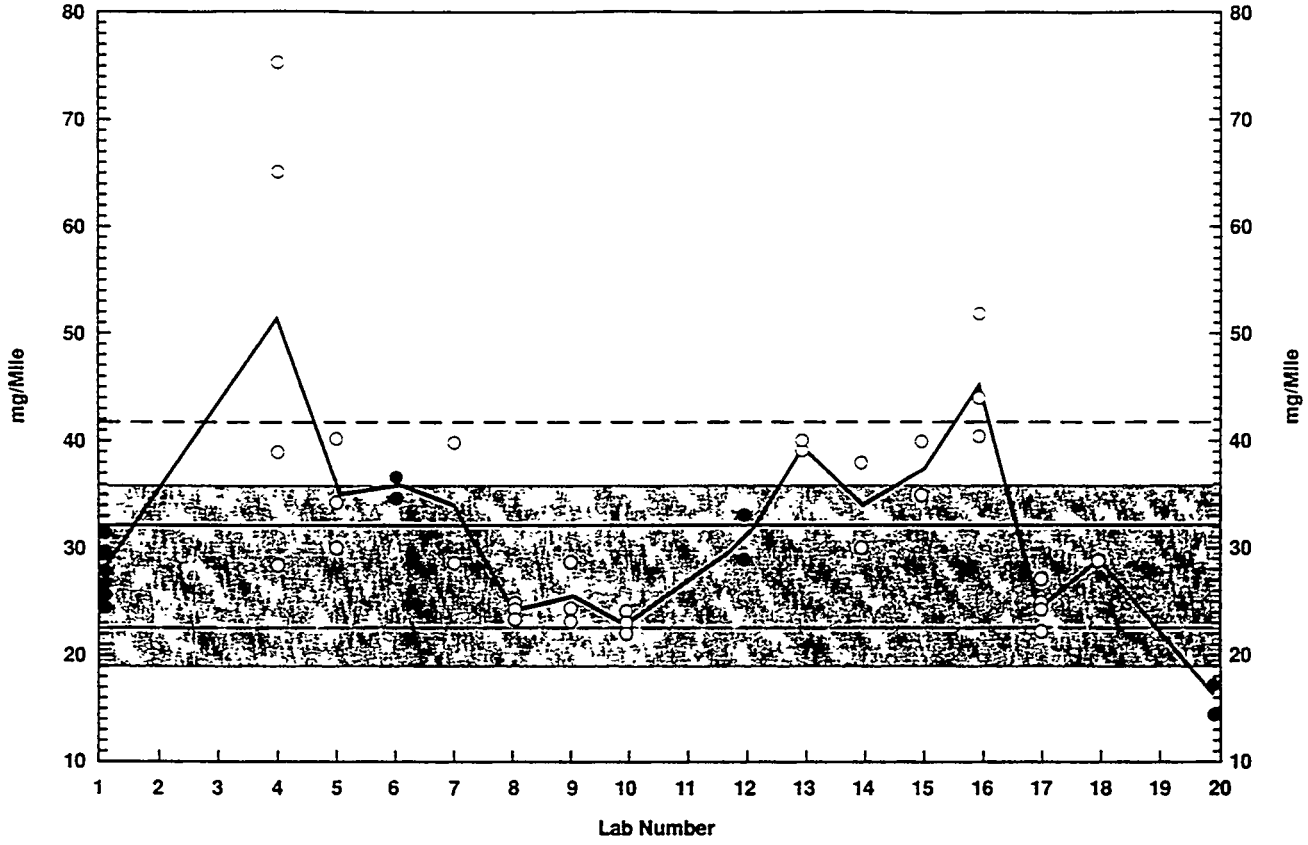
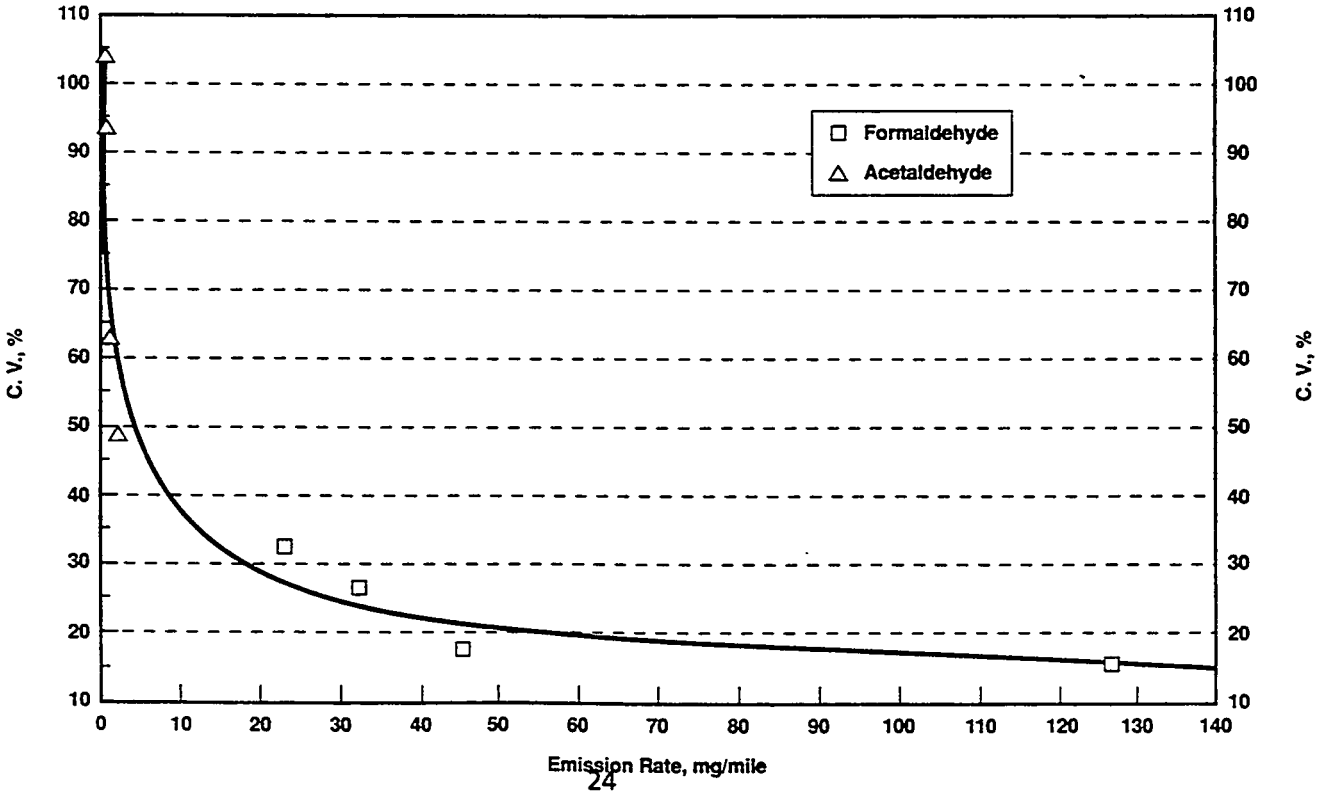


Figure 16

Variability of Aldehyde Measurements



A TECHNOLOGY ASSESSMENT OF LIGHT-DUTY METHANOL VEHICLES

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Abstract

Light duty methanol vehicle development activities over the last decade have culminated in the certification of three different vehicle models of production fuel flexible vehicles (FFVs) to California Low Emission Vehicle standards for the 1993 model year, one year ahead of the 1994 regulation requirement established by the California Air Resources Board. Steady progress in the improvement of emissions and fuel economy while maintaining good drivability and performance has characterized the development process for this technology. Emissions and fuel economy results indicate that FFVs operating on methanol (M85) can achieve advanced emission standards and reduce air toxic emissions relative to conventional and reformulated gasolines. Toxic air pollutant data from FFVs operating on M85 fuel which achieve Non-Methane Organic Gas (NMOG) emission levels close to the Transitional Low-Emission Vehicle (TLEV) standard indicate reductions in toxic (cancer weighted) risk of 50 to 80 percent for M85 fuel relative to risks associated with gasoline in FFVs and low-emission gasoline vehicles. The data support the conclusion that FFV technology is capable of achieving stringent California emissions standards while reducing air toxic emissions and improving energy based fuel economy relative to existing and reformulated gasolines.

Introduction

The State of California has actively pursued programs to support the development of light-duty methanol vehicles through co-operative efforts with manufacturers, fuel suppliers, and fleet operators since 1980. Limited numbers of dedicated vehicles were placed into demonstration fleets with local and state government agencies in the early 1980s. The largest single demonstration activity involved 1983 model-year dedicated methanol Ford Escorts in which 506 vehicles were produced at Ford's Ft. Wayne, Indiana assembly plant and placed into service in 22 state and local government fleets in California. Some of these vehicles remain in service today nearly ten years after their original deployment.

In the mid 1980s, emphasis shifted to demonstration programs aimed at encouraging development of "fuel flexible vehicle" (FFV) technology in response to limited methanol fuel availability, fueling infrastructure, and resulting vehicle user acceptance issues and other concerns. In 1987, Ford Motor Company produced flexible fuel Crown Victorias, seven of which were delivered to California for field evaluation and demonstration purposes. In 1989, 185 FFV Ford Crown Victorias were placed into fleet service as a follow-on effort. In 1988, General Motors provided its first "variable fuel vehicle" (VFV), a Chevrolet Corsica, for evaluation at the California Energy Commission (CEC) and followed up with delivery of 20 additional vehicles to California in 1989.

Since that time close to 6,000 additional methanol fuel flexible passenger cars and vans have been produced by Ford, General Motors (GM) and Chrysler, and placed into service in California. A major effort to market this technology in California in co-operation with the manufacturers has progressed over the past few years. This experience has been summarized recently. (Patterson 1993)

In this document, we have chosen to undertake an assessment of FFVs as the technology has reached commercial status through emissions certification to California Transitional Low Emission Vehicle (TLEV) standards. The focus of the analysis in this paper is on emissions, fuel economy and performance trends relative to gasoline vehicles and FFVs operating on gasoline. Our analysis does not attempt to assess the development process and engineering required to produce the technology nor undertake any kind of component level assessment.

Methanol Vehicle Development Trends

A summary of the vehicles currently in service in California appears in Table 1. In addition, other manufacturers have produced prototype and preproduction vehicles which are in service with various California agencies under sale, lease or loan arrangements. A list of these vehicles and their key attributes appears in Table 2. These vehicles have been provided to the Commission and local California air quality management districts for evaluation purposes, and to provide a mechanism for feedback of in-field experience and information to assist manufacturers in the vehicle development process.

The early FFV Ford Crown Victorias and VFV Chevrolet Corsicas proved the concept of fuel flexible operation in the field. In these early preproduction vehicles, the manufacturers' top priority was to make the vehicles operate and drive well on all blends of methanol and gasoline ranging from 85 percent methanol to 100 percent gasoline. Fuel economy and emissions were of secondary importance. In 1991, the major U.S. manufacturers produced new FFV and VFV models (GM produced the Lumina, Ford the Taurus and Chrysler the Spirit). These preproduction models were calibrated to achieve better emissions and fuel economy than their earlier counterparts. In 1993, manufacturers delivered production models of these vehicles with dramatically improved emissions and retained good fuel economy, as

Table 1. Current Production FFVs in California

Manufacturer & Model	Number	Displacement	Size
1988 GM Corsica	20	2.8 L	mid-size
1989 Ford Crown Victoria	183	5.0 L	full size
1991 GM Lumina	200	3.1 L	mid-size
1992 Ford Taurus	185	3.0 L	mid-size
1992 Ford Econoline	183	4.9 L	full size
1992 GM Lumina	1192	3.1 L	mid-size
1993 Ford Taurus	2128	3.0 L	mid-size
1993 GM Lumina	61	3.1 L	mid-size
1993 Chrysler Spirit/Acclaim	1739	2.5 L	mid-size
Total FFVs	5891		

Table 2. Other Prototype FFVs in California

Manufacturer & Model	Number	Displacement	Size
1991 VW Jetta	59	1.8 L	compact
1991 Nissan Stanza	1	2.0 L	compact
1991 Nissan NX 1600	16	1.6 L	mini-compact
1991 Toyota Corolla	9	2.0 L	subcompact
1992 Volvo 940-GLE	5	2.3 L	mid-size
1992 Mitsubishi Galant	2	2.0 L	compact
1992 Mercedes Benz 300SE	6	3.2 L	full size
1991 Mazda Protege	1	1.6 L	compact
Total FFVs	99		

the data will show in the latter sections of this paper. These vehicles have achieved 100,000-mile emissions certification under the California Air Resources Board's (CARB) Low Emission Vehicle and Clean Fuel Rule (LEV/CF) as a Transitional Low Emission Vehicle (TLEV).

California's Low-Emission Vehicle Standards

Achieving California's new vehicle emission standards has been and will remain a key development objective for fuel flexible vehicles, as well as dedicated methanol vehicles, which may emerge in the near future. The key elements of the LEV/CF regulations for vehicles include tailpipe emission standards which are significantly lower than federal standards, an early implementation schedule (beginning in 1994), a new and broader definition of hydrocarbon emissions which include all non-methane organic oxygen containing and non-oxygen containing species (termed NMOG), and a fuel neutral approach in establishing

hydrocarbon emission standards through the use of reactivity adjustment factors (RAFs).

The later element of the new regulations recognizes the fact that different vehicle/fuel combinations emit differing NMOG species profiles will react differently in the atmosphere under the influence of sunlight and produce different levels of ozone. By defining and applying reactivity adjustment factors, fuels such as methanol, natural gas, ethanol, liquefied petroleum gas (LPG), hydrogen, reformulated gasoline and others are regulated by the amount of ozone they generate rather than by the grams per mile of hydrocarbon emissions they produce.

As part of the LEV/CF regulations, CARB established four low emission vehicle classes with increasingly more stringent emission limits. These are the "transitional low-emission vehicle" (TLEV), the "low-emission vehicle" (LEV), the "ultra low-emission vehicle" (ULEV) and the "zero-emission vehicle" (ZEV). The emission standards associated with these vehicles and the calculated ozone levels which each would generate are listed in Table 3 (CARB 1990).

Ozone emissions, a measure of photochemical smog, have been calculated in this paper by multiplying CARB approved "Carter" maximum incremental reactivity (MIR) factors (CARB 1991) by the concentration of each hydrocarbon specie found in either exhaust or evaporative emissions profiles. This provides a comparison of emissions based upon the amount of photochemical smog they generate instead of their mass. CARB has established that each gram of methanol tailpipe emissions from TLEVs form approximately 60 percent less ozone than conventional gasoline emissions due to the lower specific reactivity of methanol vehicle emissions (CARB 1991).

Vehicle Data Base

To illustrate trends in emissions and fuel economy, three data bases have been chosen for comparative analyses. The FFV/VFV data base shown in Table 4 includes vehicle data from the Air Quality Improvement Research Program (AQIRP) (CRC 1992) and from CARB test programs undertaken to establish a generic reactivity adjustment factor (CARB 1991) for methanol vehicles achieving the TLEV NMOG exhaust emission standard. This data set also includes the three 1993 production vehicles certified to TLEV standards. Data used from these vehicles represents values certified for 100,000 miles of useful life. Table 5 includes other FFV/VFV data which has been extracted and used from the working data set from Phase I of the AQIRP to illustrate trends and results for FFV model-year comparisons. The gasoline data base shown in Table 6 includes data from vehicles tested by CARB to establish the baseline reactivity adjustment

Table 3. California Air Resources Board Low Emission Vehicle Categories and Standards[1] (g/mile)

Category	NO_x	CO	NMOG	Ozone[2]	Formaldehyde
TLEV	0.40	3.40	0.125	0.428	0.015
LEV	0.20	3.40	0.075	0.237	0.015
ULEV	0.20	1.70	0.040	0.126	0.008
ZEV	0	0	0	0	0

[1]Tailpipe emission standards applicable to all light-duty passenger cars and trucks (under 3,750 lb) beginning in the 1994 model year for 50,000-mile certifications.
[2]Ozone calculated based upon CARB determined specific reactivity for California phase 2 gasoline.

Table 4. TLEV Fuel Flexible Vehicle Test Fleet

No of Vehicles	Vehicle Description	Engine Disp.	Cyls	Fuel System[1]	EGR	Catalyst Type[2]	Catalyst Location[3]	Source[4]
1	1989 Dodge Caravan	2.5L	4	SMPI	N	TWC	UF	AQIRP
1	1990 Dodge Spirit	2.5L	4	SMPI	N	TWC	CC	AQIRP
2	1991 GM Lumina	3.1L	6	MPFI	Y	TWC	UB	CARB
1	1991 VW Jetta	1.8L	4	MPFI	Y	TWC	UB	CARB
2	1992 GM Lumina	3.1L	6	MPFI	Y	TWC	UB	CARB
1	1993 Ford Taurus	3.0L	6	SMPI	Y	TWC	UE	CARB
1	1993 Dodge Spirit	2.5L	4	SMPI	Y	TWC	CC	CARB

[1]SMPI = Sequential multi-point fuel injection; MPFI = Multi-point fuel injection
[2]TWC = Three-way catalyst
[3]UB = Under body; UF = Under Floor; UE = Under engine; CC = Close-coupled
[4]AQIRP = Auto/Oil Air Quality Improvement Research Program; CARB = California Air Resources Board

Table 5. Fuel Flexible Vehicle Fleet Model Year Comparisons

No of Vehicles	Vehicle Description	Engine Disp.	Cyls	Fuel System[1]	EGR	Catalyst Type[2]	Catalyst Location[3]	Source[4]
4	1987 Ford Crown Victoria	5.0L	8	SMPI	Y	TWC	UB	AQIRP
6	1988 Chevrolet Corsica	2.8L	6	MPFI	Y	TWC	UF	AQIRP
2	1990 Dodge Spirit	2.5l	4	SMPI	N	TWC	CC	AQIRP
2	1991 GM Lumina	3.1L	6	MPFI	Y	TWC	UB	CARB
1	1991 Ford Taurus	3.0L	6	SMPI	Y	TWC	UE	CARB
1	1993 GM Lumina	3.1L	6	MPFI	Y	TWC	UB	CARB
1	1993 Ford Taurus	3.0L	6	SMPI	Y	TWC	UE	CARB
1	1993 Dodge Spirit	2.5L	4	SMPI	Y	TWC	CC	CARB

[1]SMPI = Sequential multi-point fuel injection; MPFI = Multi-point fuel injection
[2]TWC = Three-way catalyst
[3]UB = Under body; UF = Under Floor; UE = Under engine; CC = Close-coupled
[4]AQIRP = Auto/Oil Air Quality Improvement Research Program; CARB = California Air Resources Board

Table 6. TLEV Late Model Gasoline Fleet

No of Vehicles	Vehicle Description	Engine Disp.	Cyls	Fuel System[1]	EGR	Catalyst Type[2]	Catalyst Location[3]	Source[4]
1	1989 Dodge Shadow	2.5L	4	MPFI	N	TWC	UF	AQIRP
2	1990 Toyota Celica	2.2L	4	MPFI	Y	TWC	CC/UB	CARB
1	1990 Chevrolet Cavalier	2.2L	4	TBI	Y	TWC	UB	CARB
1	1991 Ford Tempo	2.3L	4	MPFI	Y	TWC	UB	CARB
1	1991 VW Jetta	1.8L	4	MPFI	N	TWC	CC/UB	CARB
2	1992 Buick Lesabre	3.8L	6	MPFI	N	TWC	UB	CARB
1	1992 Ford Crown Victoria	4.6L	8	SMPI	Y	TWC	UF	CARB
1	1992 Ford Tempo	2.3L	4	SMPI	Y	TWC	UF	CARB
1	1992 Ford Thunderbird	3.8L	6	SMPI	Y	TWC	UF	CARB
1	1993 Buick Regal	3.8L	6	SMPI	N	TWC	UF	CARB
1	1993 Pontiac Sunbird	2.0L	4	MPFI	Y	TWC	UF	CARB
2	1993 Saturn	1.9L	4	TBI	Y	TWC	UF	CARB

[1]TBI = Throttle body fuel injection; MPFI = Multi-point fuel injection; SMPI = Sequential multi-point fuel injection
[2]TWC = Three-way catalyst
[3]UF = Under floor; UB = Under body; CC = Close-coupled;
[4]AQIRP = Auto/Oil Air Quality Improvement Research Program; CARB = California Air Resources Board

factors for TLEV, LEV and ULEV gasoline vehicles operating on industry average and California Phase 2 reformulated gasoline (CARB 1992). TLEV vehicles used in this study are listed in Tables 4 (FFVs) and 6 (gasoline vehicles). We have chosen TLEVs as the basis for making comparisons, as these vehicles are required under both California State regulations (in 1994) and federal regulations in the year 2003.

Tailpipe Emission Trends

In order to illustrate the advances in FFV technology over the years, the non-methane organic gas (NMOG) and calculated ozone emissions are shown in Figure 1 for a number of FFV models in the data base (listed in Table 5). As can be seen from this figure, the NMOG emissions and resulting ozone for 1993 production models have dropped by 20 percent to 30 percent over early prototype vehicles. Also labeled on the figure is the ozone level calculated for the gasoline TLEV NMOG standard of 0.125 g/mi times the specific reactivity of 3.42 grams ozone per gram NMOG (for an average TLEV on industry average gasoline) (CARB 1992). *The production FFVs operating on M85 produce 14 to 64 percent less ozone than the calculated limit for a TLEV operating on industry average gasoline.*

Earlier studies comparing FFVs to conventional gasoline vehicles, such as the Auto/Oil Air Quality Improvement Research Program (AQIRP) (Auto/Oil 1992) compared late model gasoline vehicles with early prototype FFVs. As shown in Figure 2, AQIRP FFVs showed only a 35 percent improvement in ozone emissions when operating on M85 and a 41 percent increase in ozone emissions when operating on industry average gasoline (RF-A) compared with late model gasoline vehicles operating on industry average gasoline. AQIRP's best reformulated gasoline (RF-C) showed a 15 percent reduction in ozone emissions in late model gasoline vehicles. By comparing newer model FFVs which have emissions in

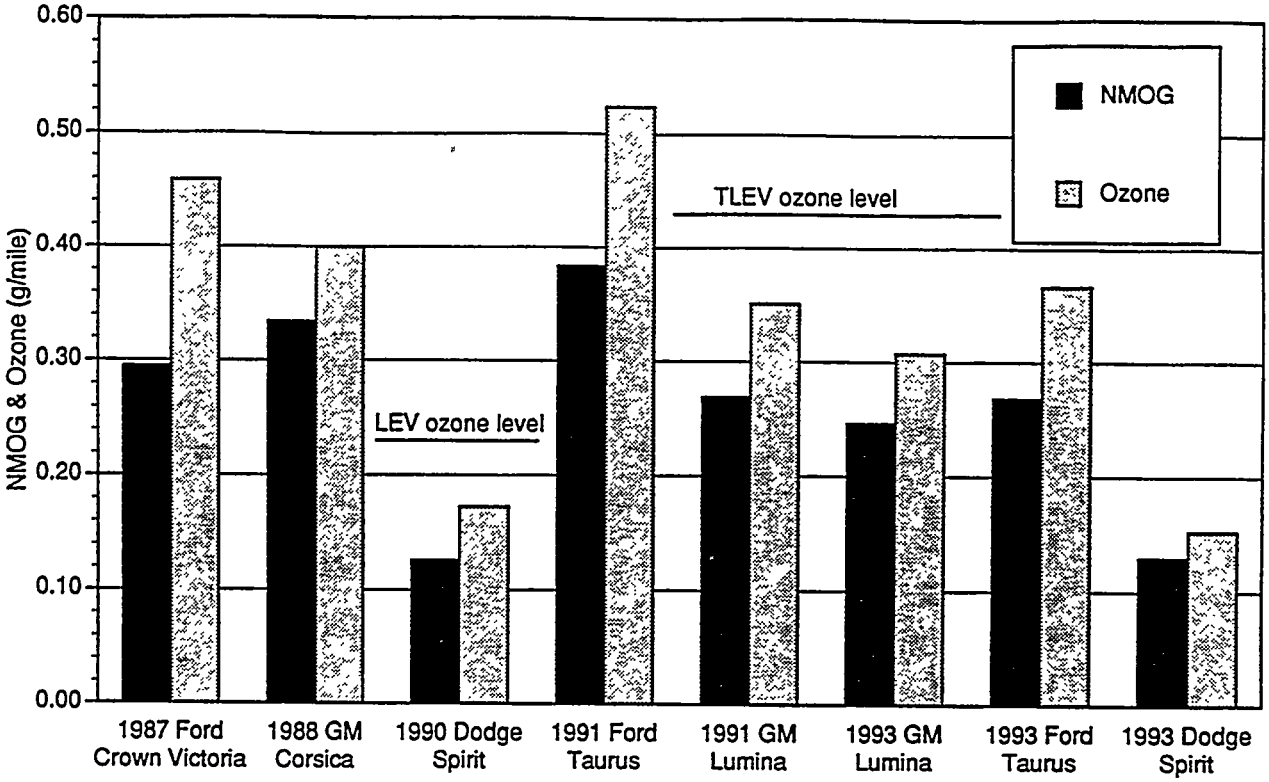


Figure 1. FFV model year comparisons of NMOG and ozone emissions

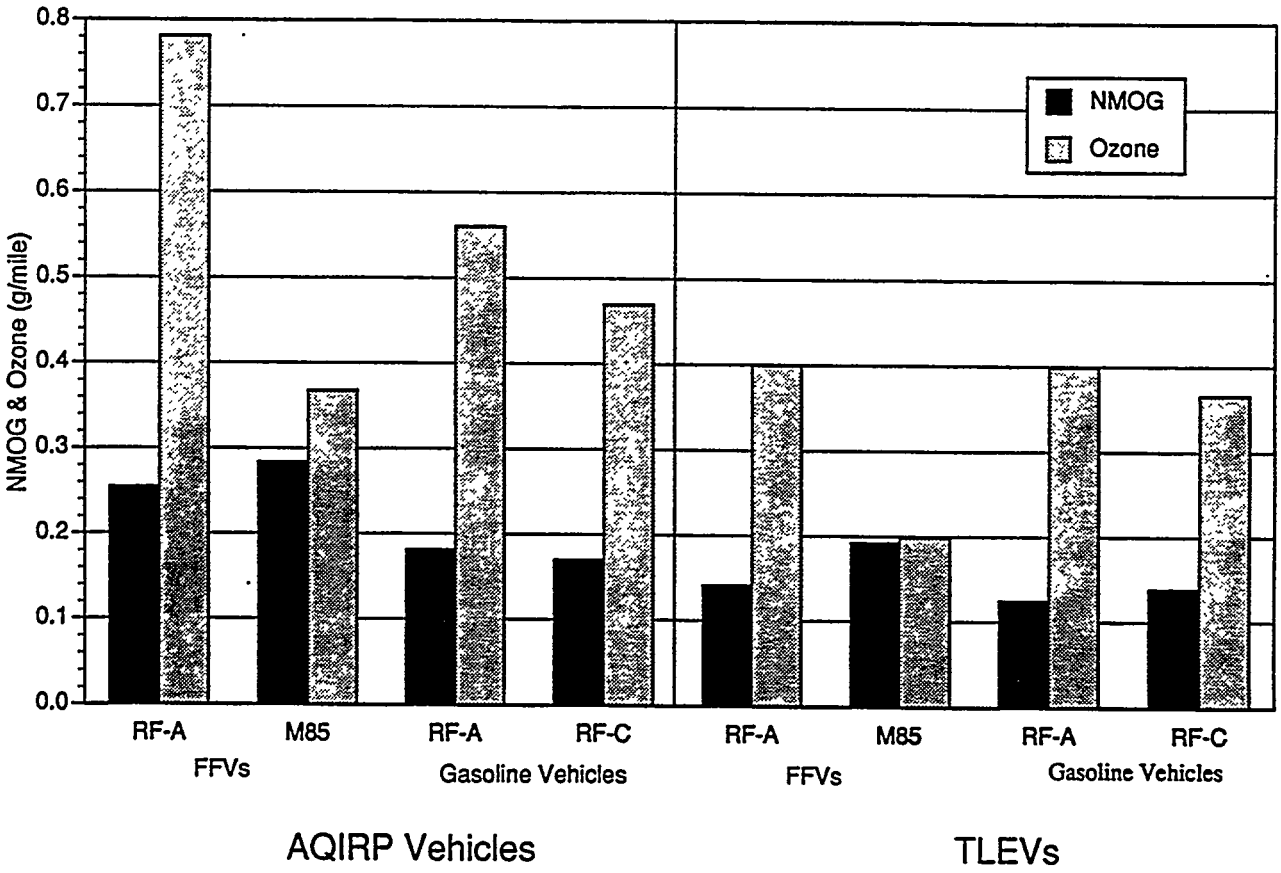


Figure 2. Comparison of AQIRP and new TLEV data

the TLEV range to late model gasoline vehicles with emissions in the TLEV range, *FFVs produce 50 percent less ozone when operating on M85 and the same ozone when operating on conventional gasoline as conventional TLEV gasoline vehicles operating on conventional gasoline.*

Figure 3 shows the improvement in FFV NO_x emissions from early prototypes to production FFVs. As can be seen from this figure, two of the three production FFVs produce NO_x levels at or below the LEV standard of 0.2 g/mile.

Formaldehyde emissions are shown in Figure 4. Formaldehyde emissions are typically higher from methanol vehicles as formaldehyde is an intermediate step in methanol combustion. Formaldehyde has been of concern with methanol vehicles, due to its air toxic designation and a rather high photochemical reactivity. However, as methanol technology has progressed, the data indicates that formaldehyde emissions have been lowered to levels consistent with the emission limits shown in Table 3. In fact, formaldehyde emissions decreased dramatically from the early prototype vehicles to the production FFVs, with production vehicles producing formaldehyde levels well within the 50,000 mile TLEV formaldehyde tailpipe standards over a 100,000 mile lifetime.

While formaldehyde tailpipe emissions from methanol vehicles can be 4 to 10 times higher than those of gasoline vehicles, *gasoline vehicles emit other highly reactive substances which react in the atmosphere to produce more ozone and formaldehyde than methanol vehicles when both vehicles achieve similar NMOG emissions.* Figures 5 and 6 show emissions profiles and ozone produced for an FFV and a gasoline vehicle which achieve NMOG mass emissions of 0.145 and 0.135 grams per mile, respectively. While not certified to the TLEV level of 0.125 grams per mile, these vehicles illustrate the relative levels of reactive emissions contributing to total ozone that would be expected from TLEV vehicles.

The increased aromatic and olefin emissions from the gasoline vehicle produce significantly more ozone than the ozone produced from the increased formaldehyde emitted by the FFV on M85. As can be seen, *gasoline vehicle aromatic emissions alone contribute more ozone than all organic emissions from FFVs.* Aldehydes (primarily formaldehyde) contributes 34 percent (and the largest share) of the ozone from FFVs, however, the combination of mass and reactivity of the olefins alone in the gasoline vehicle results in nearly twice that ozone level. Additionally, gasoline vehicle aromatics produce over three times the ozone associated with aldehydes from FFVs.

Figure 7 shows NMOG and ozone emissions for late model TLEV FFVs and late model TLEV gasoline vehicles listed in Tables 4 and 6. The ratio of ozone to NMOG emissions shown in the figure defines the reactivity of the exhaust. M85 in these FFVs again shows substantial benefits in terms of ozone over gasoline vehicles on industry average (RF-A), Auto/Oil program's best reformulated (RF-C) gasoline and California reformulated gasoline. FFVs on M85 produce over 50 percent less ozone than gasoline vehicles on industry average gasoline due to its significantly reduced reactivity. California reformulated gasoline reduces ozone emissions by about 30 percent by reducing the amount of NMOG instead of the reactivity of the exhaust.

Evaporative Emissions

Evaporative emissions play an important role in the formation of ozone from automobiles. Diurnal emissions occur when the fuel tank breathes in air at night as it cools down and then breathes out air and fuel vapors as it heats up during the day while the vehicle is parked. Hot soak emissions result after the engine is shut off and fuel "boils" out of the fuel system due to being heated by the engine. In addition, running loss emissions are evaporative emissions emitted from the vehicles while in operation.

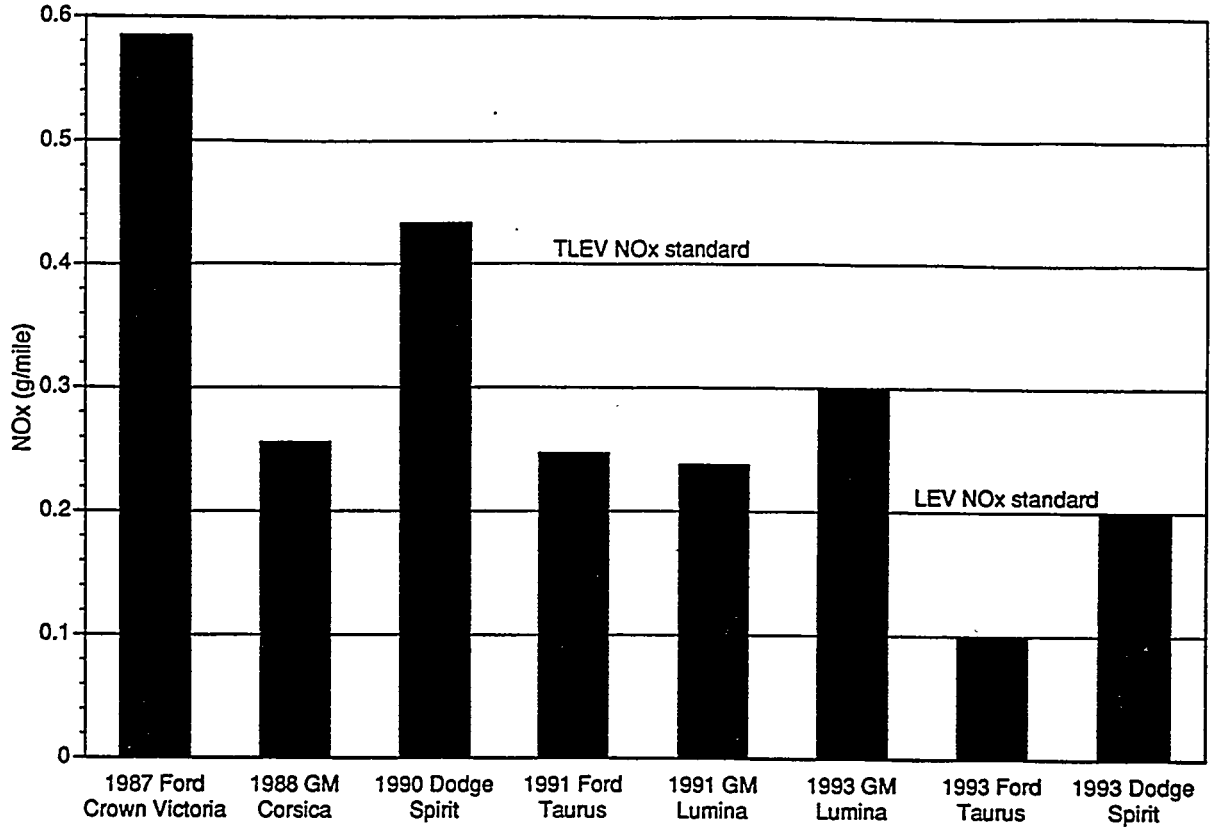
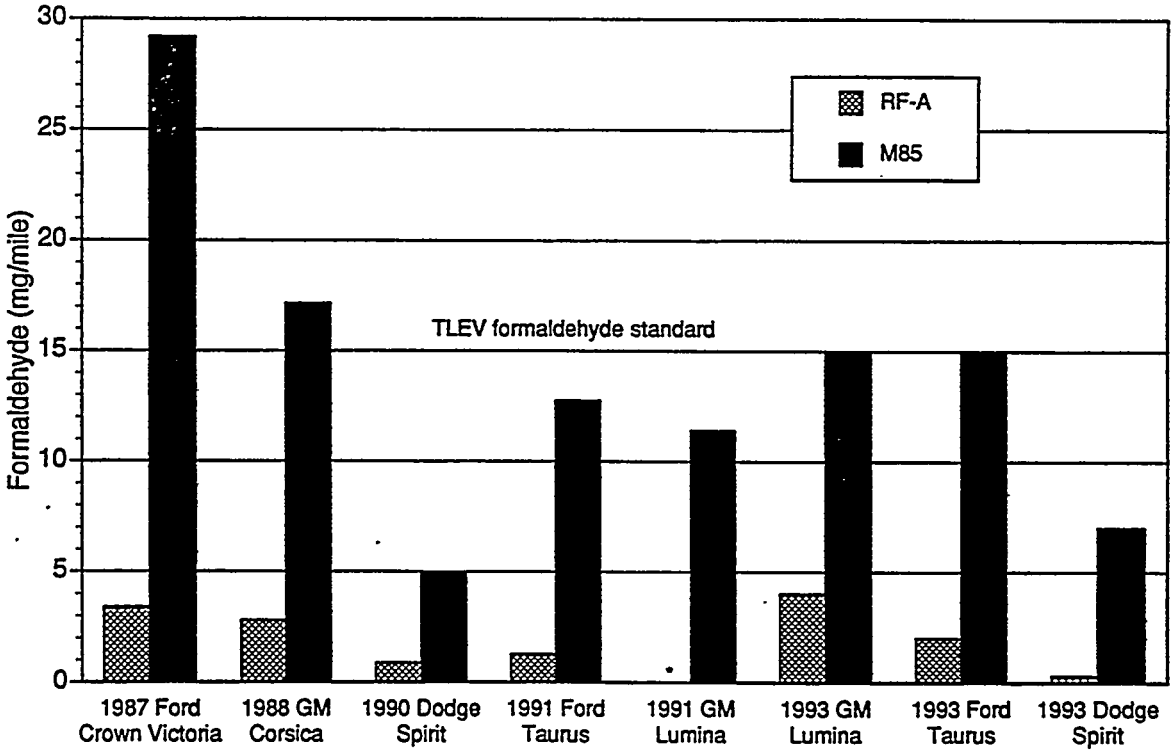


Figure 3. FFV model year NO_x emission comparisons



* Formaldehyde data not available on

Figure 4. FFV model year formaldehyde emission comparisons

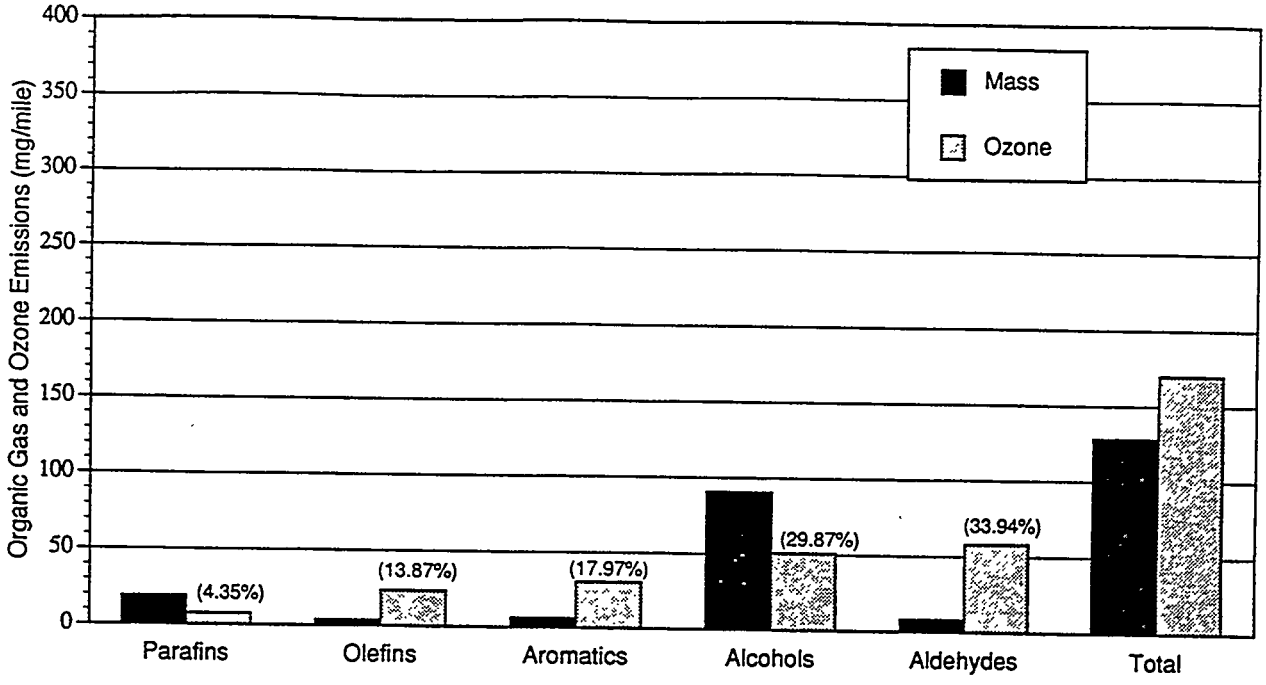


Figure 5. Breakdown of emissions reactivity for a 1990 Dodge Spirit FFV on M85

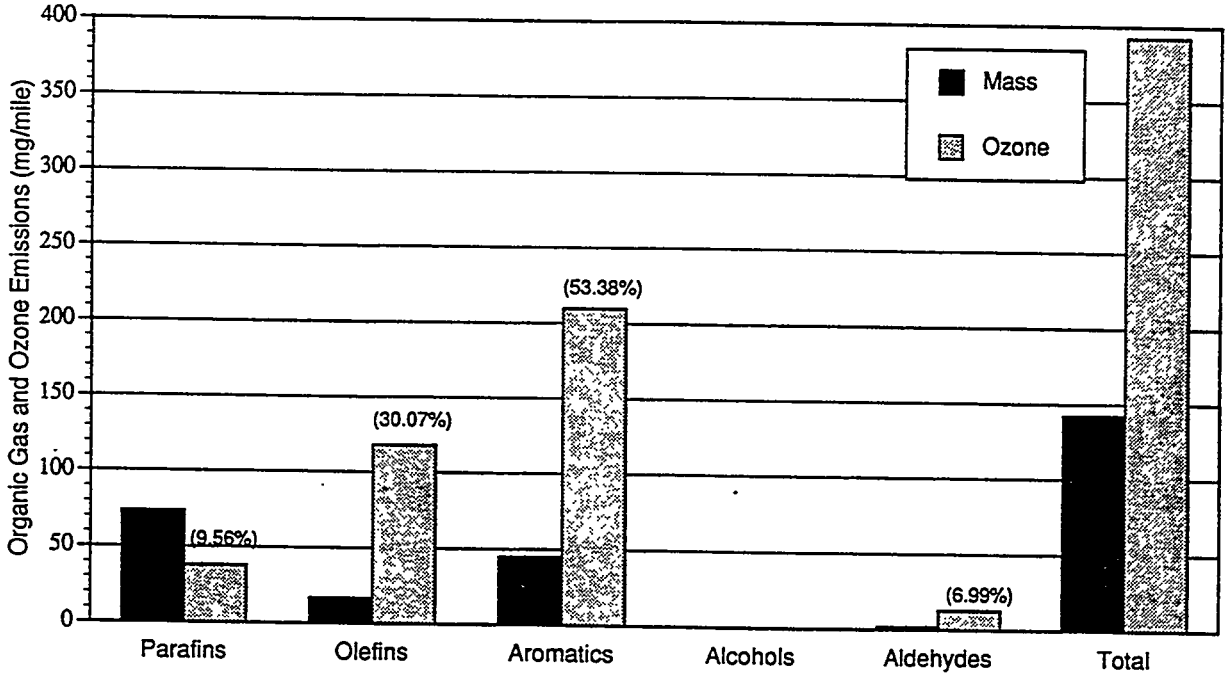


Figure 6. Breakdown of emissions reactivity for a 1991 Ford Tempo on industry average gasoline

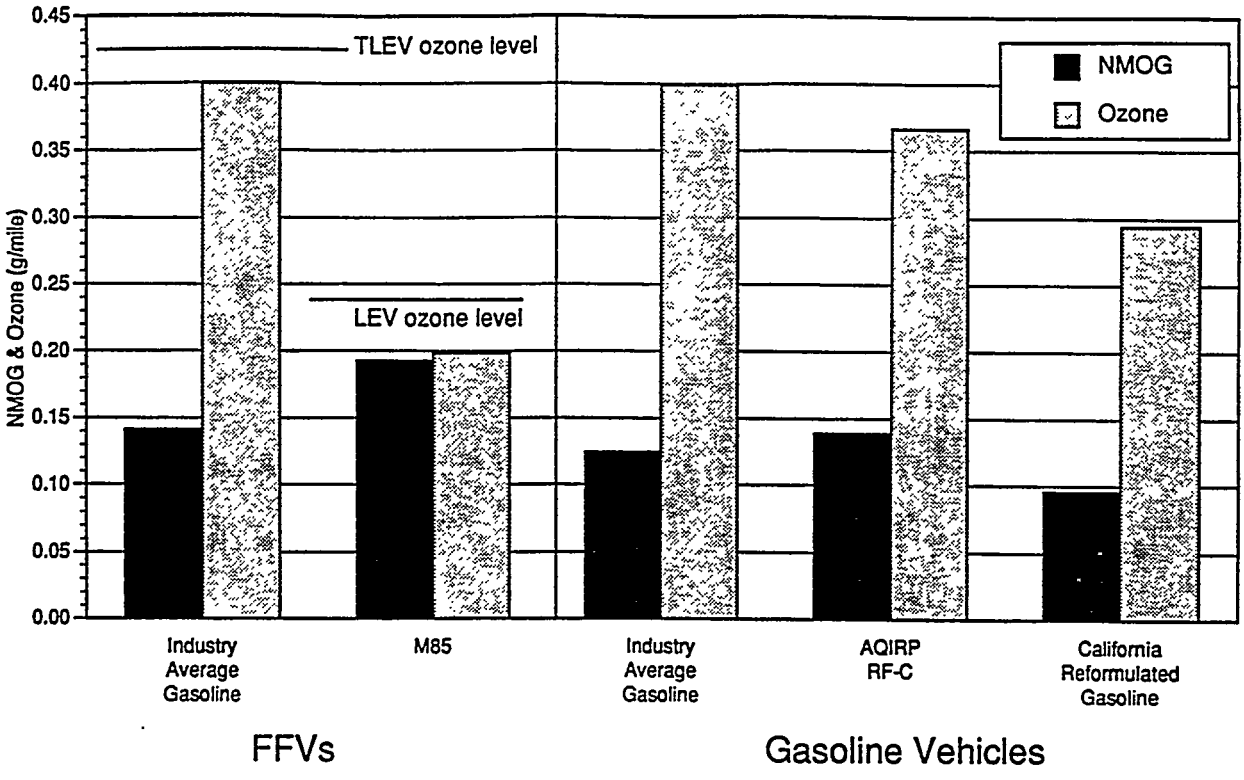


Figure 7. NMOG and ozone comparisons for TLEV FFV and gasoline fleets listed in Tables 4 and 6

M85 fuel is blended with conventional gasolines and is controlled to produce approximately the same vapor pressure as conventional gasoline. In California, the summertime gasoline Reid Vapor Pressure is currently limited to 7.8 psi, as is commercially available M85 fuel. As the percentage of methanol in the fuel tank decreases, however, (due to fueling on gasoline after fueling on methanol), the vapor pressure of the fuel mixture increases, thereby potentially increasing the amount of evaporative emissions. Some early FFV prototypes were not built to handle this increase in vapor pressure and thus had high evaporative emissions when operating on low methanol content fuel. Newer technology FFVs are designed to meet current evaporative emissions standards on the highest vapor pressure mixture of methanol and gasoline, namely 10 percent methanol and 90 percent gasoline (M10).

Limited speciated evaporative emission data exists, however, several vehicles were tested as part of the AQIRP program and some manufacturers' data is available. Figure 8 compares diurnal NMOG and resultant calculated ozone emissions for FFVs and gasoline vehicles. Figure 9 compares hot soak NMOG and ozone emissions. As seen from these two figures, the reduced reactivity of methanol evaporative emissions results in net ozone reductions. This data supports the concept of a reactivity adjustment factor for evaporative emissions from vehicles fueled with M85 and other low-reactivity fuels. Current CARB regulations do not incorporate the use of reactivity adjustment factors for any fuel in the determination of compliance with evaporative emissions standards.

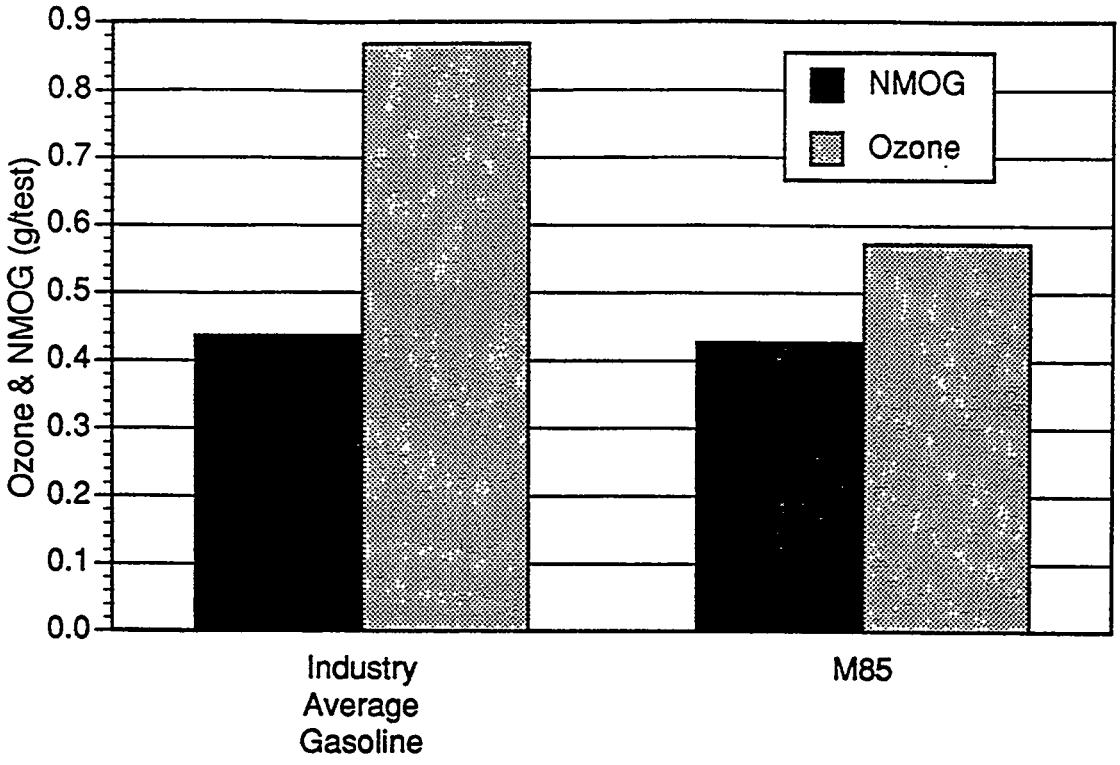


Figure 8. Diurnal evaporative emissions comparisons for TLEV vehicles listed in Tables 4 and 6

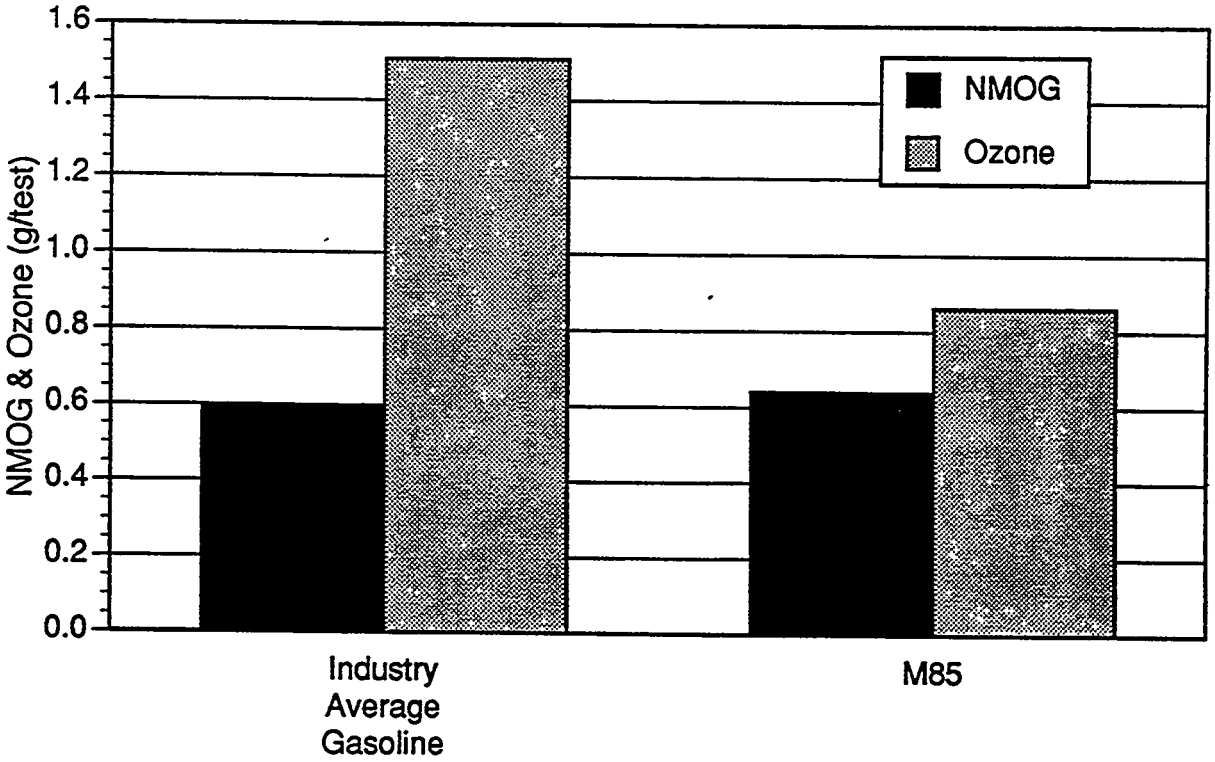


Figure 9. Hot soak evaporative emissions comparisons for TLEV vehicles listed in Tables 4 and 6

Toxic Emissions

Toxic emissions from vehicles pose a potential cancer risk. The cancer risk, estimated by the regulatory agencies, has the units of cancer incidences per million people exposed to one microgram of the toxic substance per cubic meter for a seventy year lifetime exposure. The most important toxic air emissions found in light duty vehicle exhausts are 1,3-butadiene, benzene, formaldehyde and acetaldehyde. Their relative risk factors as determined by CARB (CARB 1993)and the U.S. Environmental Protection Agency (EPA) (EPA 1993) are listed in Table 7. Gasoline exhaust emissions contain 1,3-butadiene and benzene with lower amounts of formaldehyde and acetaldehyde. Methanol, in its pure form emits only formaldehyde when combusted in an engine, but these concentrations are typically much higher than those from gasoline. M85, which contains gasoline, also produces benzene, acetaldehyde and 1,3-butadiene emissions, but at much lower concentrations than found in gasoline emissions. By taking the concentration of these compounds in a vehicle's exhaust and applying the relative potency weighting factors derived from in Table 7, the relative toxicity of the emissions from various fuel/vehicle combinations can be calculated. Figure 10 shows the relative potency of FFVs fueled on M85 and conventional gasoline (listed in Table 4), and gasoline vehicles when operating on industry average, Auto/Oil program RF-C reformulated and California reformulated gasolines (listed in Table 6) using CARB toxic risk factors. The toxic risk of each fuel has been normalized to industry average gasoline in a gasoline vehicle. As can be seen from this figure, M85 exhaust emissions from the fleet of vehicles achieving NMOG emission levels close to the TLEV standard of 0.125 grams per mile are 80 percent lower in weighted cancer potency than gasoline emissions. Furthermore, the four-fold increase in formaldehyde risk relative to gasoline formaldehyde emission risk is more than offset by gasoline's significantly higher benzene and 1,3-butadiene risk. California reformulated gasoline also shows some reduction in toxic emissions by limiting benzene.

Table 7. Unit Risk Factors of Cancer Potency (estimated cancer incidences per million people exposed to one microgram per cubic meter for a seventy year exposure)

Compound	CARB	EPA
1,3-Butadiene	170	280
Benzene	29	8.3
Formaldehyde	6	13
Acetaldehyde	2.7	2.2

Figure 11 compares risks among the various fuels and vehicles using EPA factors and CARB factors. Both sets of data have been normalized to gasoline in a gasoline vehicle. The CARB factors applied to the methanol yield 80 percent lower risk than gasoline while the EPA factors yield a 70 percent reduction in toxicity. Though not shown on this figure, the EPA factors yield a cancer risk 21 percent lower the base gasoline risk derived from the CARB factors due primarily to the EPA's lower risk factor for benzene.

Fuel Economy

M85 has an octane rating of 102, 14 octane higher than regular unleaded gasoline. However, since about 1.75 gallons of M85 have approximately the same energy as one gallon of gasoline, FFVs using M85 have only about 60 percent of the range of typical gasoline vehicles given the same fuel tank size. Currently, most of the FFVs placed in service in California have larger fuel tanks to extend the range for operation on M85. In addition, the data shows efficiency improvements for FFVs using M85 relative to gasoline as discussed below. This efficiency gain also helps to extend the range of FFVs when operating on M85. To more fairly compare different fuels, gasoline equivalent mileage is used here instead of actual mileage

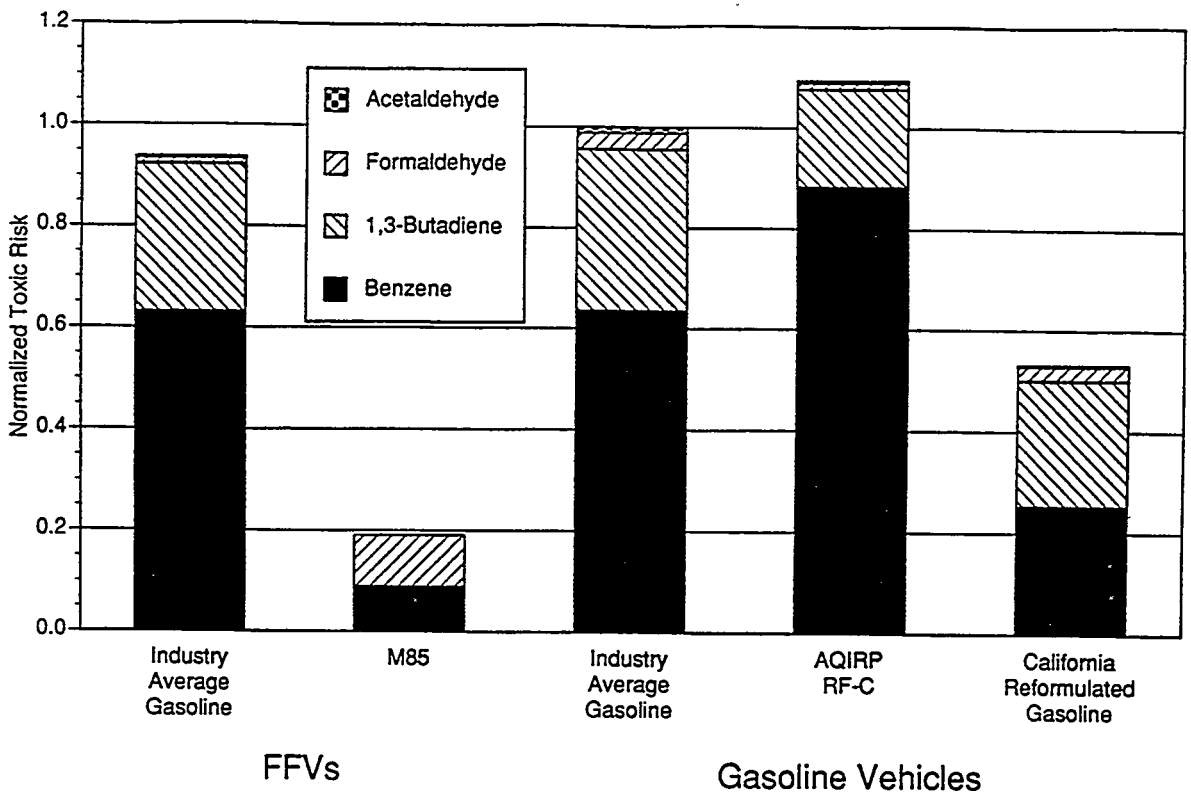


Figure 10. Normalized toxic risk comparisons of TLEV FFVs and gasoline vehicles

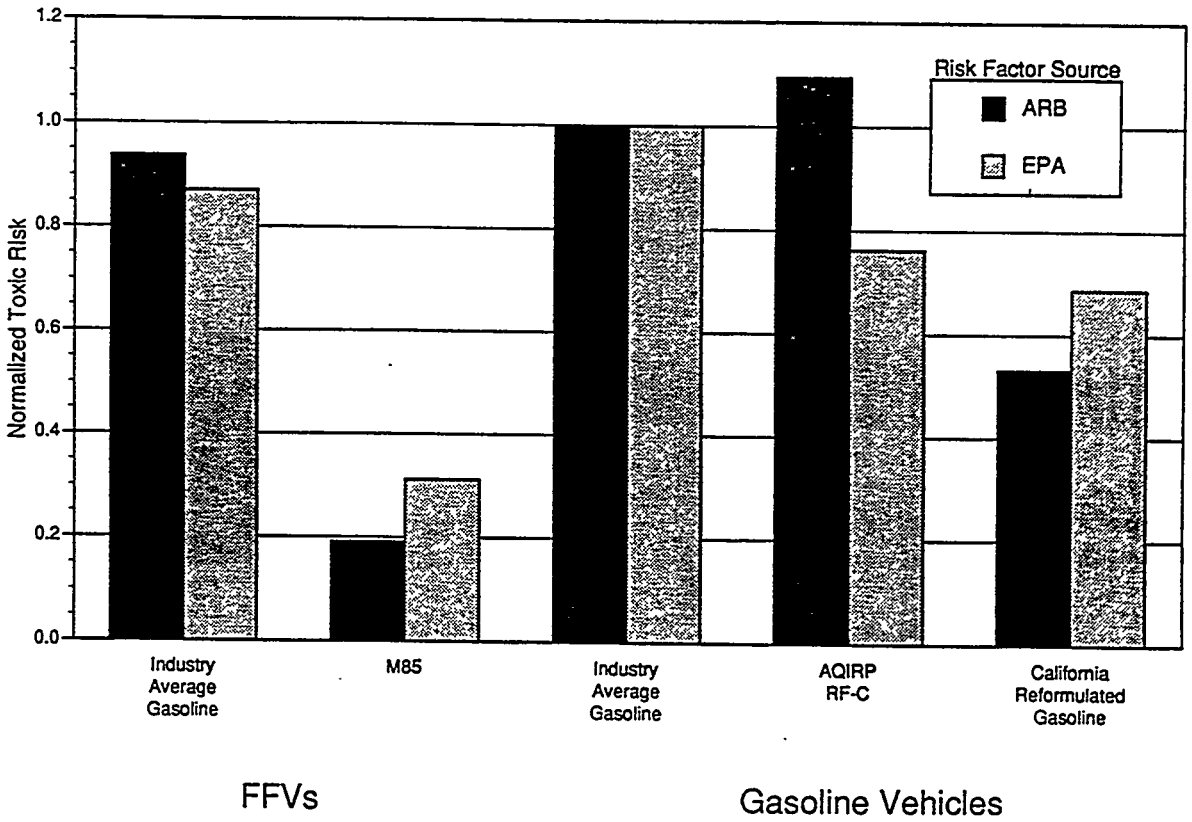


Figure 11. Normalized toxic risk comparisons for TLEV FFVs and gasoline vehicles

to compare gasoline and M85 fuel economy. Thus 20 miles per gallon gasoline equivalent is equal to approximately 12 miles per actual gallon of M85.

As shown in Figure 12, the gasoline equivalent mileage of current FFVs on M85 is slightly higher than that on conventional or reformulated gasoline. In general, about 3 to 11 percent better mileage (on a gasoline equivalent basis) is seen in the data when operating on M85 than when operating on conventional gasoline. California reformulated gasoline reduces vehicle mileage by a few percent relative to industrial average gasoline.

Figure 13 shows comparisons of production FFVs certified to the California TLEV standards on M85 and gasoline. For all three models, methanol is shown to have superior gasoline equivalent fuel economy. The results based upon city cycle data yield on average an 8-percent benefit for M85 fuel in gasoline equivalent fuel economy.

M85 Fuel Substitution Ratio Trends

The fuel substitution ratio, defined as the ratio of gasoline volumetric fuel economy to M85 volumetric fuel economy in an FFV, is useful for estimating petroleum displacement potential and calculating per mile fuel costs for the two fuels. Though we have not compared emissions — certified FFV fuel economy values with the gasoline counterpart vehicle, limited analysis and historical data suggests that an FFV will ultimately achieve the same gasoline fuel economy as the dedicated gasoline version of the same vehicle.

A review of the AQIRP Phase I data (CRC 1992) indicates that the 19 early prototypes and pre-production FFVs in that program achieved fuel economy substitution ratios of 1.63 to 1.80 for the urban (city) driving cycle of the U.S. Federal Test Procedure. Given the ratio of measured energy contents on a volumetric basis of 1.77 for M85 to industry average gasoline used in the AQIRP program, these numbers imply energy specific fuel economy gains for FFVs operating on M85 ranging from +8.7 to -1.5 percent. Only one vehicle of the 19 shows a decrease in the energy specific fuel economy on M85 relative to gasoline.

Ford, General Motors and Chrysler vehicles yield city driving fuel substitution ratios of 1.60 to 1.68 and highway cycle results of 1.63 to 1.72 gallons of M85 per gallon of gasoline in certification results. On average, data for the three models of FFVs yield an average 1.64 fuel substitution ratio for combined city and highway driving. This ratio represents about 8 percent gasoline equivalent fuel economy gain for M85 relative to gasoline. Figure 13 illustrates the comparison relative to gasoline for the three U.S. manufacturers.

Conclusions

The data presented in this paper support the following observations and conclusions:

- Fuel flexible vehicle technology can achieve stringent California emissions standards applicable to 1994 model year passenger cars as demonstrated by the certification of 1993 model year FFV and VFV vehicles by Ford Motor Company, General Motors Corporation and Chrysler Corporation.

- Application of cancer risk factors to toxic air emissions associated with FFV and gasoline vehicle technology demonstrates that methanol can reduce excess cancer risk associated with conventional and reformulated gasolines in the range of 50 to 80 percent. This conclusion holds true whether applying CARB or EPA cancer risk factors to the toxic emissions data. A 54 percent reduction in toxic risk using the EPA factors represents the least benefit achievable with M85 fuel for the data base examined.

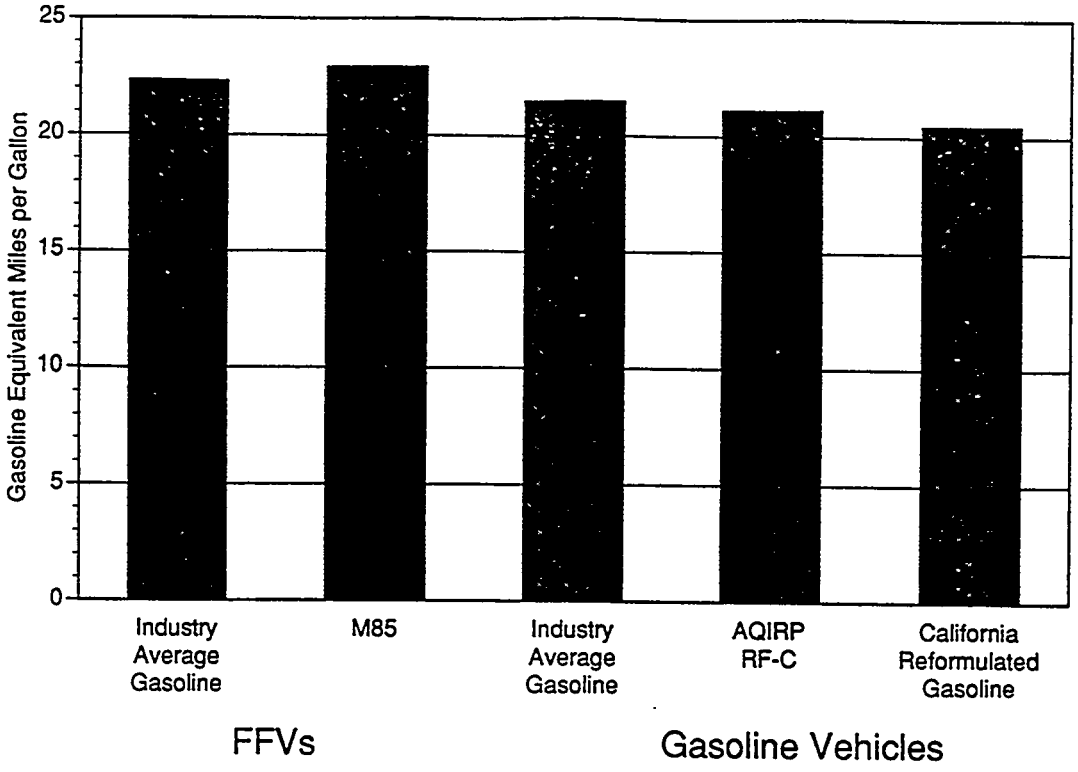


Figure 12. Gasoline equivalent fuel economy comparisons for TLEVs — U.S. Federal test procedure

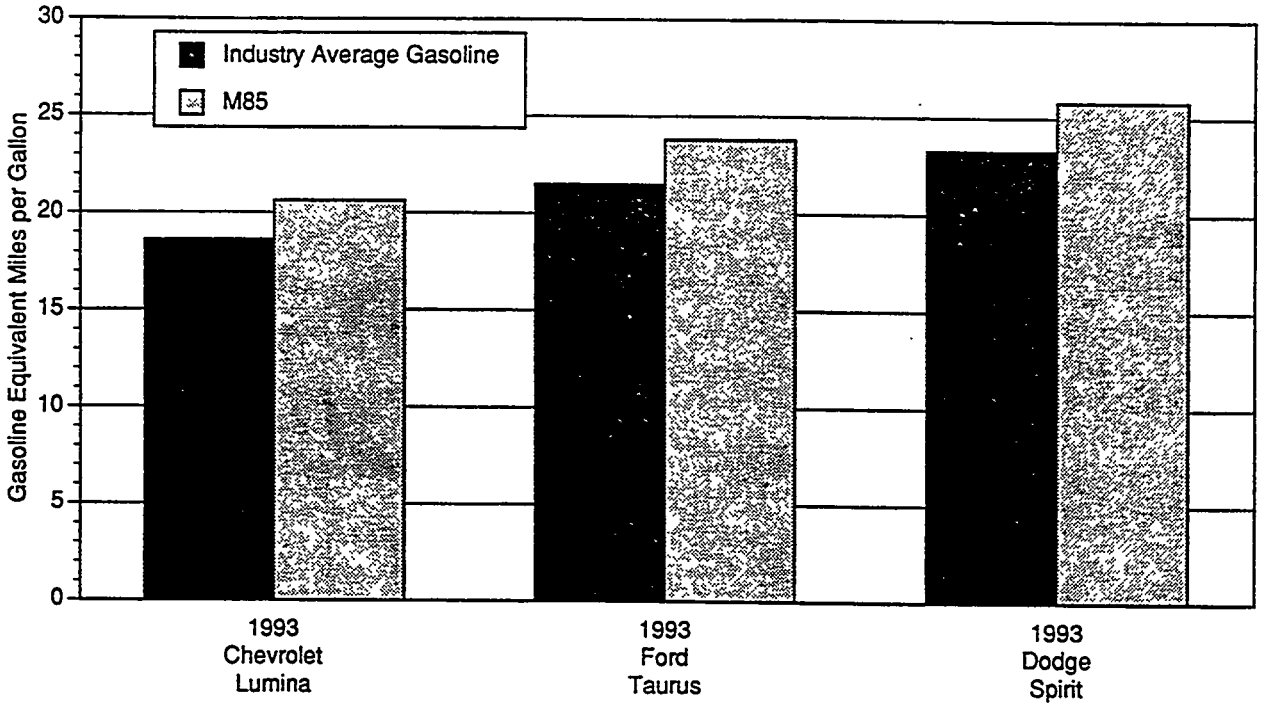


Figure 13. Production FFV gasoline equivalent fuel economy comparisons

- Ozone trends data using the CARB adopted Carter reactivity factors indicate improvement over time. Additionally, ozone results for vehicles achieving TLEV or close to TLEV NMOG emission levels show a 45 percent reduction in ozone relative to the average of FFV results of the Phase I AQIRP.

- NO_x and formaldehyde results illustrate that current FFV technology meets TLEV for formaldehyde and close to the LEV California emission standards for NO_x.

- Fuel economy trends indicate that gasoline equivalent (energy specific) fuel economy for FFVs using M85 fuel is consistently better than equivalent vehicles operating on industry average and California Phase 2 gasoline. The 1993 vehicles yield the best results to date with all three manufacturers achieving 11 percent improvements in the city cycle and combined city and highway results 8 percent better than operation on gasoline.

Disclaimer

The views expressed in this paper are those of the authors and do not necessarily reflect the views or position of the California Energy Commission or Acurex Environmental Corporation.

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CANADIAN METHANOL LIGHT DUTY VEHICLE PROGRAM

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Abstract

The Canadian Oxygenated Fuels Association, with assistance from: the federal government, three provincial governments, automobile manufacturers, fuel marketers, fuel dispensing equipment industry, and others, have initiated a National Methanol Light Duty Vehicle Demonstration Program. This program started in 1991 with the following objectives: to supply flexible fuelled methanol vehicles to fleet users to operate in the Canadian climate; to provide a methanol fuel infrastructure in those areas where the vehicles will be located; and to address technical/developmental issues in the implementation of methanol fuel in Canada. This paper reviews the main results to date.

CANADIAN METHANOL LIGHT DUTY VEHICLE PROGRAM

Introduction

The Canadian Methanol Light Duty Vehicle Program (MLDVP) was initiated as a joint undertaking of the Canadian Oxygenated Fuels Association, Natural Resources Canada (previously Energy, Mines and Resources Canada), Ontario Ministry of the Environment and Energy, Alberta Ministry of Energy, General Motors Canada (and subsequently joined by Chrysler Canada, Ford Canada and Volkswagen Canada), and two fuel retailers (Sunoco and Mohawk).

The MLDVP is a market demonstration of methanol fuelled vehicles in Canada.

Background

Over the last several years, the need for alternative clean-burning fuels has become increasingly important for North America. Energy security and clean air initiatives in the United States, and California in particular, resulted in the automobile manufacturers developing the methanol flexible fuel vehicle. This vehicle, with the capability to run on methanol, gasoline or any combination of the two, provides for a transition vehicle to help bridge the gap between today's gasoline fuel-based market and the development of the required fuelling infrastructure for methanol fuel.

In 1990, COFA approached General Motors with the concept of a Canadian methanol vehicle demonstration project, with GM providing "Canadian" versions of their 1991 VFV Lumina to a joint public and private sector program to test these vehicles in the challenging Canadian climate. Therefore, in February of 1991, the Canadian Methanol Light Vehicle Demonstration Program was initiated.

Objectives

The MLDVP was launched in 1991 as a methanol-fuelled market demonstration program with the following objectives:

* To supply flexible fuel methanol vehicles to users to operate in the Canadian environment;

* To provide a methanol fuel infrastructure in those areas where vehicles will be located;

* To address on-going technical and developmental issues in the implementation of methanol as a viable alternative vehicle fuel in Canada; and

* To communicate to the Canadian public the role of methanol fuel as a clean air alternative to gasoline and energy security considerations.

* To assess the market for clean-fuelled methanol vehicles in a Country which does not have an air quality agenda.

Implementation Phases

The MLDVP has evolved into three distinct phases:

Phase I: Technical Assessment (1991/92)

This initial phase of the program involved the technical assessment of 10 GM VFV Luminas in controlled fleets, the provision of methanol fuel infrastructure (two in-ground and three temporary facilities) to support the fleet, and the marketing of methanol fuel to the fleet market.

Phase II: Fleet Assessment (1992/94)

This phase is assessing the fleet market for up to 550 FFV vehicles from General Motors, Chrysler, Ford and Volkswagen including expanding the fuel infrastructure from two in-ground stations to twenty-five. A program office was initiated with a full-time program manager. Business plans were prepared for the three Canadian Provinces (Ontario, Alberta and British Columbia) the program is currently focussed in. A community program was initiated Kamloops, British Columbia in 1993 in association with the automobile manufacturers to assess the market for methanol vehicles with the general car-buying public.

Phase III: Market Assessment (1994/97)

This phase targets the general consumer in those regions with developed methanol fuel infrastructure. The placement of five thousand vehicles and the continued expansion of the methanol service station network is planned.

All phases include providing methanol vehicles to Environment Canada's alternative fuel emission testing program.

Current Status (September 1993)

Fuel Infrastructure. Table 1 illustrates the current status of the commercial stations placed to date in Canada under this program and includes the outlook to the end of this program year (1993/94).

Table 1. Commercial Fuel Stations

	Current	New	Total
Toronto, Ont.	2	6	8
Calgary/Edmonton	1	7	8
Medicine Hat, Alta.	-	1	1
Vancouver,	1	4	5
Kitimat,	-	1	1
Kamloops, B.C.	1	1	2
TOTAL	5	20	25

Note: In addition, 6 portable methanol stations are in place.

The fuel infrastructure installations has included both dedicated M85 and M100 with pump blending. A typical M85 installation would be as follows:

* Various dispenser/pumps including:
  - Red Jacket
  - GasBoy; and
  - Bennett.
* Steel and fibreglass tanks.
* Cross-linked polyethylene hoses and nickel plated aluminum swivels.
* Nickel plated aluminum OPW nozzles.
* 1 micron Cim-tek spin-on filters.
* Double-walled containment and vacuum monitoring and alarm systems.

The typical cost summary for these installations is documented in Table 2. This cost (in Canadian dollars) is based on a M85 installation in Calgary Alberta in 1992.

Table 2.
M85 Fuel Station Cost

Equipment	
- Tankage	$ 8,000
- Dispenser	$ 3,600
- Pump	$ 1,800
- Other	$ 7,000
	$20,400
Installation	
-Contractor	$15,500
Permits/Engineering	$14,100
TOTAL	$50,000

Note: Installation category included cardlock and contractor supplied equipment. The cost in U.S. dollars is approximately $38,500

The alternative method of blending M85 at the fuel dispenser was installed at one location. It used the following equipment:

* Wayne/Dresser electronic blending dispenser.
* Red Jacket submersible pump.
* Fibreglass tank.
* Cross-linked polyethylene hose and nickel plated aluminum swivels.
* Nickel plated aluminum OPW nozzle.
* 1 micron Cim-tek spin-on filter.
* Double-walled containment, vacuum monitoring and alarm system.

A typical pump blending installation would be as shown in Table 3. These costs (in Canadian dollars) are based on a pump blending installation in Toronto, Ontario in 1992.

Table 3.
Pump Blending Fuel Station Cost

Equipment	
- Tankage	$11,700
- Dispenser	$10,000
- Pump	$ 1,800
- Other	$ 6,850
	$30,350
Installation	
-Contractor	$23,150
Permits/Engineering	$16,500
TOTAL	$70,000

Note: Installation included contractor supplied equipment. The cost in U.S. dollars is approximately $54,000.

It was quickly determined that a third type of methanol refuelling infrastructure was required to support the demonstration program. This requirement was for a portable methanol fuel station which could be utilized to support central refuelling of FFV's in fleet use. The system was designed, tested and manufactured by Clemmer Industries of Waterloo, Ontario. Figure 1 illustrates the current version of this tank system.

The portable station is available in sizes up to 7,500 litres and currently includes a GasBoy commercial-use pump (modified for M85 use by Clemmer). The current cost of the system in Figure 1 is approximately $6,000 (Canadian). A "Weights and Measures" pump is currently being tested at a Department of National Defence fleet demonstration site in Toronto, Ontario. This pump uses a new Clemmer Dissimilar Metals Limiting Kit in a GasBoy methanol island pump.

Methanol Vehicles. The MLDVP was initiated with 10 vehicles from General Motors Canada in 1991. Chrysler Canada and Ford Canada subsequently joined the program in 1992 offering limited numbers of vehicles for the Canadian marketplace. Table 4 illustrates the current status of the FFV's placed to date including the outlook to the end of this program year.

Table 4. Vehicles

	Current	New	Total
Ontario	35	100	135
Alberta	10	250	260
British Columbia	50	100	150
TOTAL	100	450	550

The vehicles made available to the program by calender year is as follows:

1991 General Motors Lumina

1992 General Motors Lumina

1993 Chrysler Spirit/Acclaim
Ford Taurus
VW Jetta/Golf

1994 Chrysler Intrepid
Chrysler Spirit/Acclaim
Ford Taurus
VW Jetta/Golf

Methanol Fuel Pricing. A key factor in the conduct of this demonstration is the ability of the Canadian methanol industry to compete with regular grade gasoline on price and an energy equivalent basis. This is due to the fact that three Canadian provinces (Ontario, Alberta and British Columbia) have given methanol fuel road tax exemption in order to make up for the initial higher distribution costs associated with an alternative fuel launch. In addition, the federal government exempts methanol fuel from the excise tax.

In addition, it is the position of the Canadian methanol industry that M85 fuel will continue to be competitive with regular gasoline as long as road taxes are on an energy equivalent basis to Gasoline. A recent study commissioned by the methanol industry ("Economics of Canadian New Methanol Supply", Syngen Enterprises Ltd., Berkeley, California, 1992.) found that for Canada's major market area (southern Ontario), transportation economies of scale would more than off-set the imposition of fuel taxes.

Main Findings

Although the demonstration program is still at an early stage in its life-cycle, there is considerable field experience to present the main findings to date.

1. Given that methanol vehicles are priced equivalent to gasoline versions, and the fuel priced equivalent to gasoline, the lack of a significant refuelling infrastructure is the main constraint to FFV vehicle sales to the fleet market. (This result is also supported by a recent survey of FFV fleet users by the National Association of Fleet Administrators.)

2. The lack of regulations applicable to methanol fuel and the various regulatory organizations (for example, Fuel Safety, Fire Code, Weights and Measures) lack of familiarity with methanol fuel, results in more stringent requirements than for gasoline, and typically results in longer than expected approval periods.

3. Most, if not all current offerings of "methanol compatible" infrastructure components are not M85 compatible over the long term. A comprehensive fuel quality monitoring program for all dispensing sites is a necessary program activity. In fact, one of the first supporting projects initiated by COFA is a report "Methanol Fuel Systems Guide", currently in its fourth revision, published by COFA.

4. The key to a cost effective launch of methanol fuel is the availability of low cost, portable refuelling stations. Once high volume through-put sites are identified, in-ground stations can be developed.

Recommendations

There are several recommendations which follow from the work to date in the Canadian Methanol Light Duty vehicle Program. They are summarized as follows:

1. There is an immediate requirement for proven, methanol compatible dispensing equipment including dispensers, nozzles and hoses.

2. There is a need to investigate a low cost temporary refuelling infrastructure such as an above-ground tank with an island pump for retail public sites.

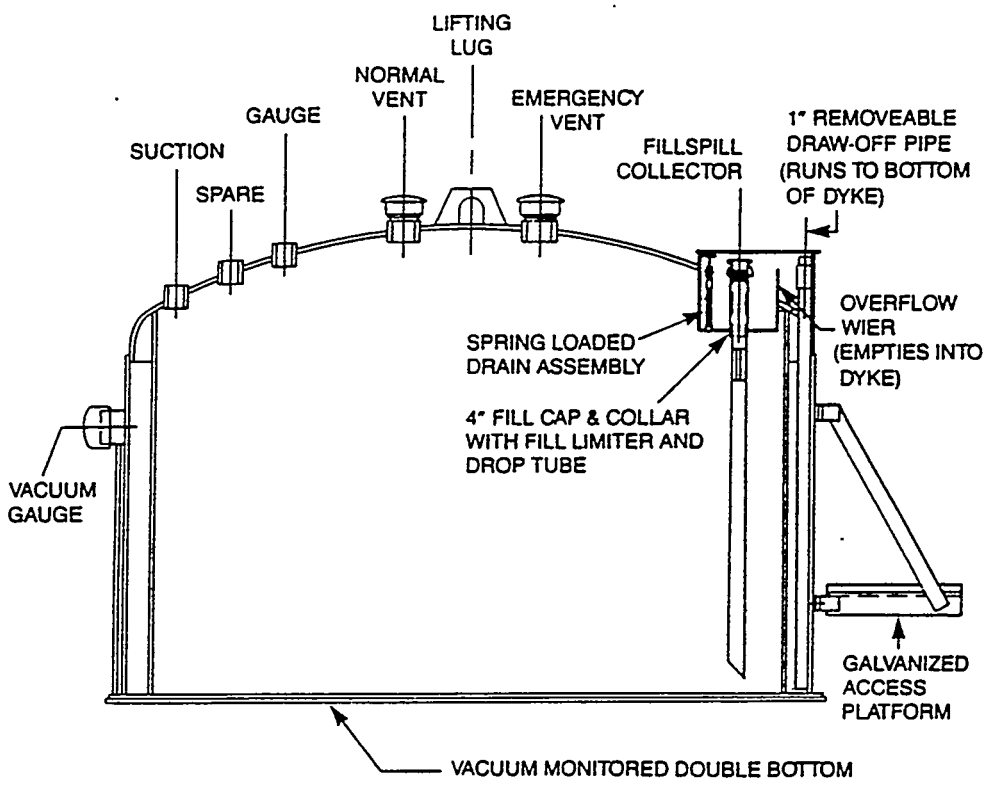
3. There is a need to investigate the feasibility of retrofitting existing gasoline installations for use with methanol fuel.

4. There is a need for governments to place a high priority on including methanol in all fuel regulatory regimes, including fire codes, fuel specifications, and fuel safety regulations.

5. There is a need and role for government leadership in encouraging a flexible fuelling infrastructure. By this we mean a fuelling infrastructure which is fully compatible with gasoline and methanol fuel.

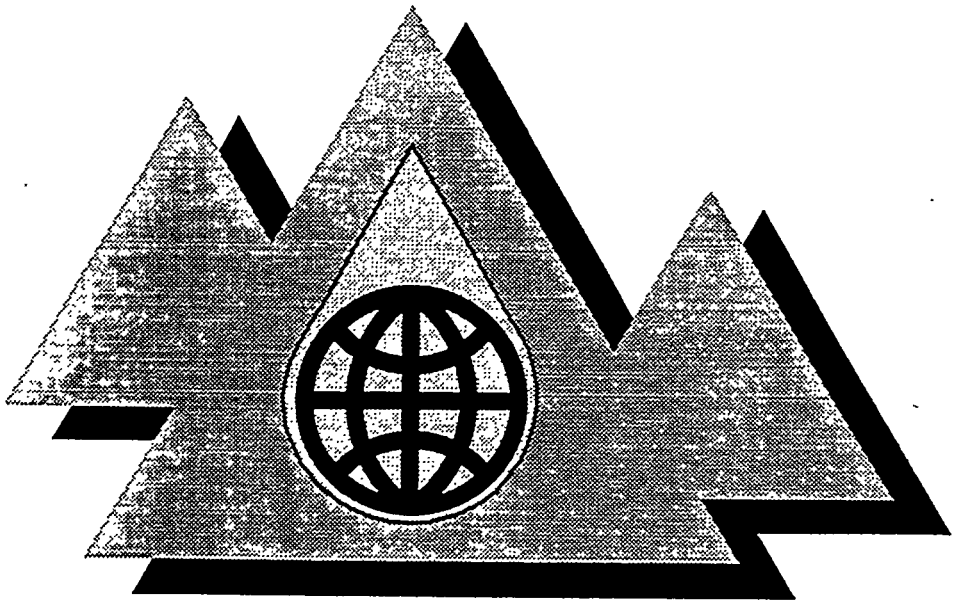
Fleet Installations

Clemmer Tank Diagram



- Methanol fuel portable station designed by Clemmer Industries;
- GasBoy commercial-use pump included; and
- Cost approximately $6,000.

Figure 1. Portable Methanol Fuel Station



Fuel Specification, Additives, and Evaluation

GENERAL MOTORS SPECIFICATIONS FOR FUEL METHANOL AND ETHANOL

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Abstract

Fuel alcohols, such as M85 (blend of 85 percent by volume methanol with hydrocarbons) and E_d85 (blend of 85 percent by volume denatured ethanol with hydrocarbons), are inherently involatile at low temperatures and may contain soluble or insoluble contaminants. Existing fuel specifications do not adequately address these properties, which may adversely affect vehicle performance and durability. To improve customer satisfaction with alcohol-fueled vehicles, we developed new fuel specifications for M85 and E_d85. This paper presents and discusses these specifications, which are based on studies of fuel effects on cold starting, vapor flammability, and durability.

Introduction

As part of demonstration programs with several states and the Federal Government, General Motors developed the Chevrolet Lumina Variable Fuel Vehicle (VFV). The methanol version of the VFV operates on methanol-gasoline mixtures up to 85 percent by volume methanol (M85) and the ethanol version operates on ethanol-gasoline mixtures up to 85 percent denatured ethanol (E_d85). Currently, GM has sold about 1700 methanol VFV's, mostly in California, and about 400 ethanol VFV's, mostly in the Midwest. The quality of M85 and E_d85 fuels will play a major role in their commercial success or failure for a variety of reasons [1]. First, methanol and ethanol fuels are inherently lower in volatility than gasoline fuels, so they must be carefully formulated for good cold starting and warm-up, and to minimize the occurrence of flammable mixtures in the fuel tank. Second, alcohols are good solvents for ionic materials and are, therefore, easily contaminated during manufacture, storage, and distribution.

To ensure sufficient fuel quality, we reviewed existing American Society for Testing and Materials (ASTM) and California Air Resources Board (CARB) specifications for methanol and ethanol fuels, and conducted appropriate studies to explore the relationships between fuel properties and vehicle operation. Our studies showed that existing standards needed revision. Because the development of industry standards can be slow, GM has written its own specifications, which are presented in this paper and compared to existing specifications.

ASTM and CARB Specifications

The starting point for developing GM specifications for M85 was the ASTM D-2 Proposal P 232 [2]. CARB also adopted a specification for M85 [3]. Table 1 compares selected properties from both specifications.

ASTM has not yet proposed a specification for E_d85 fuels. However, specification D 4806 [4] covers the ethanol used to make gasohol (10 percent by volume denatured ethanol in gasoline). D 4806 is relevant because the manufacturing plants that make ethanol for gasohol will likely be the same as those used to make ethanol for E_d85. In contrast, CARB has adopted a specification for E_d85. These specifications are compared in Table 2.

Although the CARB and ASTM requirements were good starting points for fuel specifications, they do not ensure good performance of vehicles operating on M85 and E_d85. Additional or tighter specifications were needed to improve cold starting, reduce vapor flammability, enhance fuel system durability, and minimize fuel filter plugging.

GM's M85 and E_d85 Specifications

Tables 3 and 4 show General Motors specifications GM 4713M and GM 4729M for M85 and E_d85 respectively. We developed these specifications to solve volatility-related and contaminant-related performance issues. GM instructs owners of variable fuel vehicles to use fuels meeting these specifications and requests fuel suppliers to make the appropriate fuels available. The following sections discuss and justify differences between GM and existing specifications.

Temperature Ranges

In General Motors' M85 and E_d85 specifications, four ambient temperature ranges, "high," "intermediate," "cool," and "cold," are defined according to the ASTM volatility classes given in Tables 3 and 4. "High," "intermediate," and "cool" correspond to the summer, intermediate, and winter classifications defined in ASTM D-2 Proposal P 232. The "cold" classification in the GM specifications has no parallel in the ASTM proposal. We have added it to ensure reliable wintertime starting performance and reduced probability of flam-

Table 1. Proposed ASTM and CARB Specifications for M85

PROPERTIES	ASTM P232 *(as of 7/2/93)*	CARB *(as of 3/12/92)*
Methanol plus higher alcohols, min, vol. %	85	84
Hydrocarbons, volume %	13-15	13-16
Vapor pressure at 37.8 C, kPa (psi)		
Summer (ASTM classes A, A/B, B/A,B)	48-62 (7-9)	48-62 (7-9)
Intermediate (B/C, C/B, C, C/D, D/C)	62-75 (9-11)	62-75 (9-11)
Winter (D, D/E, E/D, E)	75-90 (11-13)	75-90 (11-13)
Higher alcohols (C2-C8), max, vol %	2.0	2.0
Acidity as acetic acid, max, mass %	0.005	0.005
Inorganic chloride, max, mass %	0.0001	–
Total chlorine as chlorides, max, mass %	0.0002	0.0002
Gum, unwashed, max, mg/100 ml	100.0	–
Gum, washed, max, mg/100 ml	5.0	5.0
Particulates, max, mg/L	–	0.6
Lead, max, g/L	0.002	0.002
Phosphorus, max, g/L	0.0002	0.0002
Sulfur, max, mass %	0.015	0.004
Water, max, mass %	0.5	0.5

Table 2. ASTM Specification for Fuel Ethanol and CARB Specifications for E85

PROPERTIES	ASTM D 4806 *(denatured fuel ethanol)*	CARB E85 *(as of 3/12/92)*
Ethanol, min, vol. %	91.9	79
Hydrocarbons, volume %	2-5	15-21
Vapor pressure at 37.8 C, kPa (psi)		
Summer (ASTM classes A, A/B, B/A,B)	–	45-60 (6.5-8.7)
Intermediate (B/C, C/B, C, C/D, D/C)	–	50-65 (7.3-9.4)
Winter (D, D/E, E/D, E)	–	60-70 (8.7-10.2)
Other alcohols, max, vol %	–	2.0
Methanol + ketones, max, vol %	0.5	–
Acidity as acetic acid, max, mass %	0.007	0.007
Inorganic chloride, max, mass %	0.0040	–
Total chlorine as chlorides, max, mass %	–	0.0004
Gum, unwashed, max, mg/100 ml	–	–
Gum, washed, max, mg/100 ml	5.0	5.0
Particulates, max, mg/L	–	0.6
Lead, max, g/L	–	0.002
Phosphorus, max, g/L	–	0.0002
Sulfur, max, mass %	–	0.004
Copper, max, mg/L	0.03	0.07
Water, max, mass %	1.25	1.25

Table 3. GM Specification for Fuel Methanol - M85 as Dispensed to the Vehicle (GM4713M)

PROPERTIES	VALUES				TEST METHODS
Ambient temperature range	High	Intermediate	Cool	Cold	
ASTM volatility classes (see ASTM D4814)	A, A/B, B/A, B	B/C, C/B, C, C/D, D/C	D, D/E, E/D	E	
Methanol plus higher alcohols, min, vol. %	84	84	79	74	ASTM D-2 Proposal P 232 (annex A1)
Hydrocarbons, vol. % (see Note 1)	14-16	14-16	14-21	14-26	Difference between 100 & sum of (methanol+water)
Vapor pressure at 37.8 C, kPa psi	52-62 7.5-9	62-79 9-11.5	72-93 10.5-13.5	83-103 12-15	ASTM D4953, D5190, D5191
Cold starting performance index, min (Note 2)	--	--	--	120	(Note 2)
Higher alcohols (C2-C8), max, vol %	2.0				ASTM D-2 Proposal P 232 (annex A1)
Acidity as acetic acid, max, mass %	0.005				ASTM D1613
Chloride ion, max, mass %	0.0001				Ion chromatography (Appendix B)
Total chlorine as chlorides, max, mass %	0.0002				ASTM D2988 or D3120 (mod.)
Conductivity, max, micro S/m	300.0				ASTM D1125
Gum, unwashed, max, mg/100 ml	100.0				ASTM D381
Gum, washed, max, mg/100 ml	5.0				ASTM D381
Particulates, max, g/L	0.0001				ASTM D2276 (teflon membrane filter)
Lead, max, g/L	0.002				ASTM D5059
Phosphorus, max, g/L	0.0002				ASTM D3231
Sulfur, max, mass %	0.005				ASTM D3120, D1266, D2622 (mod.)
Water, max, mass %	0.5				ASTM E203
Appearance	This product shall be visibly free of suspended or precipitated contaminants when viewed using a strong beam of light.				
Luminosity (Note 3)	Shall produce a luminous flame throughout the entire burn duration.				ASTM D-2 Proposal P232 (Appendix X2)

Note 1: The hydrocarbons shall have a maximum end point of 225°C by Test Method D 86, oxidation stability of 240 min. minumum by Test Method D 525 and No. 1 maximum copper strip corrosion by Test Method D 130. The hydrocarbons must also meet sulfur, benzene, aromatic, olefin, maximum T90, and maximum T50 gasoline specifications applicable for the state or region (if any). The hydrocarbons may contain aliphatic ethers as blending components as are customarily used for motor fuel.

Note 2: Cold starting performance index = $VP+(1.2VP - 50)\frac{C5/C4}{(1+C5/C4)}$ where VP is vapor pressure, kPa, (using a Reid vapor pressure equivalent method such as ASTM D4953) and C5/C4 is the ratio of total mass of 5-carbon hydrocarbons to that of 4-carbon hydrocarbons using the gas chromatographic technique described in Journal of Chromatographic Science, Vol. 28, pp. 624-627.

Note 3: Use of gasoline containing 30 volume % aromatics of typical carbon number distribution for the non-methanol portion of the M85 has been generally demonstrated to meet the luminosity requirement. Some commercially available gasolines at 30 volume % aromatics level have been shown not to meet the luminosity requirement. In general, luminosity increases with increasing aromatic content.

Table 4. GM Specification for Fuel Ethanol - E85 as Dispensed to the Vehicle (GM4729M)

PROPERTIES	VALUES				TEST METHODS
Ambient temperature range	High	Intermediate	Cool	Cold	
ASTM volatility classes (see ASTM D4814)	A, A/B, B/A, B	B/C, C/B, C, C/D, D/C	D, D/E, E/D	E	
Ethanol, min, vol. %	79	79	74	69	ASTM D-2 Proposal P 232 (annex A1)
Hydrocarbons, vol. % (see Note 1)	19-21	19-21	19-26	19-31	Difference between 100 & sum of (ethanol+water)
Vapor pressure at 37.8 C, kPa psi	38-59 5.5-8.5	48-65 7-9.5	59-76 8.5-11	66-83 9.5-12	ASTM D4953, D5190, D5191
Cold starting performance index, min (Note 2)	--	--	--	75	(Note 2)
Acidity as acetic acid, max, mass %	0.005				ASTM D1613
Chloride ion, max, mass %	0.0001				Ion chromatography (Appendix B)
Total chlorine as chlorides, max, mass %	0.0002				ASTM D2988 or D3120 (mod.)
Conductivity, max, micro S/m	300.0				ASTM D1125
Gum, unwashed, max, mg/100 ml	100.0				ASTM D381
Gum, washed, max, mg/100 ml	5.0				ASTM D381
Particulates, max, g/L	0.0001				ASTM D2276 (teflon membrane filter)
Lead, max, g/L	0.002				ASTM D5059
Phosphorus, max, g/L	0.0002				ASTM D3231
Sulfur, max, mass %	0.005				ASTM D3120, D1266, D2622 (mod.)
Water, max, mass %	1.0				ASTM E203
Appearance	This product shall be visibly free of suspended or precipitated contaminants when viewed using a strong beam of light.				
Corrosion inhibitor	30 ptb Petrolite T-3222 or equivalent				
Denaturant	Only hydrocarbon denaturants are permitted; methanol, ester, and ketone denaturants are unacceptable				

Note 1: Ethanol-E85 fuels are typically a blend of 85% denatured ethanol (containing about 5% hydrocarbon denaturant) and 15% hydrocarbons by volume. The hydrocarbons shall have a maximum end point of 225°C by Test Method D 86, oxidation stability of 240 min. minumum by Test Method D 525 and No. 1 maximum copper strip corrosion by Test Method D 130. The hydrocarbons must also meet sulfur, benzene, aromatic, olefin, maximum T90, and maximum T50 gasoline specifications applicable for the state or region (if any). The hydrocarbons may contain aliphatic ethers as blending components as are customarily used for motor fuel.

Note 2: Cold starting performance index = $VP+(1.2VP - 50)\frac{C5/C4}{(1+C5/C4)}$ where VP is vapor pressure, kPa, (using a Reid vapor pressure equivalent method such as ASTM D4953) and C5/C4 is the ratio of total mass of 5-carbon hydrocarbons to that of 4-carbon hydrocarbons using the gas chromatographic technique described in Journal of Chromatographic Science, Vol. 28, pp. 624-627.

mable mixtures in the fuel tank in Class E gasoline areas.

Vapor Pressure

Minimum vapor pressures are specified to ensure good cold starting and driveability and to minimize the occurrence of flammable mixtures in the fuel tank. General Motors VFVs have flame arresters in the filler neck and in-tank electrical components designed and tested to prevent ignition of flammable fuel-air mixtures. Despite the fact that a fire in the fuel tank is very unlikely, fuels should still be formulated to minimize the occurrence of flammable in-tank fuel-air mixtures.

Using a model described previously [5], we calculated upper flammable limit temperatures (the temperature at which the fuel-air mixture reaches the rich flammable limit in an enclosed tank) as a function of vapor pressure. We calculated these temperatures using a rich limit equivalence ratio of 2.5 and a vapor-liquid ratio of 50. The high vapor-liquid ratio simulates an effectively empty tank, which would give the highest flammability limit temperature. Flammability limit temperature, calculated at the minimum vapor pressures specified in Tables 3 and 4, are shown in Figure 1. Upper flammable limit temperatures decrease for both M85 and E_d85 as the ambient temperature ranges change from "high" to "cold." Although minimum vapor pressures for E_d85 are 13-17 kPa (2.0-2.5 psi) lower than those for M85, upper flammability limit temperatures are approximately equal within each temperature classification. Our modeling shows that GM specifications reduce wintertime upper flammability limit temperature by 3-4°C relative to existing industry specifications.

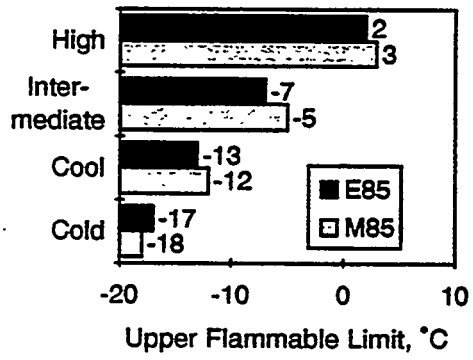

Figure 1. Upper flammable limit temperature calculated based on minimum vapor pressures from Tables 3 and 4

For M85 fuel, we established maximum vapor pressures to match the maximum gasoline vapor pressures for each corresponding volatility class in ASTM D 4814 [6]. We control maximum vapor pressure to avoid excessive evaporative emissions and hot weather driving problems. The GM specifications limit maximum vapor pressures for E_d85 fuels at values 17-21 kPa (2.5-3.0 psi) greater than the minimum vapor pressure, to provide a reasonable range of blending flexibility.

Cold Starting Performance Index

Previous studies [5, 7] have shown that specifying minimum vapor pressure by itself is not sufficient to insure reliable starting at temperatures to -29°C. Instead, we developed the Cold Starting Performance Index (CSPI) [8], defined by Equation 1, to describe cold starting with fuel alcohols.

$$CSPI = RVP + (1.2 \cdot RVP - 50) \cdot \frac{C5{:}C4}{1 + C5{:}C4} \quad (1)$$

In the above equation, RVP and CSPI both are in units of kPa, and C5:C4 is the mass ratio of total five-carbon hydrocarbons (C5) to total four-carbon hydrocarbons (C4) in the liquid fuel. C5:C4 accounts for the important effect fuel composition has on cold starting.

Figure 2 shows the poor correlation between RVP and minimum reliable starting temperature (MRST) for M85s formulated with various compositions and amounts of hydrocarbons. Methanol contents ranged from 78 to 87 percent for C5:C4=1.5 fuels and were 85 percent for C5:C4=6 and C5:C4=0.5. The poor correlation in Figure 2 is a result of the effect of hydrocarbon composition on MRST. Four of the fuels had an RVP of about 79 kPa, which exceeds the minimum RVP specification in

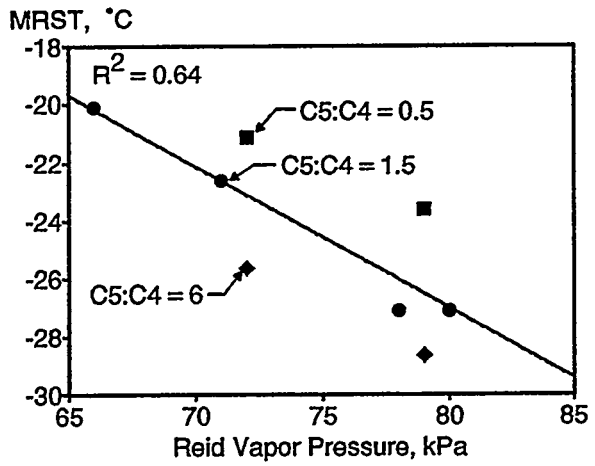

Figure 2. Effect of Reid vapor pressure on minimum reliable starting temperature (MRST) with M85

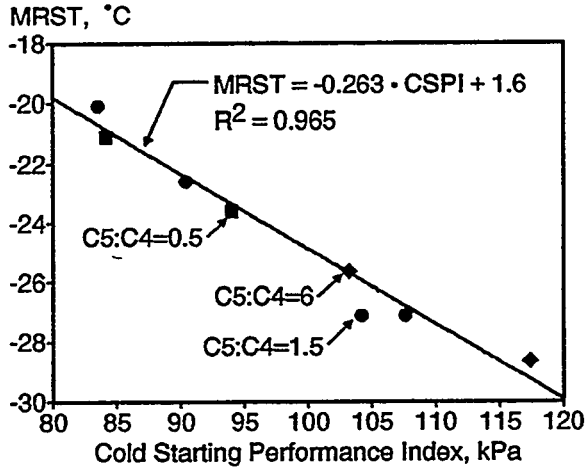

Figure 3. Effect of Cold Starting Performance Index on minimum reliable starting temperature (MRST) with M85

ASTM P 232. However, the C5:C4=6 fuel started reliably at -28.5°C, 5°C lower than the C5:C4=0.5 fuel.

Figure 3 shows the same MRST data as a function of CSPI. Regardless of C5:C4 and methanol content, all data points are now closely grouped about the correlation line. Thus, because it explicitly includes C5:C4, CSPI is an excellent predictor of minimum reliable starting temperature. At a CSPI of 120 kPa, MRST was below -29°C.

We have specified a minimum M85 CSPI of 120 kPa for the Cold classification (see Table 3). On the basis of our results, this specification provides reliable starting below -29°C, about 7°C lower than that of a low C5:C4 fuel just meeting the minimum RVP requirements of ASTM P 232.

A similar cold starting study conducted with E_d85 showed good correlation between cold starting performance and CSPI, with a minimum CSPI of 75 kPa required for starting at -29°C. Therefore, 75 kPa is the minimum CSPI specified for the "Cold" temperature classification for E_d85 (see Table 4). Our data showed that at temperatures down to -20°C, specification of minimum Reid vapor pressure by itself is adequate. Therefore, the Cold Starting Performance Index is not required for the High, Intermediate, and Cool classifications.

Chloride Ion

Previously, specifications for M85 permitted as much as 2 ppm (0.0002 mass percent) chloride ion contamination. We evaluated the suitability of this specification by testing complete VFV fuel systems. These fuel systems were operated for approximately 3200 hours with one of three fuels: a baseline M85 fuel containing no added chloride ion, an M85 doped with a chloride ion concentration of one ppm, or an M85 doped with a chloride ion concentration of two ppm. Chloride ions were introduced by adding sodium chloride. Conductivities of the fuels were roughly 250, 450, and 700 µS/m for the 0, 1, and 2 ppm chloride ion concentrations, respectively.

We found increased levels of chloride ion, and the associated increased conductivity, to accelerate corrosion, reducing the durability of many fuel system parts, especially at the two ppm level. For example, Figure 4 shows severe damage to an anodized aluminum fuel rail connector with two ppm added chloride. With one ppm added chloride (see Figure 5) and with zero ppm added chloride (not shown) no damage

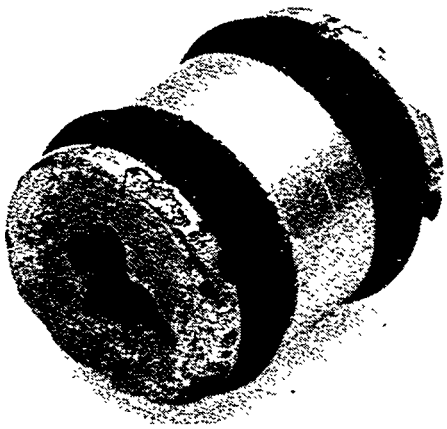

Figure 4. Fuel rail connector tested 1955 hours in M85 with two ppm added chloride

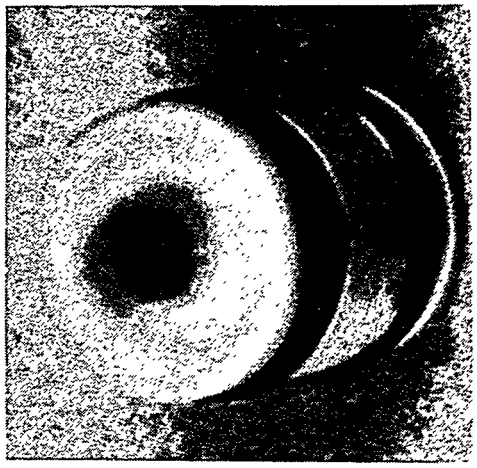

Figure 5. Fuel rail connector tested 3412 hours in M85 with one ppm added chloride

to the parts was apparent, despite the longer test time.

Addition of chloride ion also caused a number of fuel pump failures. Fuel pump life averaged 488 and 1400 hours with two and one ppm chloride, respectively, added to M85. The stainless steel shells of the pumps tested with two ppm chloride were also badly corroded. The pump operated in M85 without added chloride was still operable after 3210 hours and had only minor pump shell corrosion.

On the basis of these results we specify a maximum chloride ion concentration of 0.0001 mass percent (1 ppm) for M85 and E_d85. This is consistent with the recently revised ASTM P 232 specification for M85.

Conductivity

The GM specifications include a maximum for conductivity because the rate of galvanic and electrolytic corrosion is proportional to the conductivity of the fluid (see Appendix A). In addition, conductivity is an easily measured indicator of the presence of ions, such as chloride ions, which can catalyze free corrosion reactions. Our experience has been that methanol fuels have a conductivity of approximately 100 μS/m, if they have not been contaminated by handling. Measurements show that contamination by one ppm chloride ion will increase conductivity by 200 μS/m. Therefore, our specification maximum of 300 μS/m is consistent with the conductivity of methanol fuel that has been contaminated by one ppm of chloride ion, and limits corrosion due to any ions. For E_d85 we experienced corrosion-related fuel pump failures with a 422 μS/m conductivity fuel and no failures with a 125 μS/m fuel. On the basis of these results we also adopted 300 μS/m as the limit for E_d85. Neither ASTM P 232 for M85 nor the CARB specifications for M85 and E_d85 includes a conductivity specification.

Particulates

Modern automobiles have relatively coarse filters in the fuel tank to protect the in-tank fuel pump, and fine filters after the pump to protect the fuel injectors. Plugging of both filters has been a major problem for methanol VFVs in the field. Our analysis of these plugged filters shows the cause to be aluminum corrosion products, primarily aluminum hydroxide. The major source of the aluminum has been unprotected aluminum nozzles and other aluminum components of service station dispensing systems.

To determine the quantity of aluminum hydroxide required to plug filters, we tested a vehicle operating on fuel containing M85 to which 1.0 mg/L aluminum hydroxide was added. Figure 6 shows pressure drop across the in-line filter plotted as a function of accumulated miles.

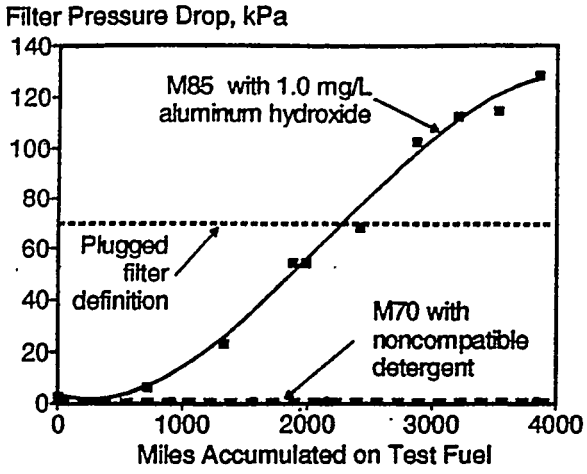

Figure 6. Vehicle study of in-line filter plugging

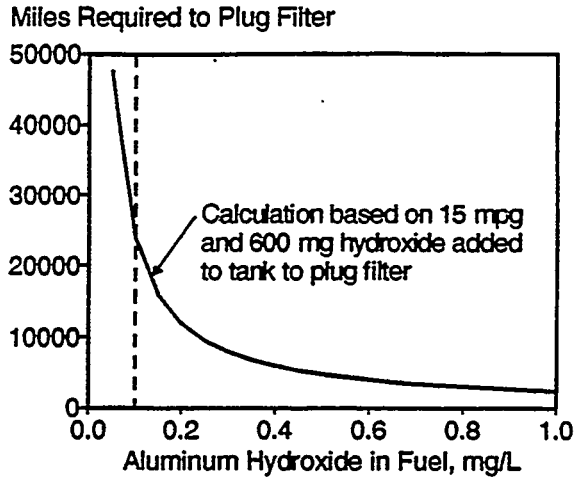

Figure 7. Effect of aluminum hydroxide concentration in M85 on fuel filter life

(As the filter plugs, the resultant flow restriction results in an increased pressure drop across the filter.) The filter was plugged after less than 2500 miles, at which time only about 600 mg of aluminum hydroxide was added to the tank. Figure 6 also shows results for a mixture of methanol and gasoline containing a detergent not compatible with methanol. Although the mixture was noticeably hazy, pressure drop did not increase because the separated phase passed right through the filter.

Figure 7 shows the calculated miles required to plug the in-line filter as a function of aluminum hydroxide content of the fuel. The aluminum hydroxide concentration in the fuel must be no more than 0.1 mg/L to provide a filter life of approximately 25,000 miles. However, no suitable method is available for measuring aluminum hydroxide in the fuel at this concentration. Instead, the GM specifications limit total particulates, as measured by filtration, to 0.1 mg/L, because we find aluminum hydroxide to be the major particulate in dispensed M85 fuel. It is important to recognize that this limit applies to the fuel as it is dispensed into the vehicle. We applied the same limit to E_d85 fuel because aluminum hydroxide would plug the filter as quickly in E_d85 as it would in M85. However, filter plugging has not yet been a problem with ethanol VFV's.

Alcohol and Hydrocarbon Content

For "high" and "intermediate" temperatures, minimum methanol content is 84 volume percent and hydrocarbon content ranges between 14 and 16 percent. At "cold" temperatures, these specifications permit methanol concentrations as low as 74 percent. This allows increased hydrocarbon content and broadens the range of fuels that meet starting requirements.

For "high" and "intermediate" temperatures, E_d85 is nominally 85 volume percent denatured ethanol. Because denatured ethanol generally contains about 5 percent hydrocarbons, the nominal ethanol content is about 80 volume percent. We selected a minimum ethanol concentration of 79 volume percent, to provide blending tolerance. Minimum ethanol contents are reduced to 74 and 69 volume percent for the "cool" and "cold" ranges, respectively, to permit volatility requirements of the blend to be satisfied using typical hydrocarbon refinery streams.

These specifications do not require finished gasolines to be used for the hydrocarbon portion of M85 and E_d85. In fact, our experience [5, 8] indicates that light hydrocarbon streams may be more suitable for fuel methanol in the "cold" temperature range and for E_d85 in all temperature ranges.

Acidity

The acidity of fuel alcohol has a major impact on its corrosion of metals [9]. Therefore, to protect fuel system materials, a maximum acid concentration of 0.005 mass percent (50 ppm) is specified for both M85 and E_d85. This is consistent with ASTM P 232 for M85 and is lower than the 0.007 mass percent specification in ASTM D 4806 for ethanol that is to be diluted with gasoline.

Sulfur

Sulfur contamination can adversely affect catalytic converter efficiency [10]. The maximum level specified, 0.005 percent, is similar to the 0.004 percent specified by CARB, but below the 0.015 percent limit specified in ASTM P 232.

Water

For M85, maximum water content is 0.5 percent by mass, equivalent to that of ASTM P 232. For E_d85, the maximum water content is 1 mass percent by volume. A higher limit is acceptable for E_d85, because ethanol-hydrocarbon blends tolerate more water than methanol-hydrocarbon blends.

Appearance

The appearance requirement, like total particulates, limits insoluble contaminants in the fuel. Because contaminants such as aluminum hydroxide are difficult to see, it is important that the inspection be performed using strong backlighting through a clear sample container. The total particulate specification of 0.1 mg/L should be, in general, more restrictive than the appearance requirement.

Corrosion Inhibitor

During development of GM's ethanol-fueled VFVs it was discovered that E_d85 fuel, without corrosion inhibitor, caused fuel pump failures that had not been observed with M85. These failures were corrosion-induced, and apparently a result of the higher level of dissolved contaminants in ethanol compared to methanol. We found that addition of a corrosion inhibitor did not solve this problem but improved other aspects of fuel pump durability. Therefore, we included a requirement for such an additive in the specification. Meeting this requirement should not be a problem for fuel ethanol manufacturers, because they already routinely add corrosion inhibitor.

Denaturant

To avoid excise taxes, the Federal Government requires the addition of denaturants to fuel ethanol. The GM E_d85 specification requires that denaturants consist of only hydrocarbons. This is consistent with ASTM D 4806 and is common practice in the fuel ethanol industry.

Other

The GM limits for M85 and E_d85 for total chlorine, gum, lead, phosphorus, and luminosity are identical to those for ASTM P 232.

Summary and Conclusions

Our studies show a need for improvement in existing ASTM and California Air Resources Board specifications for fuel methanol and fuel ethanol. Therefore, we developed and recommend General Motors specifications to improve vehicle cold starting performance and durability. Key aspects of GM's specifications are summarized below.

- We adopted a new cold temperature classification and corresponding minimum Reid vapor pressure that, compared to existing specifications, reduces the temperature at which flammable mixtures occur during the winter.

- Reid vapor pressure specifications do not adequately control the fuel's wintertime starting performance. Instead, we developed and specify a Cold Starting Performance Index (CSPI), which accounts for fuel composition effects on starting. Fuels with the specified CSPI provide significantly improved cold starting.

- Ionic fuel contaminants increase corrosion by increasing fuel conductivity. Certain ions, such as chloride, also chemically enhance corrosion. To improve fuel system durability, we control conductivity to 300 •S/m and chloride ion concentration to one ppm. The one ppm chloride ion limit has recently been implemented in ASTM P 232 for M85.

- The most prevalent service problem with M85-fueled vehicles has been premature filter plugging due to fuel contamination by aluminum corrosion products. To ensure reasonable filter life, we specify a maximum particulate contamination of 0.1 mg/L for both M85 and E_d85 fuels.

It will be a major undertaking to establish a fuel distribution and dispensing infrastructure for M85 and E_d85 that provides customers convenient access to good quality fuels. The development of such an infrastructure is the greatest technological hurdle to widespread sales of M85 and E_d85 fuels and to their use in variable fuel vehicles.

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12. Deborah M. Esch and Noel M. Potter, General Motors NAO R&D Center.

Appendix A. Conductivity Effect on Fuel System Corrosion

Faraday's Law of electrolysis states that the amount of chemical reaction (corrosion, in this instance) that occurs at an electrode is directly proportional to the electrical current that passes through that electrode into the solution. This electrical current is, in turn, related to the voltage applied, various interfacial impedances, and the solution resistance [11]. Expressing the solution resistance in terms of conductivity we obtain:

$$CR = \mathfrak{F}ki_{corr} = \mathfrak{F}E/\Sigma(R_i + G/\kappa) \qquad (A\text{-}1)$$

where CR is the corrosion rate, $\mathfrak{F}$ is the Faraday constant, k is a proportionality constant, i_{corr} represents the electrical current flow through the solution-metal interface, E represents the voltage between the anode and cathode, κ represents the electrical conductivity of the solution, G is a geometric factor, and ΣR_i represents various interfacial impedances, some of which are voltage dependent.

If the interfacial impedances are small relative to G/κ, as it can be in alcohol fuels, the corrosion rate becomes conductivity limited and the above equation simplifies to a form in which CR is directly proportional to the conductivity:

$$CR = \mathfrak{F}kE\kappa/G \qquad (A\text{-}2)$$

Appendix B. Ion Chromatography Procedure for Chloride Ion in Alcohol Fuels [12]

Workup for 0 to 75% alcohol

1. Add 20 ml of water, 50 mL of sample and 2 drops of concentrated. NaOH (600 g NaOH/L) to a separatory funnel.
2. Mix thoroughly and let stand until separated
3. Draw off water phase.
4. Follow evaporation procedure (below) to further purify sample before injection into the Ion Chromatograph (IC).
5. Note: efficiency of extraction is 80 to 100%. A second extraction may be used to improve efficiency

Workup for > 75% alcohol

1. Evaporate 50 to 100 mL of sample + 20 drops of concentrated NaOH just to dryness at about 100°C in nitric acid washed beakers (don't use HCl for wash).
2. Evaporate at least two similarly prepared reagent blanks to dryness (pure alcohol + 20 drops NaOH).
3. Dissolve the residue of the above evaporations in 5 to 10 mL of deionized water and dilute to 50 mL
4. If needed, filter the solutions with an ACRO LC3A disposable syringe filter.

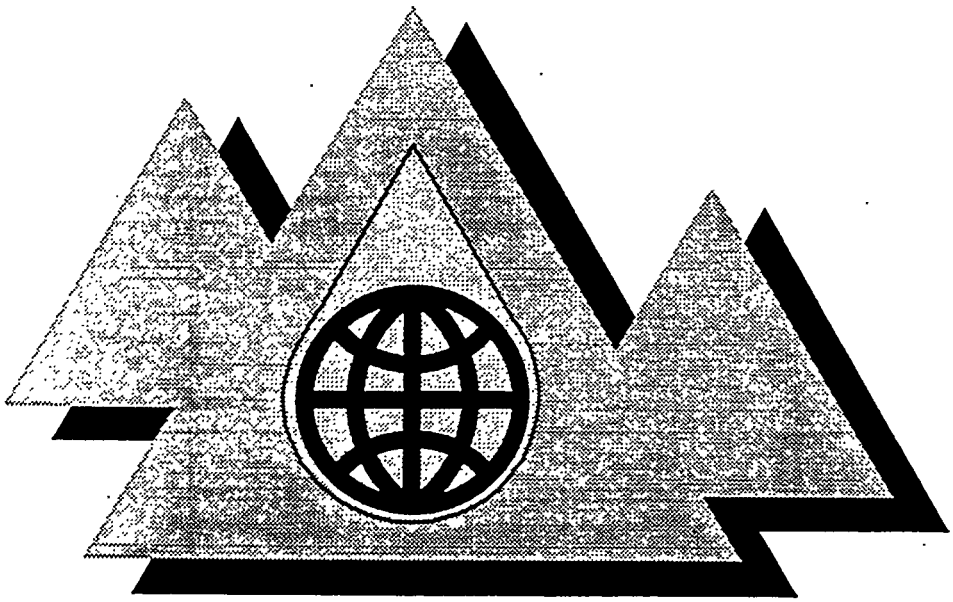
Instrument Parameters:

A Dionex 2010I Chromatography system was used for this work
Columns: DIONEX AG4 Precolumn and DIONEX AS4 Separation Column
Eluant: 1.5 mM $NaHCO_3$ + 1.2 mM Na_2CO_3
Flow: 2 mL/min
Total Conductivity: 12.8 µS
Conductivity Range: 10 µS
Injection Loop: 50 µL
Integrator: Baseline compensating.
Approximate retention time: 1.8 to 1.9 min.

Analysis and Calculations

1. Results should be based on a calibration curve with at least three standards covering the expected Cl^- concentration range.
2. Calculate concentrations based of sample size and dilutions.
3. Correct final results by the average reagent blank result
4. If the reagent blank correction is >0.1 mg/L, report the blank correction also.

*Note: A Dionex 2010I Chromatography System was used for this work.



Fuels in Commerce, Fuel Quality, and Fuel Formulation

METHANOL FUEL FORMULATION ISSUES

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Abstract

There are a number of issues regarding the formulation or quality of methanol fuels that have become apparent in the demonstration of light- and heavy-duty methanol vehicles in California. This paper will outline and provide some discussion of the following issues:

1. Additives to M100 for flame luminosity improvement.
2. The potential impacts of gasoline deposit control additives and methanol fuel distribution system corrosion products on the reliability and component durability of methanol fuel flexible vehicles.
3. Additives to methanol for fuel injector and fuel pump durability improvement in diesel cycle engines.
4. The impacts on fuel injector durability and NOx emissions of the use of M85 in two-stroke, heavy-duty methanol engines designed for M100.
5. M100 ignition improver additive prices vs. heavy-duty methanol engine design cost savings.
6. Fuel grade methanol: what is it, what are the potential cost savings in production and transport, and will it make methanol competitive with gasoline and diesel?

Introduction

The California Energy Commission has been sponsoring methanol vehicles and methanol fuel formulation and distribution since 1979 to achieve fuel diversity and improve air quality. Key to the success of these activities are public-private partnerships with other government agencies, automobile manufacturers, heavy-duty engine and vehicle manufacturers, and fuel suppliers. Cooperation between the partners is instrumental to the successful introduction of methanol vehicles and fuel distribution into the market.

A number of issues regarding the formulation or quality of methanol fuels have become apparent in the demonstration of light- and heavy-duty methanol vehicles in California and elsewhere. This paper will outline and provide some discussion of these issues.

Discussion

The following sections identify and discuss some of the issues facing efforts to commercialize methanol and vehicles capable of using methanol. The intent is to provide some general information and to stimulate discussion toward providing solutions to these issues.

M85 in FFVs vs. M100 in dedicated vehicles

Many feel that fuel flexible vehicles (FFVs) operating on M85 (85 percent methanol, 15 percent gasoline) represent a compromise that falls short of the low-emission potential of methanol fuel. While this may be true, the compromise provides extremely important market advantages for FFVs. These advantages will remain until methanol fuel can become conveniently available throughout the U. S. to support a market for dedicated methanol vehicles running on M100. Without this compromise, efforts to expand the use of methanol would necessarily focus on dedicated methanol vehicles and centrally-operated fleets. This market constitutes only about 10 percent of vehicle sales and traditionally does not receive auto industry attention sufficient to develop and market unique vehicle technology. On the other hand, FFVs can be and are being marketed to both fleets and individuals.

The full range of customers can purchase FFVs now, use methanol when they can find it, and use gasoline when they can't. They can enjoy the full utility expected of a gasoline vehicle along with the opportunity to use methanol more often in the future as the availability of methanol expands. This seems to translate into the opportunity to *accelerate* the acceptance of methanol by the marketplace and to support a growing methanol fuel station infrastructure *sooner* than with dedicated methanol vehicle technology. FFVs and M85 offer the potential to *accelerate* and *improve* conditions to establish a market for potentially lower-emission and higher efficiency dedicated M100 vehicles in the future. FFVs and M85 take advantage of market dynamics rather than fight these very strong forces. The growing methanol/vehicle market being nurtured in California and elsewhere provides a much stronger platform for supporting the development of optimized dedicated methanol vehicle technology in the future than would exist without the FFVs and the M85 fuel distribution network. People that become familiar and comfortable with FFVs will be good candidates to become customers for more advanced methanol vehicles in the future. What the methanol fuel formulation requirements will be for future methanol engines, remains to be discovered.

Flame luminosity additives to M100

The potential air quality benefits of engines designed for optimized low-emission performance with M100 for the light-duty market have intrigued regulators and sustained support for methanol. Some concepts for the development of new M100 engine technology show the potential to achieve very low levels of smog forming emissions with high efficiency and performance. (Last 1993) This section summarizes the results of a major effort to identify additives to M100 that would provide the luminosity of M85 while maintaining the low emission properties of M100.

M85 is used in California and elsewhere, based on extensive automobile industry research, to provide sufficient flame luminosity to allow the detection of an accidental fire. (The gasoline in M85 also improves cold-start performance, reduces cold-start emissions, and prevents casual ingestion). Luminous flames allow people in the vicinity to take steps to avoid and to extinguish a fire. Experience in California demonstration programs has shown that the lack of luminosity in an M100 flame may complicate its

acceptance by local fire marshals and other permitting authorities with safety and hazard prevention responsibilities. Consequently, the California Air Resources Board (ARB), the California Energy Commission (CEC), and the South Coast Air Quality Management District (SCAQMD) sponsored a major effort by Southwest Research Institute (SwRI) to identify fuel additives that might provide adequate flame luminosity while maintaining or improving upon emission levels seen with M85 in FFVs.

SwRI screened over 200 single and multiple compound candidate additives and developed laboratory test procedures to generate repeatable luminosity values over a range of concentration levels. Initial screening showed that both M85 and ethanol provide a minimum threshold visibility measured between 1 and 2 lux with the laboratory test apparatus. This level was accepted by the sponsors as a target for comparison of alternatives. An extensive initial literature search to identify potential additives and the nomination of additional candidate compounds by fuel suppliers, automobile manufacturers, and others lends confidence to the conclusion that as many candidates as possible were considered. Development of mechanisms of luminosity generation lead to identification of additional candidates. (Fanick 1993)

Testing shows that some compounds provide luminosity during the early portion of a burn and others provide luminosity near the end of a burn. This behavior relates to the volatility of the compounds and their ability to form azeotropes with methanol. Multiple compound candidates were assembled and tested, since the goal was to provide luminosity throughout a burn.

Many of the candidates were rejected for either insufficient luminosity at low concentrations or concerns about their long-term compatibility with use in an engine. Two multiple compound candidates, 4 percent toluene + 2 percent indan and 5 percent cyclopentene + 5 percent indan, were selected as finalists from the laboratory testing. (Indan is a heterocyclic aromatic compound with the formula C_9H_{10}). Additional subjective testing verified their luminosity performance in sunlight with outdoor burns on a variety of typical surfaces. Concrete, asphalt, sheet metal, grass, and bare soil surfaces were tested. The two final candidates performed as well as or better than ethanol and M85 in outdoor burns on most surfaces.

Emission testing of these candidate formulations in a vehicle showed that they *did not achieve lower emissions* than testing with either M85 or M100. The test vehicle was selected to represent FFV technology now entering the market that is based on gasoline engines and maintains the ability to operate and maintain emission control with gasoline as well as with mixtures containing up to 85 percent methanol. The test vehicle engine was not optimized for either M100 or the candidate formulations, so its cold-start emissions during open-loop operation may not indicate the low-emission potential of these fuels.

A subsequent effort looked at the cost and availability of the candidate additive materials. Toluene is readily available at relatively low prices, while indan and cyclopentene are not. SwRI researched the availability of process streams containing indan, cyclopentene, or their precursors. They concluded that special processing equipment would be needed which would add substantially to the price of an additivized M100. The conclusion is that *M85 provides cost-effective luminosity as well as better emission performance for FFVs now entering the market than identified alternative methanol fuel formulations.*

Fuel quality impacts on FFVs

FFVs being demonstrated in California have experienced occasional drivability problems traced to clogging of the fuel "sock" filter/strainer in the tank and the in-line filter. This section will discuss corrosion in fuel storage and dispensing systems, protection to reduce corrosion, filtration to remove the products of corrosion, and the potentially complicating effects of some gasoline deposit control additives.

Inadequate or non-existent fuel filtering at the M85 dispenser and corrosion products from unprotected aluminum dispenser components downstream from a dispenser filter have been identified as causal factors for vehicle fuel filter clogging. Other contaminants, which appear to play a less significant role but can easily be minimized, are decomposition products from non-compatible dispenser hoses and incorrect dosage of (gasoline) deposit control additives in M85 supplies.

Aluminum corrosion and filtration

The importance of adequate fuel filtration at the dispenser is evidenced by Ford Motor Company

(Ford) experience with 1989 Crown Victoria FFVs in the City of Los Angeles fleet. From January to June 1992, 11 out of 42 vehicle in-line filters were replaced for plugging. In some cases, fuel pumps were also replaced. Analysis of a filter from another available fleet showed that 50 percent of the external contamination was under 2 microns in size and another 20 percent was in the 2 - 5 micron range. Based on this, it was decided to replace a 10 micron non-compatible M85 filter on the fuel dispenser with a 1 micron "micro-glass" filter. This was installed in June 1992. Subsequently, the incidence of filter plugging on the vehicles was reduced to 7 from June to October 1992 and none since. This type of 1 micron dispenser filter has since been installed at most of the 49 California Program stations with excellent results.

Experimental and field data reported by General Motors (GM) and corroborated by Ford experience shows that aluminum corrosion products form a gel that intermittently blocks the fuel tank sock filters. Some of the material passes through the sock and collects permanently on the finer mesh in-line filter. Collection of this gel on the filter substrates increases the pressure drop across the filters. This results in cavitation or increased load on the electric fuel pump causing excessive noise and drivability problems, and can lead to premature fuel pump failure.

Aluminum hydroxide ($Al(OH)_3$), the main corrosion product of aluminum in methanol, will be a potential problem as long as there is unprotected aluminum in the fuel dispensing system to start a chemical reaction. It is an insidious problem, because even small quantities can form a thin, sticky layer that can effectively plug even a large fuel filter and shut down a vehicle. GM supplied data from FFV testing shows that doping the fuel with aluminum hydroxide at the rate of 1.0 mg/L of fuel (0.3 mg/L of aluminum) plugs the in-line filter in 2,500 miles of driving and coats the sock filter heavily in 2,900 miles; eg, about 700 mg of aluminum hydroxide. This compares to a Ford measurement of 112,000 milligrams of Arizona fine dust retained by a similar filter with no effect on vehicle performance.

Aluminum corrosion products obviously need to be prevented or filtered out before reaching the vehicle. Contact with aluminum need not be absolutely prevented upstream of a suitable dispenser filter, however, unprotected downstream aluminum components must be eliminated. Filters are installed in or on fuel dispensers to collect upstream aluminum corrosion products. The filter may or may not be located downstream of internal metering components, depending on the availability of a suitable location for installation of the filter. In any case, there are still some aluminum components downstream of the filters that must be upgraded to eliminate exposure of unprotected aluminum to methanol fuel. Soak testing and field experience at Ford has determined that adequate protection for aluminum can be provided by anodizing to 0.002 inches minimum or electroless nickel plating to 0.0003 inches minimum thickness.

Evidence of the effectiveness of the "belt and suspenders" approach (protect and filter) was obtained by Ford in two experiments. The first was a check of aluminum content ahead of and after the in-line (20 micron absolute) fuel filter in a vehicle that showed that fuel contaminated at a 6 mg/L level was filtered down to 0.3 mg/L. The second was experience gained from New York Thruway M85 installations that generated no filter plugging complaints in FFVs when equipped with 1 micron filters and nickel-plated nozzles.

The minimum practical level obtainable by providing 1 micron filtration at the dispenser despite contact with aluminum upstream is about 0.1 mg/L. Evidence of this was obtained by Ford by monitoring a March 1993 delivery of M100 in an aluminum tanker truck from Los Angeles harbor to Phoenix, Arizona. After passing a sample of the delivered fuel through a 1 micron fuel filter, the aluminum content was found to be 0.1 mg/L. The average filter service interval at this level would be about about 25,000 miles, based on GM filter/fuel consumption figures. Based on the GM case and an average 40 liter refill, the level of aluminum contamination allowable in a weighted sample of unpurged and purged nozzle samples of M85 fuel required to obtain a 120,000 mile service interval for FFV fuel filters would be no more than immeasurable 0.006 mg of aluminum per liter of fuel! For this level of longevity, aluminum would have to be eliminated upstream as well as downstream. However, the GM test was a worst case scenario. Ford expects that a 0.1 mg/L maximum standard enforced on unpurged nozzle samples will be sufficient due to the dilution of 1 liter of unpurged fuel from an inactive dispenser in a fillup of 40 liters (of purged fuel).

Dispenser hoses and gasoline deposit control additives

Other contaminants that have been found in FFV fuel filters include plasticizers and other chemicals that leach out of dispenser hoses, and (gasoline) deposit control additives dosed at gasoline levels into M85. These two sources not only have been found in small quantities on vehicle fuel filters, but have been found to elevate the conductivity of M85, thus creating potential fuel mixture control problems in the FFV engine.

Plasticizer leachate is not a problem in some M85 locations outside of California due to the use of cross-linked polyethylene dispenser hoses. This product, developed for the chemical industry, is fully methanol compatible, but is not available in coaxial form for Stage II vapor recovery applications (generally required in California). "Stage I" refers to vapor recovery during transfer of fuel from a truck tanker to an underground storage tank; "Stage II" refers to vapor recovery during vehicle refueling. Coaxial hose designs have become normal practice for Stage II vapor recovery, with a 13/16 inch OD inner product hose located inside a corrugated 1.5 inch OD vapor hose, the combination being much more serviceable and less cumbersome than two hoses strapped together.

The best solution to date for coaxial hose is to use a high acrylo-nitrile content inner hose, presoaked for 24 hours to wash out the majority of the plasticizer. Ford compatibility testing indicates that this hose can survive a 2,000 hour soak test in M85 without any evident material degradation. During the first 24 hours, however, the M85 soak medium transforms into a nearly opaque, amber, and even more highly conductive liquid that is highly undesirable to have in a vehicle fuel tank.

Ford research has confirmed that polybuteneamine deposit control additives used in some gasolines (and therefore in some FFVs) are not completely soluble in methanol. The data shows that at normal dosages in the gasoline blended into M85, the worst (least soluble in methanol) additive is only 90 percent dissolved; ie, 10 percent of the additive remains on a 1 micron filter in a single pass. It is suspected that the small residual may exacerbate the tendency of any dissolved aluminum to form a filter-clogging gel in an FFV refueled with such gasolines when the tank contains some methanol (however, this has not been verified in the field).

General Motors testing of an M70 formulated with gasoline containing a noncompatible gasoline detergent additive *without added aluminum hydroxide* does not show increasing pressure drop across a fuel filter. GM concludes that aluminum hydroxide contaminated fuel is the most likely cause of filter-related service problems. No testing of the combination of the detergent additive with aluminum was reported. (Halsall 1993)

Application of a polybuteneamine deposit control additive to blended M85 at a standard gasoline dosage can create sticky deposits on the surfaces of all dispenser equipment and FFV fuel system components in contact with the fuel. Both nozzles from one affected site became disabled due to the sticky coating after dispensing about 8,000 gallons. Chemical laboratory testing at Ford has shown polybuteneamine deposit control additives to be only moderately soluble in methanol blends at dosages higher than if applied to the gasoline portion only. Polyetheramine additives are somewhat more soluble in methanol and thus less likely to collect on M85 fuel station dispenser filters. But, there does not now appear to be a concern about polybuteneamine additives in gasoline added to an FFV containing some methanol if that methanol does not have excessive aluminum contamination. *It is clearly necessary to avoid adding gasoline deposit control additives to M85 at normal gasoline concentrations.*

Successful examples

Two fleets have avoided problems with contaminated fuel because they follow Ford-recommended blending and dispensing hardware practices. The New York fleet consists of 15 Crown Victorias started into service in October 1992 and fueled from a Ford-approved Stage II aboveground M85 site. No vehicle downtime has been attributed to contaminated fuel. The Dearborn (Michigan) Police fleet consists of 45 1993 Taurus FFVs of which 30 are dedicated to running captive M85 from the Ford Research and Engineering Center Superstation. The vehicles were put in service between May and August 1993, and the station uses non-Stage II components over an underground storage tank. Again, no downtime has been attributed to contaminated fuel.

Summary of fuel quality impacts

Ford and GM experience indicates that to minimize vehicle downtime due to contaminated

M85, the fuel must meet recommended chloride ion, conductivity, particulate, and aluminum content specifications *as dispensed from an unpurged nozzle.* To do this requires the best practices for fuel blending and dispenser equipment:

- additives (dose only the gasoline)
- M85 filtration (1 micron)
- eliminate contact with or protect all aluminum (anodize to 0.002 inches minimum or electroless nickel plate to 0.0003 inches minimum)
- use cross-linked polyethylene or equivalent hose for Stage I systems
- use presoaked high acrylo-nitrile hose for Stage II systems until a better hose becomes available for coaxial installations.

A question remains: How much filter clogging is the result of a few fuel stations that may not have installed components identified as methanol-compatible vs. how much will be resolved by a general upgrade of components in all of the stations? Removal of such known "don'ts" as unprotected aluminum "drop" tubes (typically used with gasoline storage tanks and known to corrode quickly in the presence of methanol) is clearly a top priority. Anodized or nickel-plated nozzle bodies are now recognized as necessary due to observed high levels of aluminum corrosion when fuel sits in contact with the cast aluminum for long periods between customers. This was earlier thought to be unnecessary with frequent refueling events to minimize residence time and thus the opportunity for methanol to corrode susceptible components.

California Program M85 stations are in a general upgrade process of installing nickel-plated dispenser nozzles and cross-linked polyethylene hoses or black iron pipes for the transfer adapter. Cross-linked polyethylene hoses have been found to be too stiff for assembly in a coaxial dispenser hose. Development of new hose technology such as a teflon-lined coaxial design is needed. And, there is still the issue of compatibility of the outer hose that may be exposed to methanol if a customer repeatedly tries to top-off or overfill after initial nozzle shutoff.

Even when fully compatible components become widely accepted and are generally available, continued vigilance will be necessary until methanol fuel station equipment becomes standard practice. Maintenance personnel primarily familiar with gasoline component requirements and not necessarily motivated to give a high priority to methanol customer satisfaction may tend to install readily available gasoline components as quick fixes.

More attention to quick resolution of these issues is important to remove potential barriers to greater market acceptance of methanol FFVs. First priority goes to improvement in protection of aluminum components and filtration downstream of those that aren't protected.

M85 in heavy-duty methanol engines

The development of heavy-duty methanol engines has primarily focused on M100 fuel. The Detroit Diesel Corporation (DDC) 6V-92TA methanol engine is commercially available for transit bus use and is certified at very low emission values. 150 of these engines are also used in the Katz Safe School Bus Clean Fuel Efficiency Demonstration Program which specifies M85 to avoid concerns about flame luminosity in the extremely safety-conscious education environment. The School Bus Demonstration Program's use of DDC 6V-92 engines operating on M85 initially experienced shorter life of fuel injectors than was expected when compared to M100 in transit buses. Initial life of schoolbus injectors with M85 without additives was as low as 5,000 miles vs. 20,000 miles with M100 with additives in transit buses. Later experience shows approximately fourfold increase in injector life when fuel and lubricating oils containing Lubrizol additive packages specified by DDC are always used. (Deterville 1993)

Certification of DDC 6V-92TA engines for 1993, calibrated for a variety of methanol and ethanol fuel formulations, shows a range of NOx emissions from 1.7 g/bhp-hr for M100 to 4.1 g/bhp-hr for M85. For reference, the current heavy-duty NOx standard of 5 g/bhp-hr continues through 1997 for trucks. The standard goes down to 4 g/bhp-hr for transit buses in 1996. It is generally accepted that the higher NOx result for M85 does not reflect as much maturity and design optimization as the M100 result; however, it remains to be seen if NOx emissions are necessarily higher with M85 and how low NOx emissions can be from this engine with further calibration effort with M85. A Navistar DTM-466 tested at the Los Angeles County Metropolitan Transit Authority Emissions Test Facility shows an increase in NOx emissions from M100 to M85 of about 40 percent. On the other hand, the Ford 6.6L MX engine, designed for spark-ignited stoichiometric operation on

M85 to facilitate 3-way catalyst emission control, has NOx emissions of only 1.2 g/bhp-hr, the lowest of any heavy-duty methanol engine tested. (Wiens 1993)

Additives to methanol for diesel-cycle engines

Some manufacturers of heavy-duty methanol engines, Detroit Diesel Corporation and Caterpillar Inc., have specified the use of lubricity/corrosion inhibitor additive packages for their engines designed for M100 and M85. Discussion of an additional additive, Avocet ignition improver, is in a different section. DDC requires a Lubrizol additive at 0.06 percent concentration and Caterpillar requires Bardahl Maxlub at 0.025 percent concentration. These additives provide lubricity for the injector pumps and fuel injectors that would normally get lubrication from diesel fuel. The Lubrizol additive also provides detergency to control fuel injector tip deposits formed from condensing lubricating oil vapors. The concentration may be increased to 0.09 percent to better control fuel injector tip deposits. DDC methanol engines also use a lubricating oil formulated with a Lubrizol additive package with low ash properties to work together with the fuel additive detergent to control fuel injector tip deposits. Maxlub also contains corrosion inhibitors to protect components in fuel systems that have not been redesigned with methanol-compatible materials.

Since there may be an opportunity for widespread availability of an M100 in nationwide fuel stations with the use of blending pumps, it would be desirable for any additives needed in M100 for heavy-duty diesel cycle engines to be compatible with blending into M85 for FFVs, the principal early market. The blending pump approach would otherwise only be able to dispense M85, principally for the FFV market. Heavy-duty methanol vehicles could carry small containers of required fuel additives, but this is distinctly less desirable since even occasional failure to add them may compromise the service life of sensitive components.

The key issue here is whether "additivized" M100 will be compatible with the requirements of OEMs for M85 dispensed into their FFVs. General Motors indicates that the lubricity additives are acid based and would lead to unacceptable conductivity in M85 for FFVs. High conductivity accelerates electrolytic and galvanic corrosion of metallic fuel system components and may also interfere with the capacitive methanol-content sensor that is the heart of FFVs from GM, Chrysler, and most import manufacturers.

M100 ignition improvement vs. compression ignition engine design changes

Design changes to compression ignition (diesel) engines to use methanol fuels involve three principal methods. A fundamental characteristic of diesel fuels is ignition quality, measured by Cetane rating. This is a measure of a fuel's ability to autoignite under diesel engine combustion chamber pressures and temperatures with a minimum delay from injection to ignition. Methanol fuel is characterized by a low Cetane rating and, unless measures are taken, will experience unacceptable ignition delay when injected into a diesel combustion chamber. Ignition delay is a function of temperature; a sufficiently high temperature in the combustion chamber will accelerate ignition to achieve acceptable delay times.

There are typically two or three methods used to generate the combustion chamber temperatures necessary for acceptable methanol ignition:

1. Glow plugs, similar to those used in passenger car and light truck indirect-injection diesel engines. Glow plugs can be energized for cold starting only (DDC 2-stroke) or may be controlled to maintain a desired temperature to extend glow plug life and minimize alternator load.

2. Increased compression ratio (DDC raises compression from 17:1 to 23:1)

3. Exhaust gas recirculation (this is readily accomplished in 2-stroke engines by bypassing some mechanical blower airflow to reduce the flow of cylinder scavenging air, maintaining higher combustion chamber temperatures for the next combustion cycle). It may be possible to accomplish sufficient internal exhaust gas recirculation to facilitate methanol ignition in 4-stroke engines by the use of variable valve timing technology.

An alternative method is to employ an ignition improver in the fuel that imparts diesel-like ignition quality. Avocet is a proprietary nitrate-ester ignition improver additive available from ICI Americas Inc. that has been tested in a variety of heavy-duty methanol engine conversions.

The ignition-improved methanol fuel allows a diesel engine to function normally with only fuel system material compatibility and fuel injection quantity changes. The result is elimination of diesel smoke and some reduction of NOx emissions, while retaining diesel-like fuel efficiency.

Unfortunately the use of Avocet at the 5 percent level (M95A) necessary for good ignition in unmodified diesel combustion systems is expensive. It typically adds 10 cents per gallon to the fuel price for every percentage of Avocet concentration. This cost can be reduced by making some mechanical changes in the engine to attain acceptable ignition quality with lower Avocet concentrations. These changes can be any, or any combination, of the three ways described above to increase cylinder temperatures prior to injection. Also, in fairness to the chemical supplier, current Avocet pricing is limited by small-scale production. The supplier makes a credible claim that increased quantities will substantially reduce the price.

Fuel-grade methanol

There has been much discussion of the potential for a lower price "fuel-grade" methanol. Chemical grade methanol is produced and marketed around the world for a variety of uses, including formaldehyde-urea resin glues for wood building products and cleaning of electronic circuit boards. Since it is widely known that methanol is an aggressive solvent that tends to pick up the "flavor" of any susceptible materials it comes in contact with, it is very important for methanol marketers to maintain a reputation for high-purity standards. This leads to the use of specialized equipment and procedures in tankers and other storage and transport modes to maintain high purity. Tanks that have previously stored other products are typically steam cleaned with mechanical scrubbing of all surfaces before methanol can be loaded. Some of this emphasis on cleanliness could be relaxed, resulting in a saving to fuel users if (or when) a "fuel-grade" market can be established. Production plants could reduce final distillation of the product, also providing cost savings. However, this implies production facilities dedicated to the fuel market, a step that seems unlikely in the short term while the fuel market is relatively small compared to the chemical market.

If a standard for "fuel-grade" methanol can be established that maintains the benefits of good combustion and low emissions while reducing the extra costs associated with producing, transporting, and storing the higher purity chemical-grade product, the expectation is that prices will be substantially lower. It seems obvious that contamination of methanol with gasoline or gasoline components would not constitute a problem if the product is used to blend M85. Allowance of co-mingling with gasoline component transport vessels would also facilitate the integration of methanol into established petroleum fuel transport systems (both tankers and pipelines). Establishment of a market for fuel-grade methanol would also allow the price for chemical-grade methanol to maintain its own level and not be affected by a demand established for lower-price fuel methanol. These markets are distinctly different and this would maintain independence.

However, little research has been accomplished to provide confidence that parts of the chemical-grade specification can be *relaxed* without compromising vehicle durability and low emissions. The emphasis has, rather, been on identifying sources of contamination in storage and dispensing systems that need *more* control to achieve adequate durability of engine components.

Summary of Conclusions

1. Additives have been identified to provide flame luminosity improvement for M100. However, they are not economically available and have not been shown to improve emissions of FFVs.

2. FFV fuel filter clogging must be controlled by some combination of removing unprotected aluminum components from fuel storage and dispensing systems, protecting aluminum components in contact with the fuel, dosing only the gasoline fraction of M85 with gasoline deposit control additives, and by filtering to 1 micron before dispensing fuel into FFVs. This is needed to provide acceptable reliability and component durability.

3. M100 additives are identified by diesel-cycle engine manufacturers for fuel injector and fuel pump durability improvement.

4. M85 can be used in two-stroke heavy-duty diesel cycle engines to avoid concerns about

flame luminosity. Initial poor fuel injector life can be improved through correct use of OEM-specified fuel and lubricating oil additives.

5. Avocet can facilitate the use of methanol (M95A) in heavy-duty diesel-cycle engines and minimize the need for extensive engine combustion system modifications to improve ignition. The cost for the additive must be compared to the cost for engine modifications to determine the most cost-effective approach.

6. Fuel-grade methanol is a concept that may or may not provide a way to reduce the price of methanol in the future to better compete with gasoline and diesel. The ability of engines and fuel systems to withstand moderate levels of certain impurities will determine the success of this alternative.

Acknowledgment

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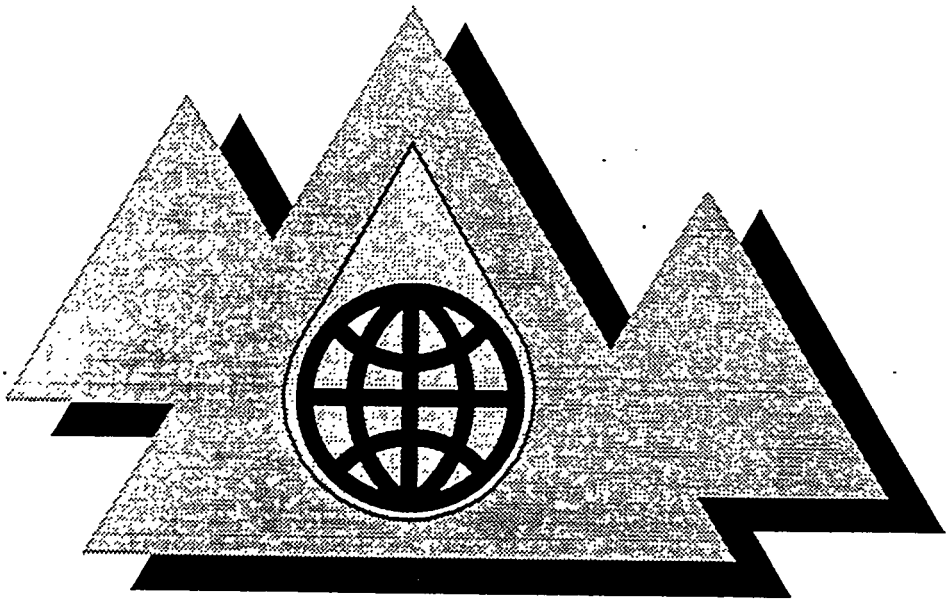

Biochemical Process Routes

BACTERIA FOR POWER ALCOHOL
YEAST FOR BREAD AND BEER

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Abstract

Zymonomas offers the following advantages over yeast, using starch - or sucrose-based renewable resources:

- Shorter fermentation time
- Reduced contamination risk because of its fast growth and ethanol production
- Higher ethanol tolerance
- No fusel oils, glycerol or lactic acid formation. Ethanol is almost parmaceutical grade, reducing the BOD in the effluent markedly
- Cascading inoculum technique eliminates regular cleaning and sterilization of fermenters, allowing a faster turn around time.
- Significant reduction of foaming and less cooling because of less heat produced from the lower required cell population, and a higher temperature tolerance
- Centriguation and biiomass recycle can be eliminated and replaced by the cascading technique
- Distiller's dried grain (DDG) contains higher protein, 34% against 30%, and is FDA approved
- Sterilization of raw material an obsolete requirement
- Liquid effluent recycle of 50% possible

These advantages that bacteria, *Zymomonas mobilis*, holds over yeast allow for a more economical and environmentally friendlier way of producing power alcohol. This paper provides the detail and background which support these claims.

BACTERIA FOR POWER ALCOHOL
YEAST FOR BREAD AND BEER

Introduction

Yeasts have been used and constantly developed over the centuries for making fermented drinks such as beer and for bread. It is through many of the yeasts by-products that these flavors have been encouraged, however, in the power alcohol industry, flavor is not a requirement. The requirement for this industry is efficiency and economics. *Zymomonas mobilis* is a bacteria which has been developed for this purpose. The technology is more friendly to the environment and is generally referred to as the *Zymomonas* Ethanol Technology, or Zytech. (Doelle & Doelle, 1989; Lawford, 1988).

The unique features of the plump facultative anaerobic rod *Zymomonas* are:

(a) to convert quantitatively sucrose, glucose and fructose into ethanol, which does not allow significant by-product formation such as glycerol or fusel oils;

(b) to uncouple growth in favor of ethanol production resulting in small cell requirements for high ethanol productivity rates;

(c) to possess two separate enzymes for glucose and fructose utilization, allowing the formation of a mutant blocking fructose conversion to ethanol.

The biochemical uniqueness of Zymomonas translated into process economic terms should therefore allow for:

1. Higher unit of pure product per unit feed;
2. Reduced total heat generation;
3. Reduced carbon loss to cell mass;
4. Eliminatiion of glycerol and unwanted by-products;
5. Fructose accumulation using fructokinase-negative mutants.

These unique features led to extensive laboratory studies, leading to scale-up commercial evaluation.

Industrial Applications

In Australia, two *Zymomonas* processes have been developed, the Sugartek and Starchtek process. The following paragraphs will discuss the advantages of *Zymomonas* technology over the yeast technology for power alcohol.

Process Performance

Sugartek Process

This involves sucrose based materials, allowing two options to be selected:

Sucrose to Ethanol

The theoretical conversion is:

1 ton sucrose -> 538 kg ethanol + 524 kg CO_2

Zymomonas mobilis in the Sugartek process converts sugar-cane syrup and all

molasses at least 94% sucrose to ethanol, depending on the sugar and salt concentrations in the substrate (figure 1).

1 ton sucrose -> 505.7 kg ethanol + 492.6 kg CO_2

Sucrose to Ethanol Plus Fructose

The theoretical conversion is:

1 ton sucrose -> 269 kg ethanol + 257 kg CO_2 + 526 kg fructose

A special mutant of Zymomonas defective in fructose utlization produces (figure 2):

1 ton sucrose -> 257.7 kg ethanol + 246.2 kg CO_2 + 523.9 kg fructose

This process has been carried out using sugar-cane syrup and C-molasses (blackstrap molasses), and was more successful on the molasses.

Starchteck Process

This process is based on using *Z. mobilis* in the conversion of starch/glucose to ethanol. The starch sources used in trials include potato, maltrin, wheat, corn, milo (sorghum) and barley.

This process can be considered depending on raw material.

Glucose Syrup

Zymomonas mobilis in the Starchtek process converts 98% of the glucose to ethanol plus CO_2 with ethanol yields of 12% (v/v) obtained (figure 3).

Dry-milled Grain

In using corn (maize), milo (sorghum) or wheat, simultaneous saccharification and fermentation give 96% starch conversion efficienceis, depending on the liquefaction efficiency. Using the Starchtek process, *Zymomonas mobilis* produced 2.7 gallons (10.2 L) per bushel (25.4 kg), or 400 L per ton of grain.

Process Advantages (figure 4)

Fermentation Time

Sugartek

(a) Ethanol. the average fermentation time for syrup and molasses is 16-24 hours. With high concentrations of salt contianing molasses, it takes up to 30 hours (figure 1).

(b) Ethanol plus fructose. the average fermentation time is 24-30 hours, depending on the concentration of the C-molasses (figure 2).

Starchtek

Depending on the starch source and solid content, *Zymomonas mobilis* fermentation ranges from 24 to 45 hours (figure 3).

Ethanol Yield

Sugartek

(a) Ethanol. A 10% (v/v) ethanol has been achieved with sugar-cane syrup and molasses, which is equivalent to a 95% ethanol yield.

(b) Ethanol plus fructose. A 96% ethanol yield can be achieved using *Zymomonas mobilis* on sugarcane syrup and C-molasses (figure 4).

Starchtek

In large scale-up experiments using sorghum (Millichip and doelle 1989), it was found 13% ethanol was obtainable, provided the Brix levels were available during prefermentation. The limiting factor in these trials in the existing plants were

that no higher than a 25-26% solid flow was allowed through the heat exchangers into the fermenters. Z. mobilis was found to tolerate 28-30% solids, producing 14% ethanol (shown only on small scale because the industries did not allow the higher solids through the heat exhangers). Yeast does not tolerate higher than 24% w/v solids with 18% w/v starch.

When the same fermentation system as yeast was used, an average ethanol concentration of 12% (v/v) was achieved.

Cooling Requirement

Less cooling water is required using the Zymomonas technology because Zymomonas mobilis has a higher tolerance to fermentation temperatures, saving on electricity costs. Furthermore, less heat is generated because of the low cell yield formation due to growth uncoupling.

Inoculum Cascading Technique

An inoculum cascading technique (Doelle et al 1989 a,b) proved to be very successful and reliable, saving the industry not only the capital but also the running and maintenance costs due to the elimination of preparation of new inocula, regular cleaning and sterilization of the fermenters. Zymomonas mobilis was grown up only once for the initial inoculation and start of the first fermenter. After a set period of fermentation, an appropriate size inoculum representing 10-20% of the fermenter mash to be inoculated, was taken from fermenter one to fermenter two, and so on, with fermenter one being refilled or left and fermented out until no residual glucose was detectable. This method has been repeated over 100 successive transfers over a six (6) month period at a 4,450 L scale, so cell recycle and centrifugation can be eliminated, saving equipment costs.

Product Purity

Ethanol and Carbon Dioxide

The ethanol produced in the *Zymononas* ethanol technology is near parmaceutical grade and the carbon dioxide contains negligible sulphur.

Effluent

Negligible fusel oils, glycerol and lactic acid are produced by Zymononas mobilis, as well as a lower BOD (Biological Oxygen Demand) due to the lower biomass requirement for fermentation. A very important product of the dry milling grain ethanol industry is distillers dried grain or DDG for animal feed. The analysis from

Table 1: Laboratory Analysis of DDGS (Distillers Dried Grain plus Syrup Addition)

	DDGS Yeast	Zymonomas
Moisture	10.7%	11.0%
Protein	30.9%	34.3%
Fiber	8.8%	7.5%
Fat	10.7%	9.5 %
Ash	5.9%	4.6 %
Starch	14.17%	12.1 %
Total Digest N.	75.44%	76.9 %
Total Sugars	0.36%	0.18 %
Std Plate Count	2,100 g^{-1}	120 g^{-1}
Bulk Density	29.6 lb ft^{-3}	25.75 lb ft^{-3}

the Zymomonas large scale process revealed a 3% higher protein content compared with the samples from the yeast process, is lighter in weight and exhibits a significantly lower microbial count (Millichip and Doelle 1989). FDA approval has been received for the distillers dried grain. This

distillers dried grains all feed, especially since *Z. mobilis* does not produce glycerol which is an undesirable product in animal feeds. The lack of glycerol in addition to the higher protein content improves the price for the animal feed significantly and also benefits the economics of the total process.

Infection Risk and Sterilization

A reduced infection risk occurs with *Zymomonas mobilis* because of its rapid growth and early production of ethanol during fermentation (figure 5).

The raw materials of both sugar-base or starch-base do NOT need to be sterilized before fermentation because of its rapid growth and fast ethanol production.

Foaming During Fermentation

Significant foam reduction is observed when using Zymononas mobilis, whereby NO antifoam is required, cutting costs of additives.

Liquid Effluent Recycle to Save Process Water

Using a starch-based fermentation the liquid effluent is recycled and the solids used for animal feed. Yeast can only tolerate 30% recylce due to the glycerol produced, which has adverse effects on the yeast. *Zymomonas* has been shown (Laboratory scale) to have no adverse effects when recycling 50% because no fusel oils or glycerol are produced.

Conclusion

The major advantages mentioned in *Zymomonas* Technology over the yearst technology are:

1. Fermentation time
2. Ethanol yield
3. Product purity
4. Reduced foaming
5. No sterilization of raw material

The combination of all of these process advantages leads to an estimated saving of 20% in process costs and 20% in capital costs of new designed production facilities.

So the yeast should be continued to be used for the flavorsome drinking beverages and breads, but the bacteria *Zymomonas mobilis* should be used for power alcohol.

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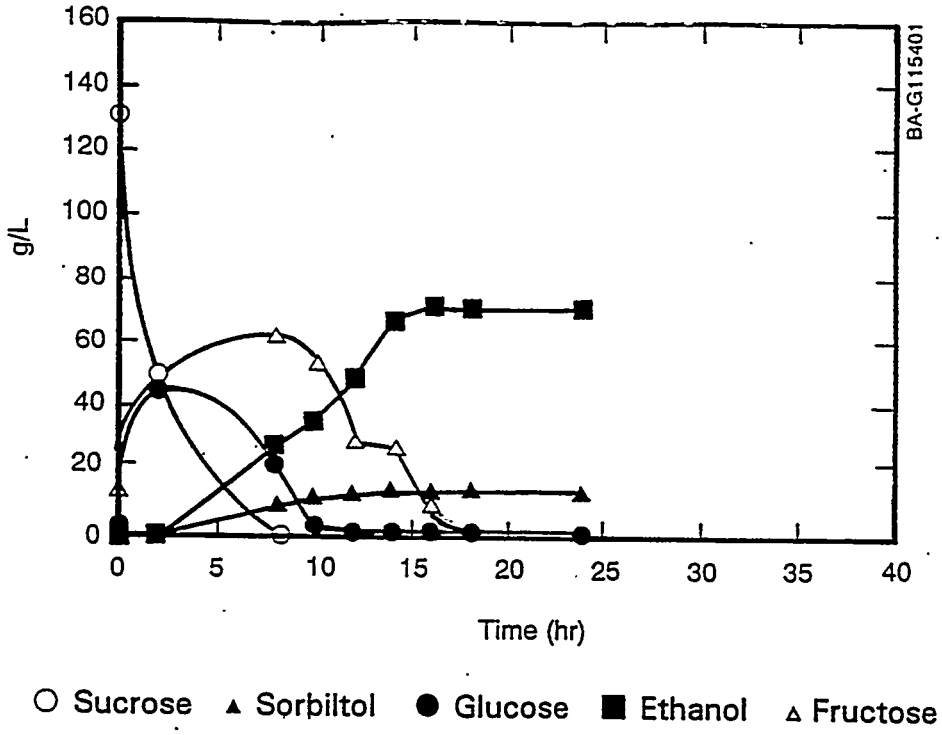


Figure 1. Ethanol formation using 50 g/l C - molasses added to 200 g/l sugarcane syrup in the presence of invertase and *Zymomonas mobilis* 2716

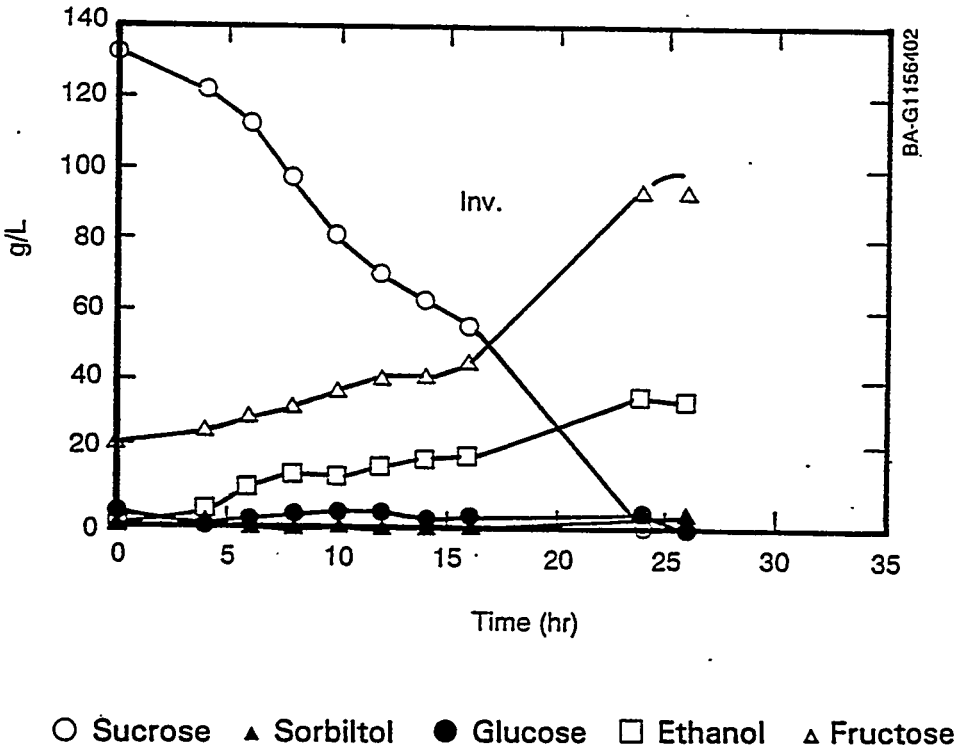


Figure 2. Fructose and ethanol fermentation from 250 g/l C - molasses, and 88.9 g/l syrup using *Zymomonas mobilis* mutant 2864.

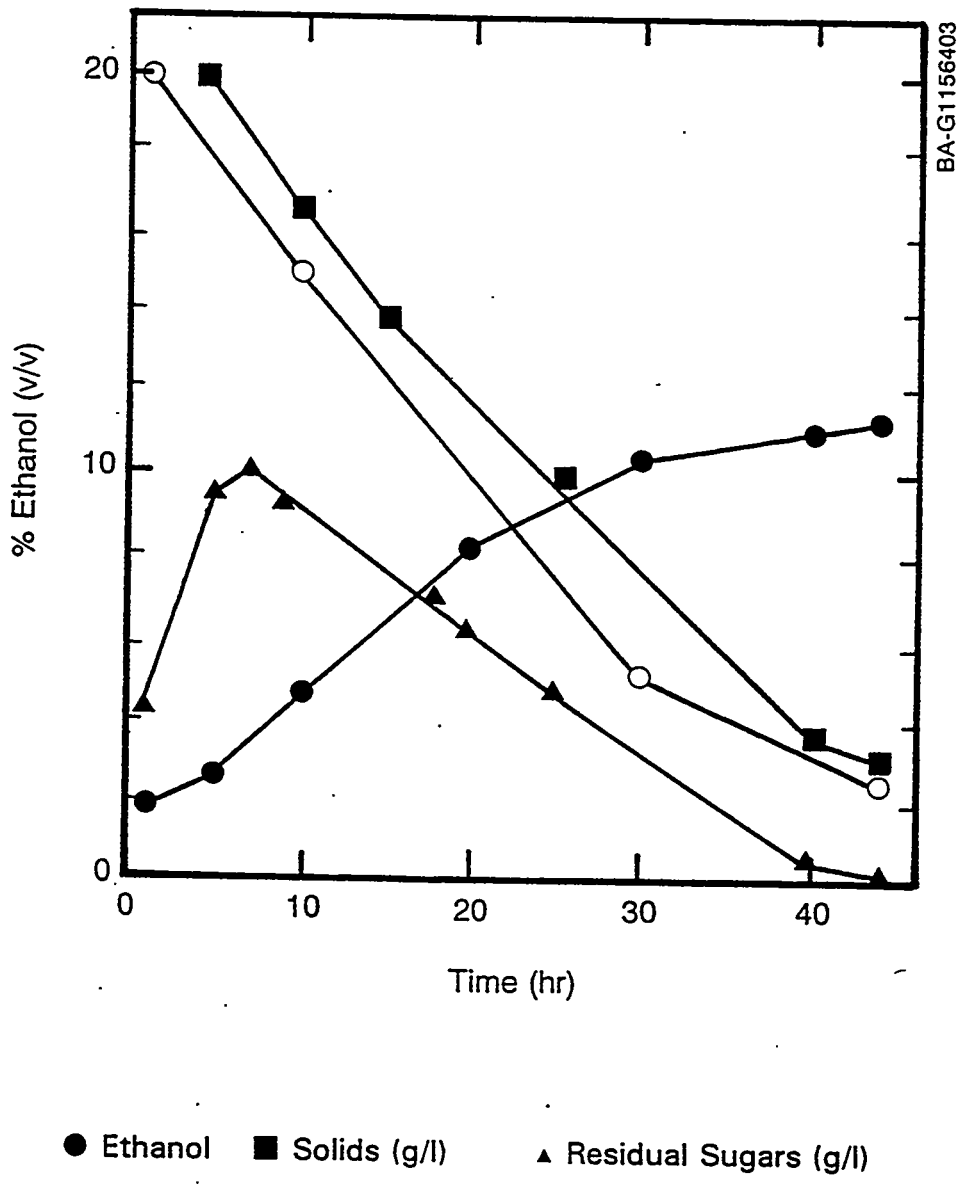
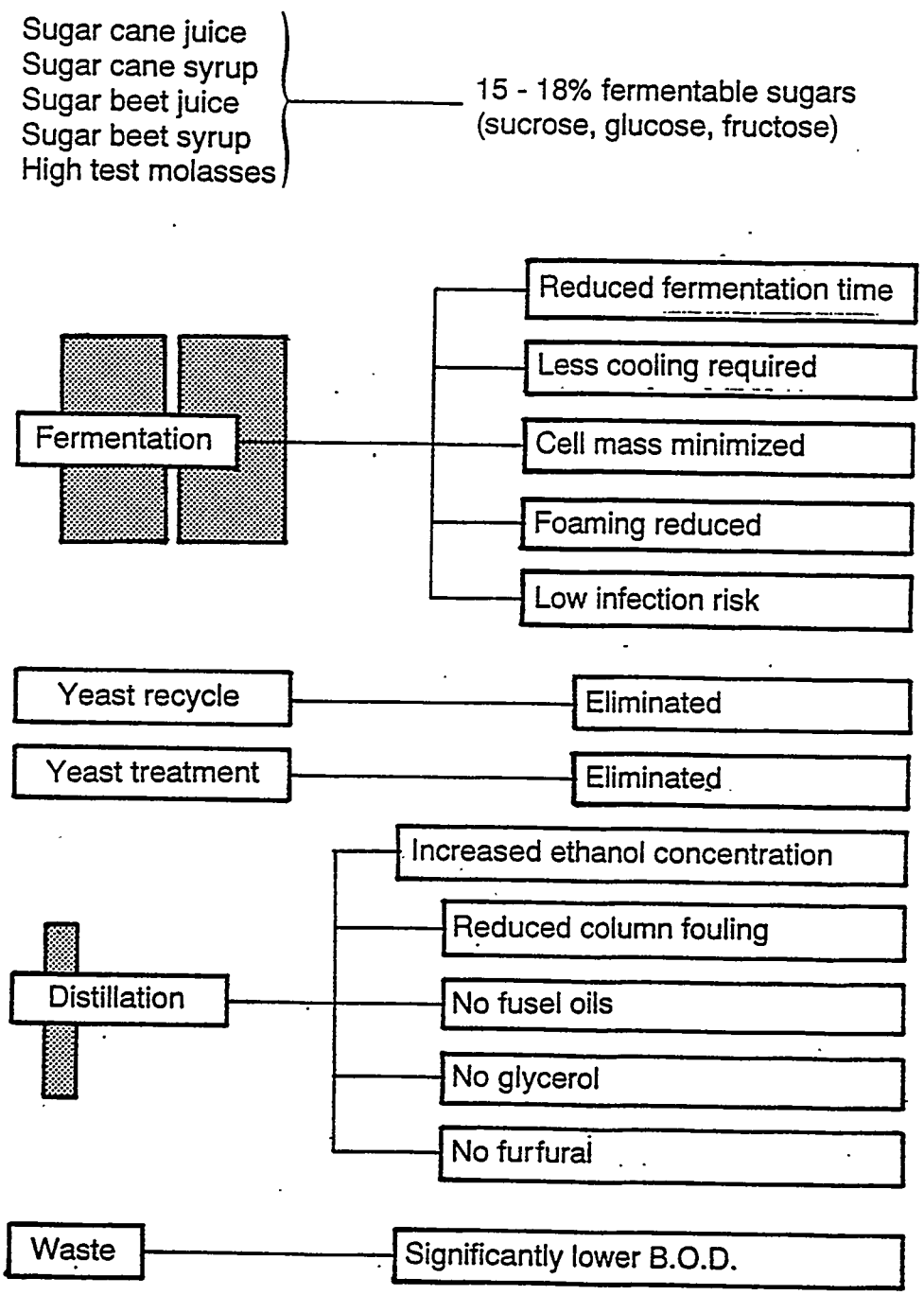


Figure 3. Simultaneous saccarification and fermentation of dry-milled milo (3,500 U.S. gallons = 13,200 l) using *Zymomonas mobilis*



SUCROTECH

Figure 4a. Process advantages of *Zymomonas mobilis* technology

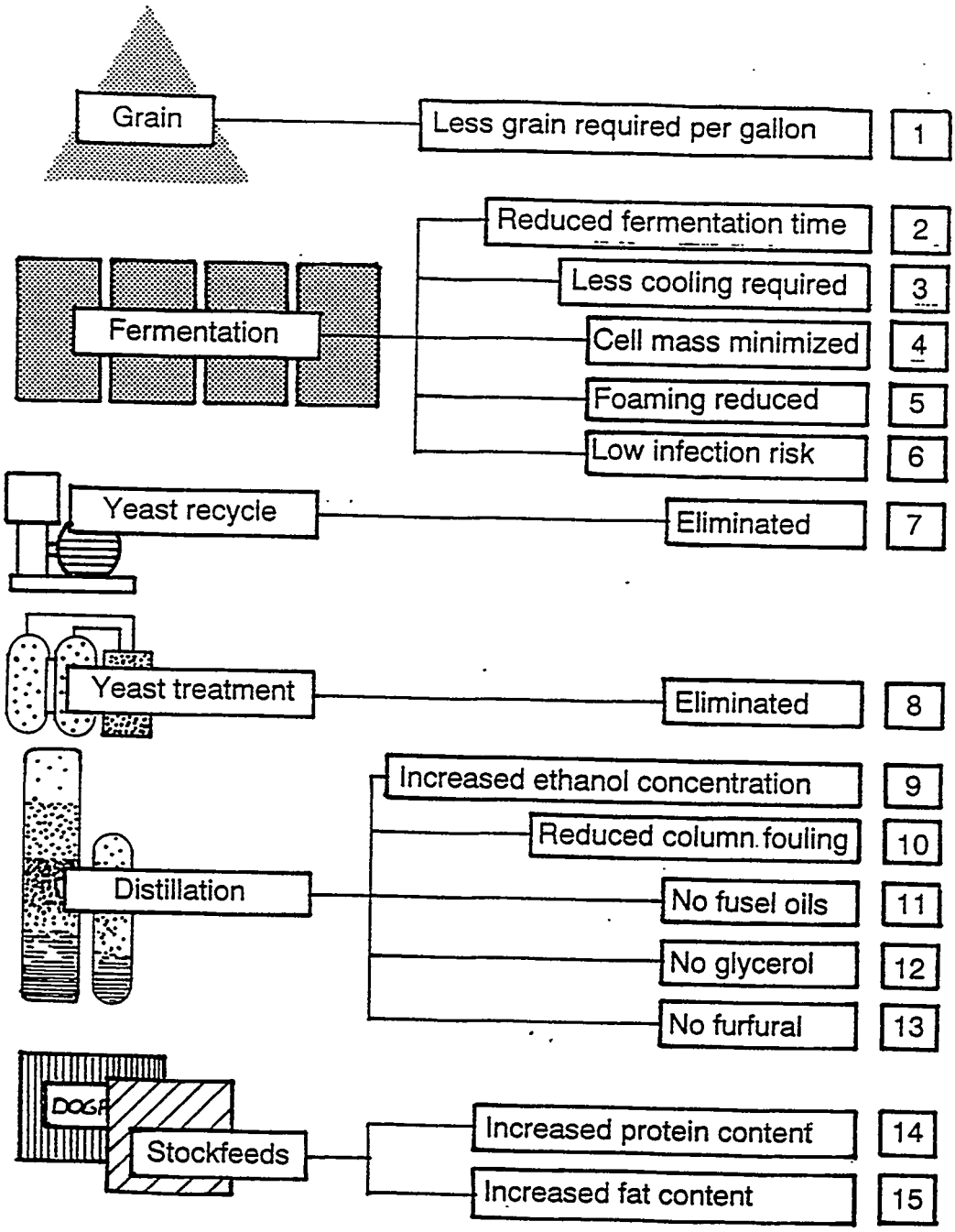


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Figure 4b. Process advantages of *Zymomonas mobilis* technology

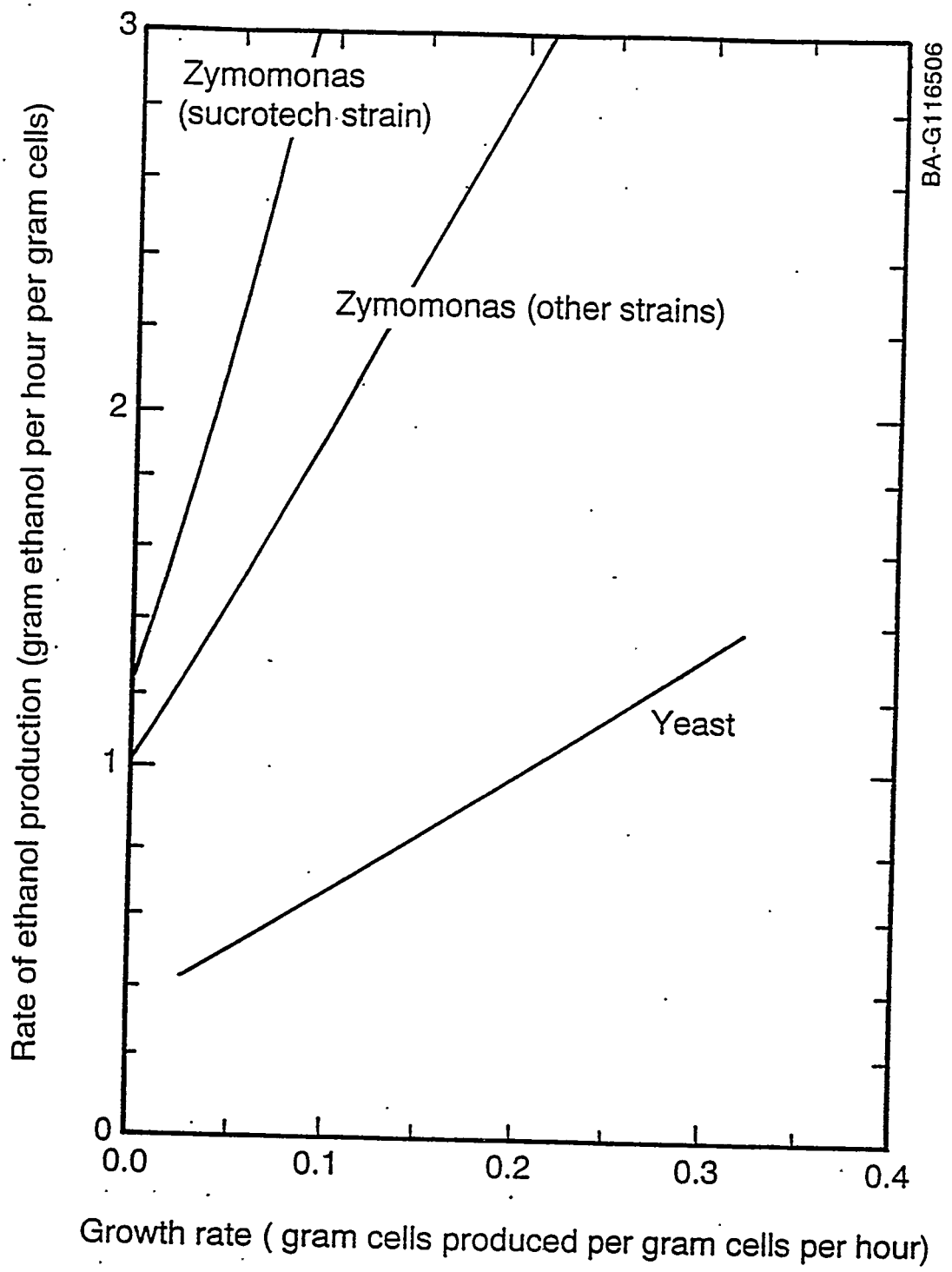

Figure 5. Comparison of the *Zymomonas* technology strain with *Zymomonas* strains and yeast

ALCOHOL PRODUCTION BY CONTINUOUS COFERMENTATION OF WHEY AND CORN

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Whey, a waste product of the cheese industry, was utilized as the liquid portion of corn starch mash and to supply about 28% of the fermentable carbohydrates as lactose for alcohol fermentation. Initially, in a continuous cofermentation of whey-corn mixture, using free cells of *Kluyveromyces marxianus* and *Saccharomyces cerevisiae*, *Kluyveromyces marxianus* from the first fermentor would take over the *Saccharomyces cerevisiae* in the second fermentor, resulting in longer fermentation by whey-corn cofermentation, using immobilized yeast, has been developed - involving a separate fermentation of the lactose from the whey using immobilized *Kluyveromyces marxianus* in the first fermentor, followed by the fermentation of the corn sugar using immobilized *Saccharomyces cerevisiae* in the second fermentor. The total fermentation time for the complete utilization of sugar was reduced to only 28 hrs (compared to 114 hrs by the conventional single culture batch process), and a final ethanol concentration of 10.9% v/v (95% of theoretical value) was obtained from whey-corn mixture. This continuous cofermentation process appears to possess a potential of significant savings in raw material an labor costs in the alcohol manufacture.

ETHANOL PRODUCTION BY CONTINUOUS COFERMENTATION OF WHEY AND CORN

Introduction

In 1990 and 1991, nearly 60 billion pounds of whey were produced in the United States. With our ever-increasing demand for cheese, it is expected that the production of whey will also be increasing. A recent report of the American Dairy Products Institute indicated that only about 47 to 48% of the whey produced was further used in human food and animal feed and the remaining 52% or about 30 billion pounds of whey are under-utilized or discarded (American Dairy Products Institute, 1990).

Whey contains approximately 5.0% lactose, 0.7% protein, 1% fat and salts (Kosikowski, 1977). With its high biochemical oxygen demand (nearly 30-50,000 ppm), discarding of nearly 30 billion pounds of whey annually puts a heavy economic burden on the cheese industry (Jones, 1974; Marwaha & Kennedy, 1988; Singh *et al.*, 1983). Dumping of huge quantities of whey down to the sewer system is costly to the dairy industry and constitutes a significant loss of a potential energy source. It is further feared that the forth coming newer EPA regulations may prohibit entirely the discharging raw whey in the municipal waste waterways. Conversion of the whey lactose to ethanol for use in gasohol (10% alcohol blended with 90% gasoline) would eliminate a costly environmental pollutant while extending our limited petroleum reserves.

Ethanol can be produced by fermentation of virtually any of the carbohydrates. The process economics of fermentation-derived industrial ethanol are greatly influenced by substrate cost. In the U.S., ethanol is produced mostly from corn via conversion of the starch to simple sugars for fermentation. The corn used for alcohol production represents up to about one-half of the process cost (Weiss & Mednick, 1983). Therefore, any substrate cost reduction would logically favor the overall economics of the process.

Alcohol production from whey has been investigated by many researchers. Early research indicated that *Candida pseudotropicalis* (*Torula cremoris*) was the most efficient among the various type of lactose fermenting yeast tested (Rogosa *et al.*, 1947). Later, it was reported that the *Kluyveromyces marxianus* (also known as *K. fragilis*) was the most efficient lactose fermenter (Yoo, 1969). Since whey contains only about 5% lactose, the major problem for alcohol production from whey is that the amount of alcohol produced from whey alone would be very small and its distillation would be very uneconomical (O'Leary *et al.*, 1977; Singh *et al.*, 1983). Attempts have been made to concentrate the lactose level and then subject it to fermentation (Burgess & Kelly, 1977; Kosikowski & Zorek, 1977; Singh *et al.*, 1983). However, these processes involve unnecessary increase in the energy input, and require large quantities of concentrated whey from a given region which restricts the number of feasible plant sites (Hacking, 1986). Still another problem for alcohol production from whey alone is that the high yielding, fast-fermenting, ethanol-tolerant *Saccharomyces* strains are unable to ferment lactose. *Kluyveromyces marxianus* ferments lactose, but its fermentation is very slow, often requiring up to 1 week to ferment 20% lactose (Gawel & Kosikowski, 1978; Moulin *et al.*, 1980). It has been demonstrated that the growth and ethanol production rate of *K. marxianus* was greatly reduced when greater than 4% ethanol was encountered in fermentation (Mumford, 1981).

As an alternative process, the combining of corn with whey to produce alcohol was studied in this and other laboratories (Freind *et al.*, 1982; Gibbons & Westby, 1983). The

advantages of this type of process are 1) the low whey requirement by a small-scale alcohol plant makes the technique more universally applicable within a given region; 2) the lactose contribution of the whey substantially lowers the corn required to produce the same amount of ethanol, then reduces the cost of ethanol production; 3) the utilization of whey increases the use of agricultural waste products for industrial products. However, a severe lag was reported in the batch cofermentation of whey-corn mixture. The cofermentation of corn whey by the conventional process with the single culture required up to 114 hr for complete sugar utilization (Gibbons & Westby, 1983). In the case of simultaneous addition of two mixed culture, i.e., *S. cerevisiae* and *K. marxianus*, *S. cerevisiae* outcompeted the *K. marxianus*, resulting in a high residual lactose concentration after 72 hr fermentation. Ultimately, employing a modified starch conversion process, a staggered inoculation for batch cofermentation of corn whey was developed in this laboratory, with the total fermentation time of 60-72 hr (Whalen, 1985, 1987). The current study was to examine the feasibility of continuous ethanol production by cofermentation of whey-corn and to further optimize the fermentation time.

Materials and Methods

Organisms and Media

Kluyvermyces marxianus NRRL y - 2415 and a distiller's yeast, *Saccharomyces cerevisiae* ss *ellipsoides* were used in this study. Stock culture of *K. marxianus* was maintained on a YLA medium containing (in 1 liter of distilled water) 5 g yeast extract (Difco), 10 g lactose, 5 g proteose peptone #3 (Difco), 5.45 g $(NH_4)H_2PO_4$, 2.42 g KH_2PO_4, 1.31 g $(NH_4)_2SO_4$, and 15 g agar. The *S. cerevisiae* was maintained on the YGA medium (substituting glucose for lactose in YLA). The medium composition used for precultivating the cells (used for inoculation and immobilization) was the same as the medium for maintenance, except the sugar content (lactose or glucose) was increased from the 10 g/liter to 100 g/liter. The media were sterilized at 121°C for 15 min. The YLA medium was used for viable counts of the yeast cells during the course of the fermentation. After incubation at 30 °C for 60 hr the colonies *S. cerevisiae* formed was much smaller than *K. marxianus*. Thus, *S. cerevisiae* were easily differentiated from *K. marxianus* on the basis of size.

Conversion Process

Figure 1 shows the scheme for whey permeate corn starch mash conversion process. Whey permeate obtained from a regional Mid-Am cheese plant (Norfolk, NE) contained 5.4% lactose, and was used as liquid portion in the whey-corn mash. Corn-starch (Argo, 7% moisture) of 1.541 kg were placed in a blender jar and mixed with whey permeate of 11 liter to make a mash volume of 12 liter. After blending, the mash was heated to 90 °C and liquefaction was carried out by using a α-amylase (Taka-Therm II L-170) at 0.12% of DSB (dry starch basis). Saccharification was carried out by using a fungal α-amylase (Clarase L-40,000) at 0.1% of DSB. All enzymes were from SOLVAY ENZYMES, Inc., Elkhart, IN. After saccharification, yeast extract (Sigma) of 0.3% was added and the mash was sterilized at 121°C for 10 min. The whey-corn mash mixture was then cooled down to be used as continuous fermentation feed.

Immobilization Procedure

The precultivated yeast cells (50 ml) were mixed with 1% sodium alginate solution (1 L) at room temperature. The resulting alginate-yeast mixture was aseptically pumped into a gently stirred 0.2 M $CaCl_2$ solution. Alginate beads (diameter 3-4 mm) entrapping a small number of growing yeast cells were formed. The beads were allowed to stand overnight at 4 °C to complete the gelation process before use.

Fermentation Method

Figure 2 is a schematic of the two-stage CSTR (Continuous Stir Tank Reactor) fermentation system. The first stage was a 2 liter New Brunswick (NBS) fermentor with working volume of 1 liter. The second stage was a 5 liter NBS fermentor with working volume of 2 to 3.5 liter, adjusted as the investigation required. In the case of free cell fermentation, the first fermentor was inoculated with 50 ml of precultivated cells of *K. marxianus* and the second one with 100 ml of *S. cerevisiae*. When the immobilized system was used to carry out the fermentation, the first fermentor contained immobilized *K. marxianus* cells and the second one *S. cerevisiae*. A Masterflex pump from Cole-Parmer was used to pump the medium, i.e. the whey-corn mash, to the fermentor. The fermentor contents were mildly agitated at 80 rpm to provide gentle mixing. The Glucoamylase (Diazyme DL-200) was diluted to 10 times and pumped into the second fermentor at different rate based on 110 DU (Diazyme Units)/kg of starch and different dilution rate. The temperature in the fermentors was automatically controlled at 30 ^{0}C. The filtered air was supplied at the rate of 0.1 v/v/min. Sampling was made once or twice a day to confirm whether or not the steady state had been achieved. If the ethanol concentration neither increased nor decreased in three residence time intervals at the specified dilution rate, it was assumed that the process had reached the steady state. This procedure was carried out over a range of various dilution rates.

Analyses

Samples were collected at appropriate time intervals and filtered (passing through 0.45 μm cellulose nitrate membrane) immediately for ethanol analyses. Our previous trials indicated that centrifugation instead of filtration of the experimental samples for ethanol determination showed lower ethanol concentration than the true value. Part of the filtered samples were stored in a deep freezer for later sugar analyses. The high performance liquid chromatography (HPLC) was employed for ethanol and sugar analyses. The HPLC system consisted of a M45 pump, U6K injector, R401 Differential Refractometer from Waters & Associates and a Spectro-Physics SP4270 integrator. Carbohydrate analysis was performed using a Waters Carbohydrate Analysis column. The ethanol content was determined by using a C_{18} DextroPak radial column.

Results and Discussion

Two Stage Cofermentation with Free Yeast Cells

According to the literature (Jones *et al.*, 1981) and our experimental tests, *K. marxianus* can't utilize maltose while *S. cerevisiae* can't utilize lactose. The mash conversion strategy was designed to result in high maltose and low glucose content in fermentation feed. The initial sugar concentration analyses showed the means of 4.72% lactose (coefficient of variation, CV= 6.5%), 6.97% maltose (CV=2.8%), and 0.85% glucose (CV=10%) present in whey-corn mash, and the rest were maltotriose and dextrin. A small amount of lactose might be converted into glucose and galactose due to the presence of a low level of lactase in fungal α-amylase. The very low level of glucose was deemed desirable since the introduction of glucose in the first fermentor would shift the fermentation from lactose to glucose.

In the two-stage CSTR cofermentation with free yeast cells, *K. marxianus* was the sole yeast involved in the first fermentor, where the lactose fermentation was the major activity. The sugar and ethanol analyses showed that *K. marxianus* performed well in the first fermentor. When the dilution rate was larger than 0.15 hr^{-1}, which is equivalent to the fermentation residence time of 6.7 hr, the residual lactose was detected (data not shown). When the dilution rate was 0.10 hr^{-1} (fermentation residence time 10 hr), the

glucose and lactose in the whey-corn mash was utilized completely and the ethanol concentration was 3.27% v/v, with a standard deviation (SD) of 0.22% (CV=6.7%). Also, as expected, maltose was not utilized at all. The population of the *K. marxianus* remained to be 135 × 10^6 cfu/ml, with a SD of 17× 10^6 cfu/ml (CV= 12%) in the first fermentor (Figure 3).

The glucoamylase was added to the second fermentor to encourage maltose and dextrin conversion into glucose which was fermented simultaneously. In the second fermentor both *K. marxianus* and *S. cerevisiae* were present after continuous process started, since the effluent from the first fermentor inevitably brought *K. marxianus* to the second fermentor. Initially, it was expected that the *S. cerevisiae* would be predominant in the second fermentor since the batch cofermentation indicated that *S. cerevisiae* would out-compete the *K. marxianus* if two of them were present simultaneously in the whey-corn mash (Whalen, 1985). However, the opposite proved to be true. Our preliminary experimental data indicated that if the continuous fermentation was initiated while the population of the *S. cerevisiae* in the second fermentor was not high enough, the *K. marxianus* coming from the first fermentor will be predominant in the second fermentor very quickly. The population of *S. cerevisiae* in the second fermentor dropped from 35 × 10^6 cfu/ml to 22 × 10^6 cfu/ml within 10 hr and was 5 × 10^6 cfu/ml by 48 hr.

If the continuous fermentation was allowed to proceed only after the *S. cerevisiae* in the second fermentor had reached a fairly high population, the process of *K. marxianus'* domination still occurred, although it did so more slowly. Figure 4 shows the viable counts of yeast, ethanol production and residual sugar concentration in the second fermentor when the initial population of *S. cerevisiae* was fairly high. The dilution rate for the first fermentor was kept at 0.1 hr^{-1} as described above and it was varied in the second one with 0.033 hr^{-1} at the beginning. No sooner did the continuous fermentation begin, the *S. cerevisiae* cell concentration dropped from 241 × 10^6 cfu/ml to 126 × 10^6 cfu/ml within 29 hr while *K. marxianus* increased from 0 to 41 × 10^6 cfu/ml in 10 hr and was 73 × 10^6 cfu/ml by 29 hr in the second fermentor. Then the population of *S. cerevisiae* continued decreasing while the *K. marxianus* maintained the population of 76 × 10^6 cfu/ml with a SD of 8 × 10^6 cfu/ml (CV=10%) at the dilution rate of 0.033 hr^{-1}. After it declined to 45 × 10^6 cfu/ml (122 hr), the population of *S. cerevisiae* seemed relatively stable. However, under this dilution rate, the sugar was not completely utilized. The ethanol concentration was 9.2 % v/v (SD=0.64%, CV=7%) with the total residual sugar being 2.51 % w/v (glucose and maltose together). When the dilution rate decreased to 0.025 hr^{-1}, the sugars were utilized almost completely (residual sugars less than 0.3%) and ethanol production increased to 10.7% v/v (SD=0.24%, CV=2%). *Kluyvermyces marxianus* maintained a population of 46 × 10^6 cfu/ml with a SD of 7 × 10^6 cfu/ml (CV=15%) at the dilution rate of 0.025 hr^{-1}. This population was lower than that at the dilution rate of 0.033 hr^{-1}, obviously due to the higher final ethanol concentration in the second fermentor. The population of *S. cerevisiae* slightly increased at the first and decreased again. When it decreased to 31 × 10^6 cfu/ml, the population of *S. cerevisiae* dropped sharply to 5 × 10^6 cfu/ml within 64 hr. Simultaneously, the ethanol concentration decreased, with the concomitant increase in the residual glucose and maltose level. This was almost identical to the situation where the continuous fermentation started while the population of *S. cerevisiae* was only 35 × 10^6 cfu/ml. Daily microscopic observation of the morphology of the two yeasts, *K. marxianus* and *S. cerevisiae*, revealed no obvious size change during the course of the fermentation. These observations suggest that *K. marxianus* would predominate over *S. cerevisiae* during two-stage continuous free cell cofermentation of whey-corn mixture no matter whether the initial population of *S. cerevisiae* was high or not. Consequently, the two-stage immobilized yeasts system was developed.

Two Stage Cofermentation with Immobilized Yeast Cells

The two-stage cofermentation with immobilized yeast was constructed as in Figure 2, based on the separate fermentation of the lactose from the whey using immobilized *K. marxianus* in the first fermentor, followed by fermentation of the corn sugar using immobilized *S. cerevisiae* in the second fermentor. When whey-corn mixture was pumped through the fermentation system, like the free cell continuous system, the immobilized *K. marxianus* was the only yeast in the first fermentor. *Kluyvermyces marxianus* would first utilize the small amount of glucose present in the whey-corn mash, then shifting to other fermentable sugars. Since it could not ferment either maltose or dextrine, *K. marxianus* would ferment lactose after exhausting the small amount of glucose. Studies were made to develop optimal dilution rates or to study the optimal residence time required for fermentation. The complete utilization of lactose could be achieved for the dilution rate of 0.08, 0.115, 0.12 and 0.14 hr^{-1} in the first fermentor. When dilution rate was 0.17 hr^{-1} or larger, the lactose was not completely converted to ethanol (Figure 5). Finally, the highest dilution rate (0.14 hr^{-1}) for complete lactose fermentation was selected for further studies.

Figure 6 shows the effect of dilution rate on ethanol production and residual sugar levels in the second fermentor where immobilized *S. cerevisiae* was used. The complete fermentation was achieved when dilution rate was 0.0496 hr^{-1} or lower. This means that the conversion of dextrine and maltose, plus the fermentation of monosaccharide and disaccharides were all accomplished in the second fermentor within 20 hr. Based on the studies on dilution rates for both fermentors, the working volume of 1 liter for the first stage and 2.8 liter for the second stage was determined for two-stage continuous immobilized system. The overall dilution rate for two-stage system was 0.0368 hr^{-1} and the total fermentation time was 28 hr. The fermentation was carried out under these conditions. The lactose and corn sugar in whey-corn mixture were completely converted to ethanol with the final ethanol concentration of 10.9 % v/v (SD=0.22%, CV=2%).

Since it is difficult to determine accurately the initial concentration of maltotriose and dextrins, glucoamylase was added to whey-corn mash in order to convert maltose, maltotriose and dextrins into glucose. This method allowed more accurate analyses of the total initial fermentable carbohydrates. After saccharification for 3 hr at 60. ^{0}C using glucoamylase, the whey-corn mash contained 10.85% glucose, 2.05% maltose and 4.57% lactose. Neither dextrins nor maltotriose was detected. According to Borglum (1981), one gram starch could be converted to 1.11 gram of glucose. Our results were in general agreement with the theoretical calculation. The fermentation efficiency of the two-stage immobilized system was 95%.

The total time required for the cofermentation of whey-corn mixture, as developed in this project, was considerably lower than that reported by earlier workers. O'Leary *et al.* (1977), and Gibbon and Westby (1983) reported a severe lag in the fermentation of the lactose from either lactase pretreated whey or whey-corn mixture by the conventional process with a single culture. In their studies, the ethanol production and sugar consumption profile showed biphasic pattern. The delayed fermentation was due to diauxie — with the lactase pretreated whey, glucose and galactose were used sequentially in that order; whereas, in experiments without the lactase pretreatment, glucose and lactose were used sequentially in that order. Gibbon and Westby (1983) also reported that the delayed fermentation of lactose lengthened the fermentation time up to 114 hr. In the batch cofermentation using simultaneous addition of the *K. marxianus* and *S. cerevisiae*, Whalen *et al.* (1985) observed a severe lag in the lactose fermentation. Because of the competition between the two yeast, the growth of more predominant yeast *S. cerevisiae* limited the

maximum population of the *K. marxianus*. As a result only 27% the original lactose was fermented after 72 hr. In the staggered inoculation, *K. marxianus* reached a high population before the addition of *S. cerevisiae*. The lactose in the whey-corn mash could be utilized in about 48 hr, while the total fermentation taking about 60-72 hr (Whalen, 1985, 1987). However, this technology presumably was not operative in the continuous process. When free yeast cell system was used for continuous cofermentation, the *K. marxianus* from the first fermentor would transfer to and predominate in the second fermentor and inhibit the growth of *S. cerevisiae*. Eventually *K. marxianus* from first fermentor would take over the *S. cerevisiae* in the second fermentor. In the two-stage continuous immobilized system, however, the lactose was used up in less than 8 hr in the first fermentor and complete fermentation of whey-corn mixture could be accomplished in 28 hr. This appears to be due to: 1) The *K. marxianus* was separated from *S. cerevisiae*, and there existed no competition from *S. cerevisiae* in the course of lactose fermentation; 2) The whey-corn mash conversion method as carried out in this study resulted in the feed with a very low level of glucose, the diauxic fermentation being minimized in the first fermentor; 3) The ethanol level only reached 3.1-3.5 % v/v in the first fermentor, thus its inhibitory effect on the growth and fermentation of *K. marxianus* was greatly reduced; and 4) Due to the immobilization, less free cells of *K. marxianus* from first fermentor could pass into the second fermentor. At the same time, the immobilized *S. cerevisiae* could maintain high population of this yeast in the second fermentor. Wada *et al.* (1980) reported that the yeast cell population inside the immobilized beads was 10 times higher than the free cell population in the fermentation broth. In our studies, the environmental conditions in the second fermentor, notably the higher *S. cerevisiae* population and ethanol concentration, would favor the *S. cerevisiae* and minimize the possibility of *K. marxianus*' domination. *Saccharomyces cerevisiae* has higher sugar uptake and ethanol production rate so that complete utilization of corn sugar could be accomplished in shorter time.

Since our primary concern at this stage was that calcium-alginate beads may not be damaged in the fermentor, the total volume of the immobilized beads was held fairly low (only about 1/2). Consequently, the ethanol productivity of current system was not very high. Also, usually the column reactor would give a much higher productivity than that of CSTR in immobilized system. However, the current system can be easily adapted by small fermentation plants without any major equipment change. The ethanol productivity could be further increased by increasing the percentage of the immobilized beads inside the fermentor. In our preliminary trials, the two-stage immobilized yeast system has been operated for 55 days without contamination or loss of efficiency, and with only very small number of damaged beads being observed.

Summary

Whey was utilized as the liquid portion of corn starch mash and the lactose content of the whey replaced 28% of the fermentable corn carbohydrates for ethanol fermentation. In a two-stage continuous cofermentation of whey-corn mixture, using free cells of *Kluyveromyces marxianus* and *Saccharomyces cerevisiae*, the *K. marxianus* from first fermentor always took over *S. cerevisiae* in the second fermentor, resulting longer fermentation time and incomplete fermentation. A two-stage continuous ethanol production from whey-corn cofermentation, using immobilized yeast, has been developed, involving a separate fermentation of the lactose from the whey using immobilized *K. marxianus* in the first fermentor, followed by fermentation of the corn sugar using immobilized *S. cerevisiae* in the second fermentor. The diauxic sugar utilization was minimized. The total fermentation time for sugar complete utilization in two-stage

immobilized yeasts system was 28 hr versus 60-72 hr required for the staggered batch process, and was 28 hr versus 114 hr required for conventional single culture batch process. The final ethanol concentration of two-stage immobilized system was 10.9% v/v with the fermentation efficiency of 95%. This continuous cofermentation process appears to possess a potential of significant savings in raw material and the length of fermentation time for alcohol manufacture. Additional studies are in progress to further optimize the system.

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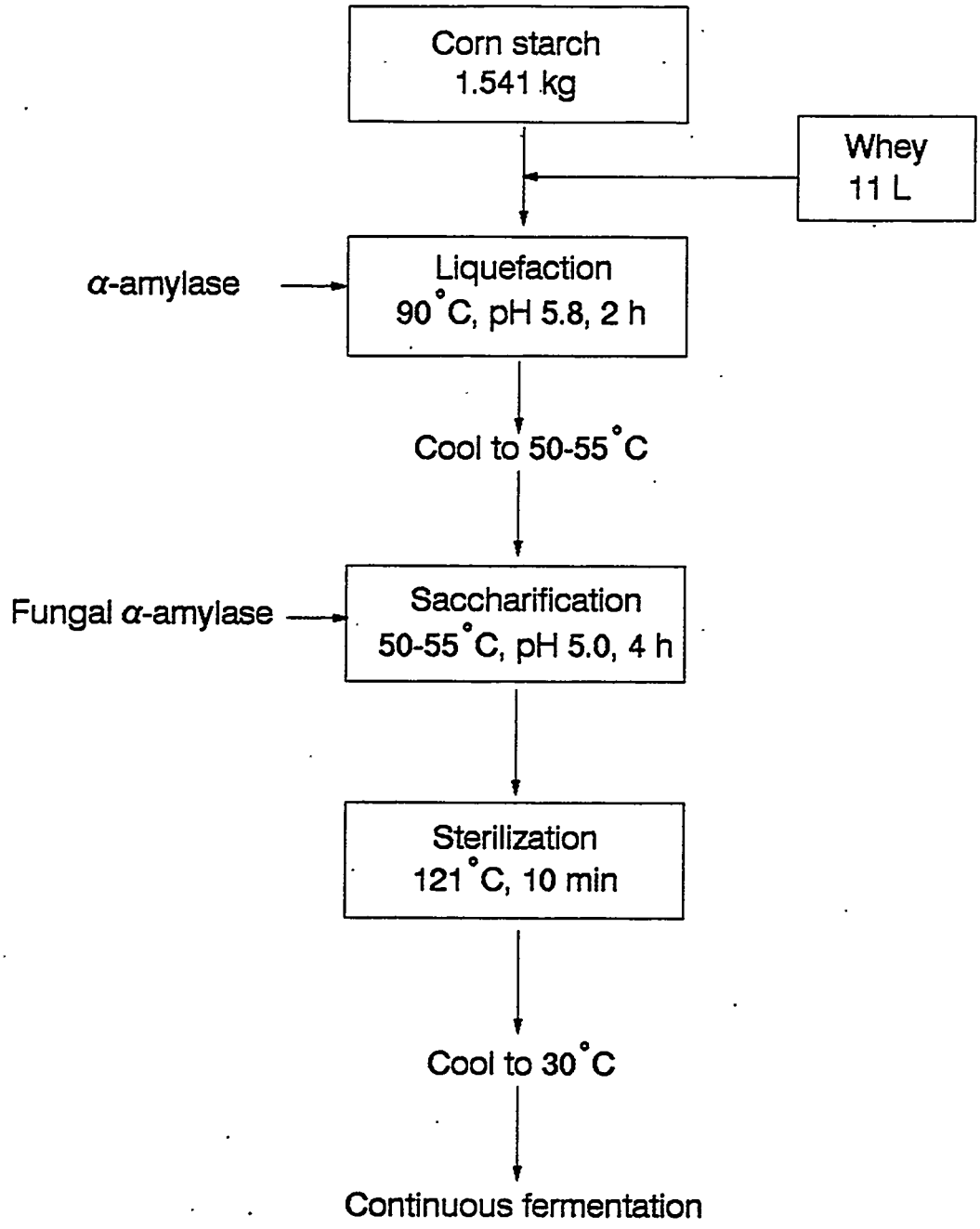


Fig. 1. Whey-corn mash conversion process scheme

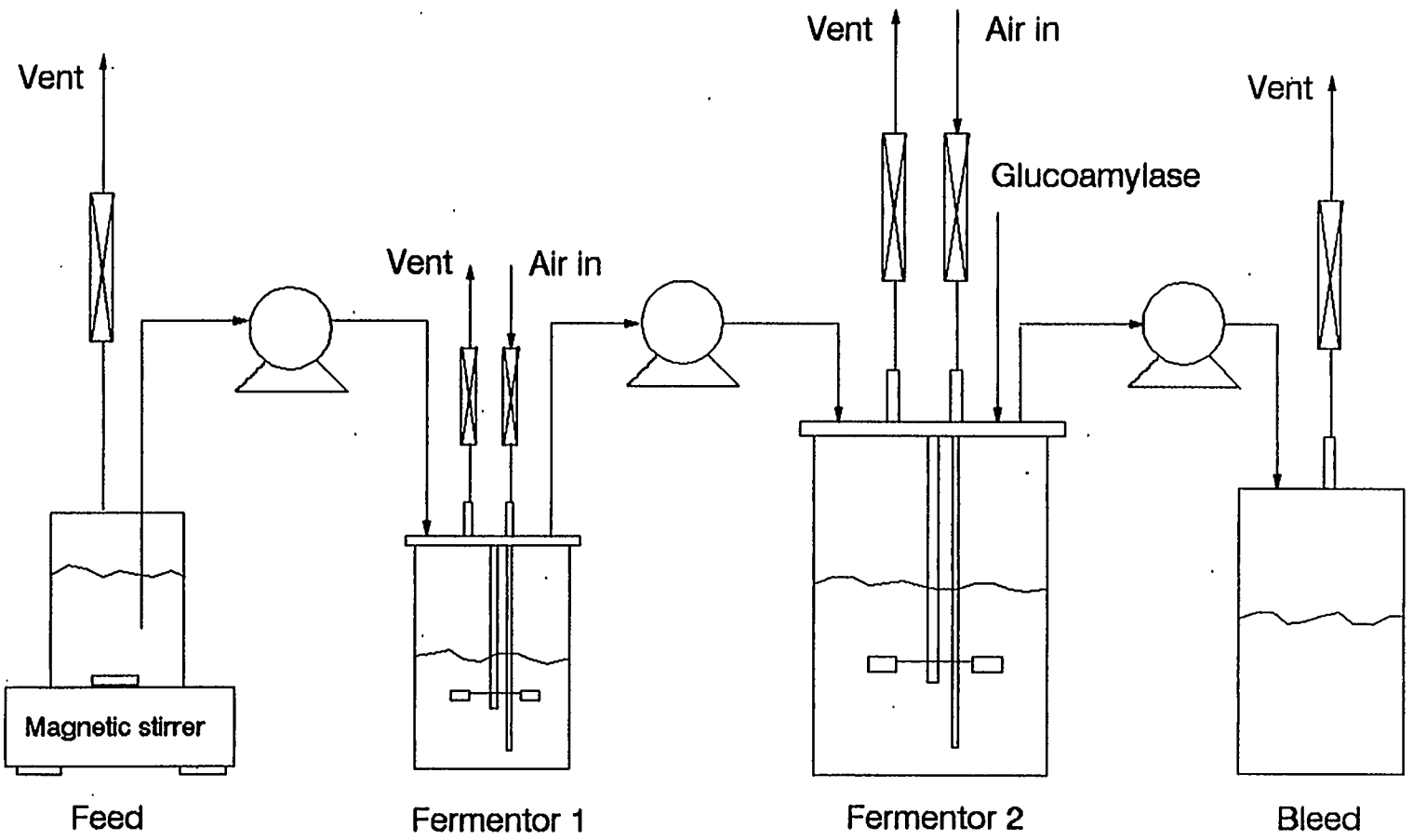


Fig. 2. Two-stage continuous whey-corn cofermentation system
Fermentor 1: free or immobilized *K.marxianus;*
Fermentor 2: free or immobilized *S.cerevisiae.*

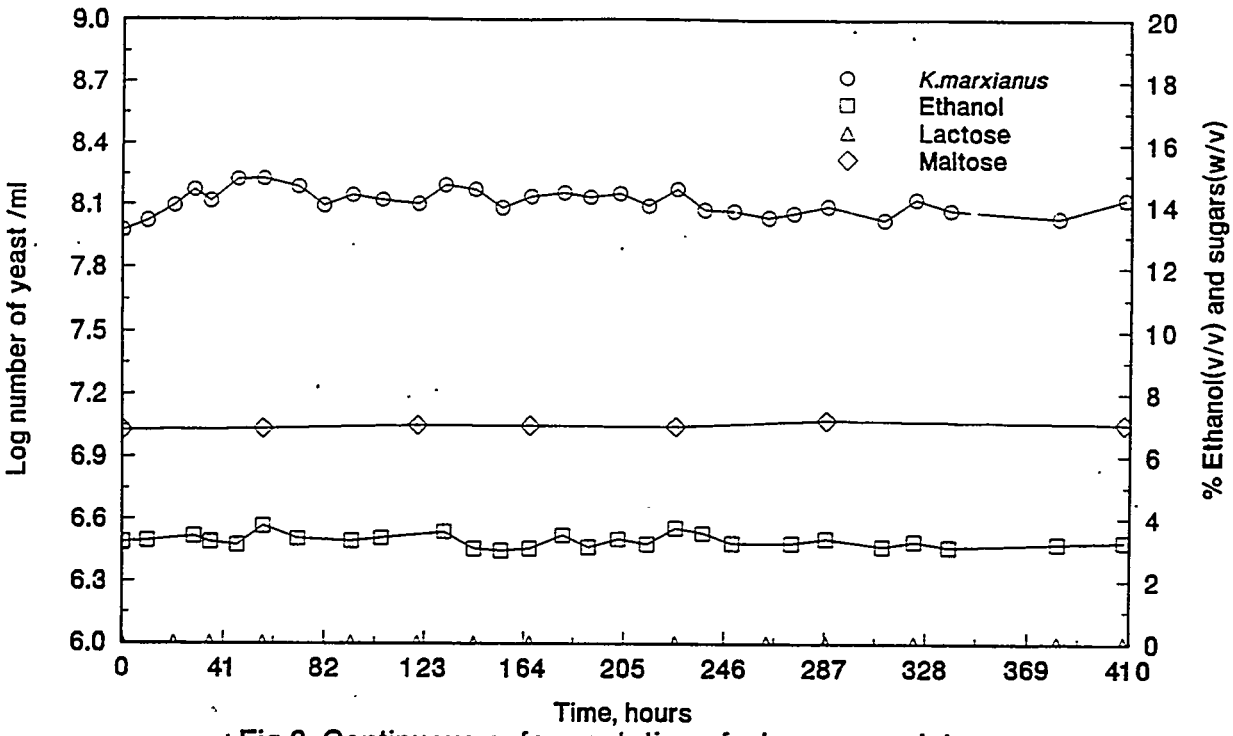


Fig.3. Continuous cofermentation of whey-corn mixture by free yeast cells in the first fermentor, D=0.1 /h.

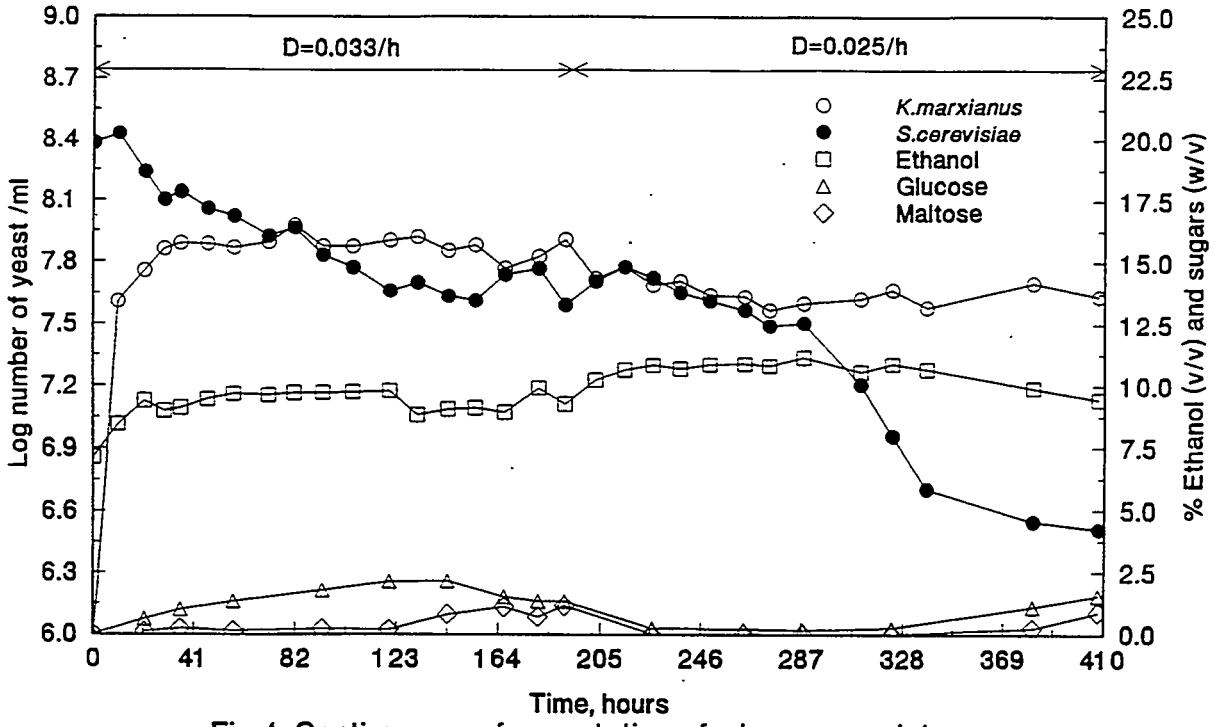


Fig.4. Continuous cofermentation of whey-corn mixture by free yeast cells in the second fermentor.

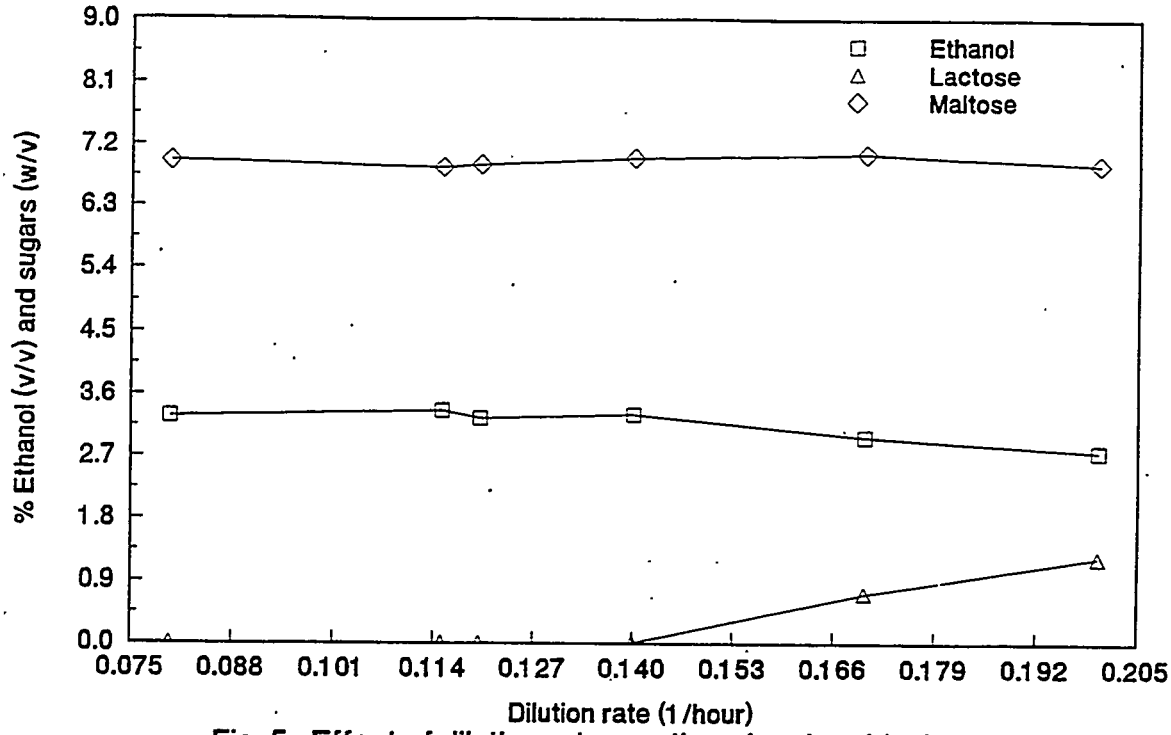


Fig. 5. Effect of dilution rate on ethanol and residual sugars in the first fermentor using immobilized *K. marxianus*

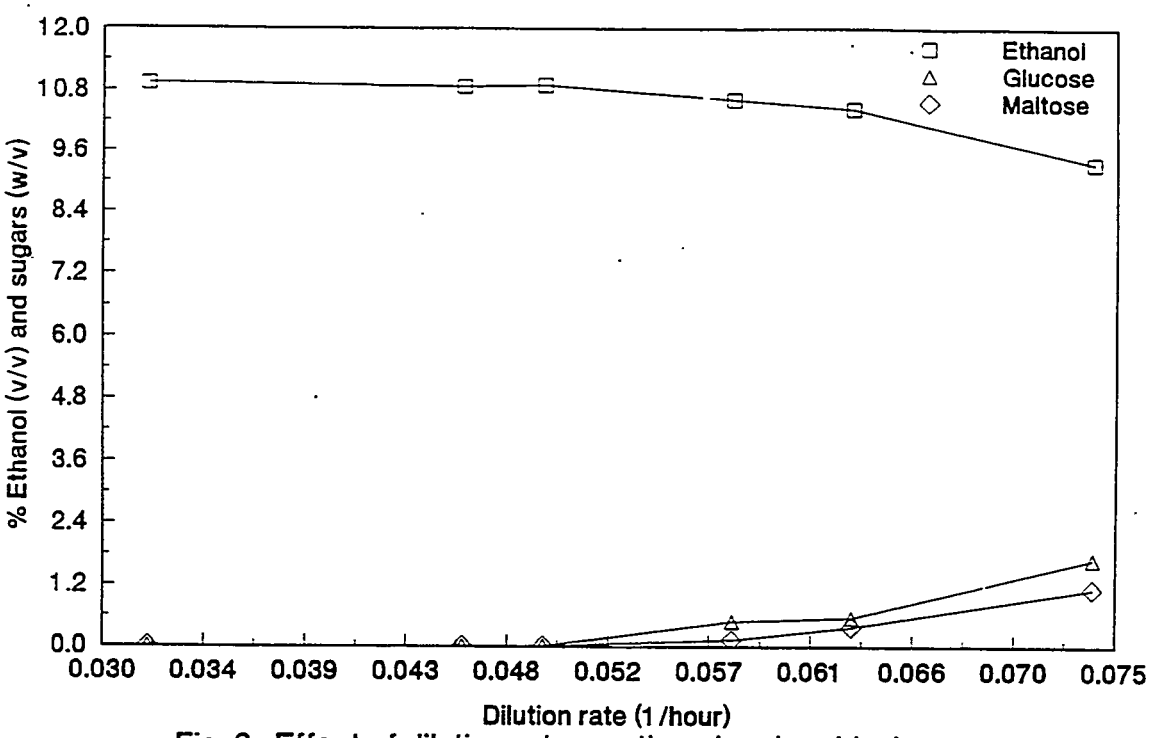
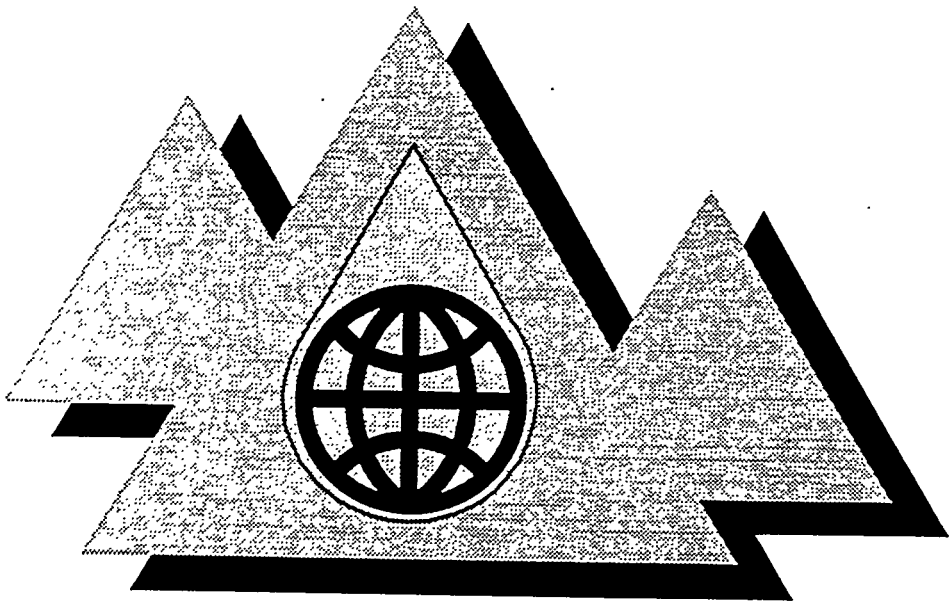


Fig. 6. Effect of dilution rate on ethanol and residual sugars in the second fermentor using immobilized *S. cerevisiae*



Bus Technology and Demonstrations

DOE FLEET TEST ACTIVITIES WITH ALCOHOL FUEL BUSES

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Abstract

The current status of the DOE Alternative Fuel Bus Data Collection Program is discussed in this paper. This program supports the activities of the U.S. Department of Energy (DOE) in fulfilling the requirements of the Urban Bus Program of the Alternative Motor Fuels Act (AMFA) of 1988. The program is a focused study of the alternative fuel buses in service at five selected transit agencies. Results from the alcohol-fuel bus activities are presented.

DOE FLEET TEST ACTIVITIES WITH ALCOHOL FUEL BUSES

Introduction

The U.S. Department of Energy (DOE) has test and evaluation programs underway for alcohol fueled transit buses. These activities are being carried out by the Alternative Fuels Utilization Program in the Office of Transportation Technologies. One part of these activities is fleet tests and demonstrations of alternative fuel vehicles. More than 4,000 alternative vehicles are currently being evaluated by DOE in fleet service in the U.S. The vehicles include a wide range of vehicle types and fuels. Among these are a number of full size, 40-foot, heavy-duty urban transit buses using methanol and ethanol fuel.

In 1988, the U.S. Department of Transportation (DOT) began funding the purchase of alternative fuel buses through a special grant program to transit agencies. As a result, there are now well over 1,000 alternative fuel urban transit buses in service today. In Los Angeles alone, the Metropolitan Transportation Authority is now operating 340 alcohol fueled buses in daily service, accumulating about 1.2 million miles each month. The Alternative Motor Fuels Act of 1988 (AMFA) directed the DOE to investigate the use of alternative fuels in urban transit buses. DOE has, therefore, selected a few transit agencies for intensive study and analysis of their alternative fuel buses.

Objective

The objective of DOE's fleet test activities with alcohol fuel buses is to further our national goals of improving our air quality and reducing our dependence on imported petroleum. The AMFA legislation specified that alternative fuel transit buses be evaluated for safety, reliability, cost, durability, and fuel economy. In addition, evaluation of exhaust emissions is a key aspect of these activities.

Use of Transit Test Fleets

Transit bus fleets are good subjects for investigating heavy-duty alternative fuel automotive technologies. Bus engines and fuel system are very similar to those of heavy-duty trucks. Findings from urban bus studies are therefore very applicable to the much larger population of heavy-duty trucks. Transit agencies are all centrally fueled, allowing the introduction of experimental fuels without concern for fuel availability elsewhere. Transit agencies usually have complete maintenance capabilities with staffs of engineers and highly skilled mechanics. This allows bus fleets to successfully maintain and accurately assess prototype vehicles and new technologies. Also, transit agencies have the advantage of being publicly funded governmental agencies which operate on a non-profit basis. This allows the trial and evaluation of new, unproved technologies to a much greater extent than a typical truck fleet could tolerate in the fiercely cost competitive business environment of the trucking industry.

Program Structure

The DOE Alternative Fuel Utilization Program in the Office of Transportation Technologies controls these activities and

their funding. The DOE has designated the National Renewable Energy Laboratory (NREL) as the government's project manager for these activities. Battelle Memorial Institute is NREL's technical support contractor for accomplishing these activities. The individual transit agencies own and operate the buses and collect the data used to evaluate the buses. They send this raw data to Battelle for processing and analysis each week. Battelle performs extensive processing, coding, and quality control on the data, then sends it in a standard electronic format to NREL's Alternative Fuel Data Center. The NREL Data Center makes the data available to the public through its computer database systems. Battelle and NREL also perform engineering evaluations of the data to make findings and conclusions available in technical reports.

The effort is known formally as the AMFA Phase 2 Alternative Fuel Bus Data Collection Program. The basic strategy of this effort is to observe about ten alternative fuel buses at six locations, along with about five well matched diesel control buses at each location. Table 1 shows the goal of the experimental design.

The transit agencies selected for this study are Peoria, IL (ethanol); Minneapolis/St. Paul, MN (ethanol and particulate traps); Miami, FL (methanol, CNG, and particulate traps); Pierce Transit in Tacoma, WA (CNG); Houston, TX (LNG). These sites were selected based upon the type of buses they have; the availability of well matched control vehicles; and their ability and willingness to provide detailed data. Table 2 shows the data items that are being collected.

Alcohol Buses

The alcohol buses in the program use two fuels; M100 methanol, and E95 ethanol. The U.S. heavy-duty bus population is dominated by two engines; the Detroit Diesel Corporation (DDC) model 6V92 and the Cummins model L10. Only the DDC 6V92 is offered in an alcohol version. Therefore, all of the alcohol buses in this program use this engine. DDC offers both M100 and E95 versions of the engine, and both are included in this program. The DDC alcohol 6V92 can be used in most of the buses available in the U.S. However, only three coach manufacturers have recently sold production alcohol buses in the U.S.: Flxible, Gillig, and Transportation Manufacturing Corporation (TMC). The buses at the Miami site are Flxible Coaches with M100 DDC 6V92 engines. The E95 buses at Peoria are TMC coaches, and the buses at Minneapolis are Gillig coaches. Both use the E95 DDC 6V92 engine. At all three locations, the diesel control buses are identical coaches in all respects except for the fuel. The alcohol and diesel control buses were ordered and built together with identical accessories and drive trains, and have DDC 6V92 engines.

The alcohol buses are all fueled on-site at the transit properties. Alcohol compatible fuel storage and dispensing systems have been installed. The vehicles use Emco Wheaton dry-break fueling nozzles to avoid spills.

Program Status

The alcohol buses are all operating in normal passenger service now. The Miami M100 buses began normal service in the summer of 1993. The Peoria E95 buses began service in the Fall of 1992. The E95

Table 1. Experimental Design

		Technology								
Agency	Engine	M100	E95	LNG Ping	CNG Si	LNG Si	DSL w/trap	DLS Control	Total Count	Bus Description
Houston	DDC 6V92			5				5	10	Mercedes
Miami	DDC 6V92	5						5	10	40-ft Flxible
Miami	Cum L10				5		5	10	20	40-ft Flxible
Minneapolis	DDC 6V92		5				5	5	15	TBD
Peoria	DDC 6V92		5				3		8	35-ft TMC
Tacoma	Cum L1				5			5	10	40-ft BIA Orion
TBD										
Total DDC 6V92		5	10	5	0	0	8	15	43	
Total Cummins		0	0	0	10	0	5	15	30	
Grand Total		5	10	5	10	0	13	30	73	

Table 2. Data Items Being Collected

Type of Data	Frequency Recorded	Data Items
Maintenance Data	For each work order:	Type of maintenance - Scheduled - Unscheduled - Roadcall Labor hours Date of repair Odometer reading Parts replaced - code Parts cost Work done code Date removed from service Date returned to service
Fuel Data	Each time a bus is fueled:	Amount of fuel Odometer reading Date
	Each month:	One sample of alternative fuel and diesel fuel analyzed per Appendix B
Oil Data	Each time oil is added	Make, type, and viscosity of oil Amount of oil Odometer reading
	Each time oil is changed:	Make, type, and viscosity of oil Amount of oil Odometer reading

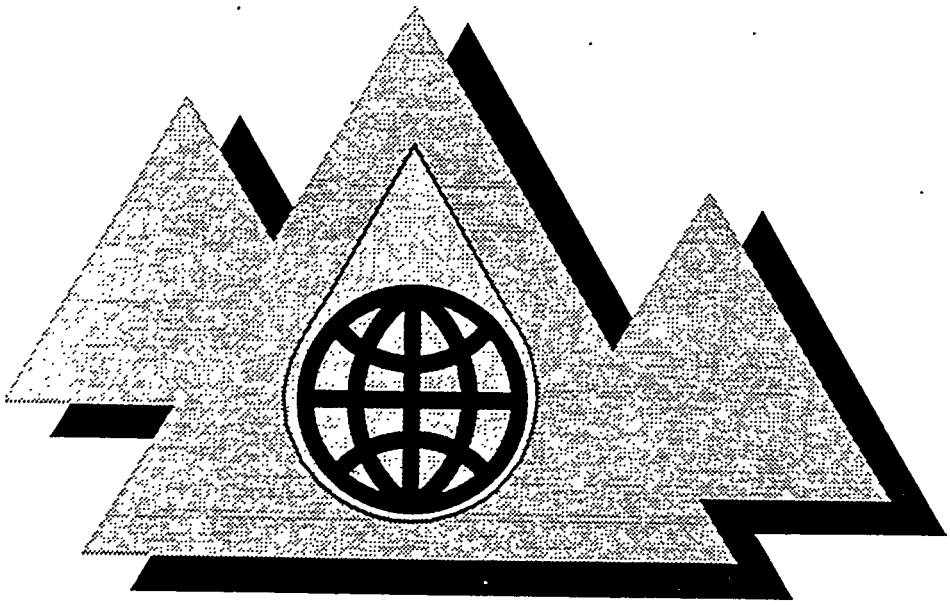
buses at Minneapolis began service in the fall of 1993.

The data collection effort at these sites is just getting underway now. Results to date are too preliminary to draw conclusions yet. Other similar buses have been running for several years at other locations, and they have reported a trend of improving reliability; a large fuel cost difference; and a substantial and persistent additional maintenance burden. Preliminary results at our three sites are consistent with these reports, though the root causes and quantitative differences remain to be established.

Overall, the alcohol buses are providing acceptable levels of passenger service in a harsh service environment. It is important to note that no injuries associated with the alcohol fuel have been reported for alcohol fuel buses since their introduction in the U.S. more than five years ago. This total safe U.S. operating experience with alcohol fuel buses is now more than 10 million miles.

Future Program Activities

The DOE bus program will continue to collect and analyze data on these buses for three years. The data now going to the NREL Alternative Fuels Data Center will be available for public review in the coming months. The program has two comprehensive analysis reports scheduled, one now expected in late 1993 and the other in the summer of 1994. An additional methanol bus site is being selected now from several in the U.S. and Canada, and will be included in the program in the coming months.



Atmospheric Photochemistry of Alcohol Fuels

REACTIVITY ADJUSTMENT FACTOR FOR VEHICLES OPERATING ON E85

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Abstract

The objective of this project is to obtain emissions data appropriate for use to establish a generic reactivity adjustment factor for ethanol. This will enable the inclusion of ethanol in the California Air Resources Board schedule of alternative fuel options for vehicles in the Transitional Low-Emission Vehicle category of low-emissions vehicles.

Four 1992 Chevrolet Lumina variable fuel vehicles that were calibrated for ethanol were used in this work. A single batch of E85 was used for mileage accumulation and emissions testing. The emissions tests for generating reactivity data were conducted after the vehicles had accumulated 4,000 miles.

The Federal Test Procedure was used for the emissions tests, which were done in triplicate for all four vehicles. Vehicle conditioning followed the Auto/Oil procedures. The exhaust speciations included aldehydes and ketones (by high performance liquid chromatography) and alcohols and hydrocarbons (by gas chromatography).

The average reactivity adjustment factor for the 12 tests was 0.68; that is, the reactivity per gram of non-methane organic gases was 68% of that of conventional gasoline. The range of reactivity adjustment factor determinations was 0.61 to 0.79 with a coefficient of variation of 7% for the 12 tests. The appropriate emission standards were met in all 12 tests.

Emission levels of toxics were low for all except acetaldehyde, which is formed by the partial oxidation of ethanol. The average emission rate for total toxics was 26 milligrams per mile. Acetaldehyde constituted nearly 80% of this total.

Introduction

The use of alternative fuels has the potential for reducing emissions of photochemically reactive pollutants from automobiles. Although the mass emissions rates are not necessarily lower than those with gasoline, the photochemical reactivity of the non-methane organic gases (NMOG) can be significantly reduced with alternative fuels. California emissions regulations recognize the benefits of lower reactivity. For vehicles certified to operate on a fuel other than conventional gasoline, the NMOG mass emission value is multiplied by a reactivity adjustment factor (RAF) applicable to the fuel and the vehicle emission control technology category. The reactivity adjusted NMOG emission rate is then compared to the emission standard to determine compliance. The RAF can be specific to the vehicle/fuel undergoing the certification process, in which case the value for the RAF is determined from the detailed analysis of the exhaust NMOG. This is referred to as a unique RAF.

Fuel specific (generic) RAFs can be (and have been) established by the California Air Resources Board. Reactivity data obtained for a variety of vehicles and vehicle models using the candidate fuel are required to determine the value for a generic RAF. There are several requirements for acceptance of reactivity data for the RAF determination. One of these is that the exhaust emissions must be in compliance with transitional low-emission vehicle (TLEV) standards. Others have to do with analytical procedures and repeatability of test results. The RAF for ethanol has not been established

because of the very limited data base. Much of the data from earlier tests was not acceptable because of failure to meet the TLEV standards. Additional experimental data are needed to provide a larger data base for the establishment of an RAF for ethanol.

Objective

The objective of this work was to obtain emissions data appropriate for use to establish a generic RAF for ethanol. This will enable the inclusion of ethanol in the California Air Resources Board schedule of alternative fuel options for use in vehicles to qualify as low-emission vehicles.

Test Methodology

Four 1992 Chevrolet Variable Fuel Vehicles were obtained from GSA/DOE. These vehicles are designed to operate on ethanol-gasoline blends over the range of 0 to 85% ethanol (E85). The fuel passes through a dielectric cell to measure the ethanol content of the fuel. The electronic control system uses this information to make the appropriate adjustment to the fuel injection system for correct stoichiometry. As received, the vehicles had accumulated very low mileage. The vehicles were driven on-road over a period of one month to accumulate 4,000 miles, the minimum required by the Air Resources Board for this type of testing.

A single batch of E85 was used for mileage accumulation and nearly all of the emissions testing. Although this type of fuel is designed as E85, the ethanol content is typically 80-82 volume percent. This particular fuel (fuel A) contained 81 volume percent ethanol. The hydrocarbon portion can be characterized as a light straight run gasoline. Two other E85 formulations were used in emissions tests. Fuel B was prepared by blending EPA certification gasoline with fuel grade ethanol; industry average gasoline was used for the hydrocarbon portion of fuel C. A limited number of tests were conducted with fuels B and C to obtain information on the effects of fuel composition on emissions. Fuel recipes and properties are given in table 1.

The Federal Test Procedure (FTP) was used for the emissions tests, which were conducted at low mileage and, for the RAF data, in triplicate for all four vehicles. Measurement of evaporative emissions is not part of the RAF test, although the diurnal heat build is required. In these tests both diurnal and hot soak emissions were measured. Vehicle conditioning followed the Auto/Oil procedure (1). The Auto/Oil procedure is designed to minimize fuel carryover effects in the evaporative emissions system and in the fuel system. The conditioning also provides ample opportunity for the vehicle's adaptive learning system to acquire the pertinent fuel property information.

The regulated exhaust emissions were measured using standard instrumental techniques. In addition, a heated flame ionization detector (FID) was used for continuous measurement of the total organic gases. The sample line and FID oven were maintained at 235°F. Limited speciation data were also obtained with the standard instruments. Methane concentration was determined by using a catalyst that quantitatively oxidizes all hydrocarbons (HC) and organic gases except for methane. This measurement was used in the computation of the emissions of non-methane hydrocarbons (NMHC) and NMOG.

The dilution air in the constant-volume-sampling (CVS) system was dehumidified and heated to 125°F upstream of the exhaust-air mixer. This treatment helped prevent condensation/adsorption of ethanol (and other polar compounds) in the CVS system and the subsequent loss in analytical samples.

The exhaust analyses included detailed speciation of the hydrocarbons and oxygenates. The speciation sampling and analysis techniques were

- Aldehydes and ketones by the dinitrophenylhydrazine method; sampling with cartridges; analysis by high performance liquid chromatography
- Alcohols by gas chromatography (GC); sampling with impingers; analysis by GC of liquid injection
- Hydrocarbons by GC; sampling of dilute exhaust into Tedlar bags; analysis by GC of gaseous samples.

The evaporative emissions analyses also included detailed speciation of the hydrocarbons and oxygenates. The hydrocarbon speciation of the evaporative emissions was done in the same manner as the exhaust emissions. The ethanol content of the evaporative emissions was determined by a GC analysis of the gas-phase sample.

The speciations are an integral part of the photochemical reactivity assessment. The value for reactivity is obtained

by multiplying the species emission rates by a species reactivity factor and summing this multiple over all NMOG. The reactivity factors are W. P. L. Carter's (2) maximum incremental reactivities which have units of grams of ozone per gram of species. The total reactivity (gO3/mile) divided by the emission rate (gNMOG/mile) gives the specific reactivity (gO3/gNMOG). The ratio of this specific reactivity to the specific reactivity for a baseline fleet operated on industry average gasoline gives the RAF. The value for the baseline specific reactivity is defined as 3.42 gO3/gNMOG for TLEVs.

Results

Initial (low mileage) tests were conducted with the three E85 fuels and EPA certification gasoline to verify that the emissions control and fuel management systems were operating satisfactorily. The regulated emissions were within EPA standards in all eight of the low mileage tests. With the E85 fuels, all four vehicles had significantly lower NMOG and CO emissions than with the certification gasoline. None of the fuel/vehicle combinations achieved the TLEV standards for NMOG without adjustment for reactivity. These results (and the EPA and TLEV emissions standards) are given in table 2. The values for HC, NMHC, and NMOG are on a hydrocarbon equivalent basis. This treatment removes the contribution of oxygen to the mass emissions. The HC, NMHC, and NMOG data in table 2 were derived from the total hydrocarbon measurement, the subtractive technique for methane, and the analyses of oxygenates (primarily ethanol and acetaldehyde). The computation takes into account the response of the heated FID to methane, ethanol, and acetaldehyde relative to propane.

The full speciation data for the low mileage tests with the E85 fuels, including reactivity computations, are given in table 3. The specific reactivities for the three E85 fuels were in the range of 1.7 to 2.2 gO3/gNMOG. This corresponds to RAFs from 0.50 to 0.65. The reactivity adjusted NMOG emissions were well below the TLEV standard in both tests with fuel A and slightly greater than the standard for fuels B and C. Although the specific reactivity was reasonably low with the B and C fuels, NMOG emission rates (with or without reactivity adjustment) were significantly greater than those with fuel A.

Brief (hot start) emissions tests were conducted at regular intervals during the mileage accumulation to ensure that no major problems developed. The results of these tests are given in table 4. The low emissions rates in all tests indicate satisfactory operation of emissions controls and fuel systems. Some differences in the results of these tests can be attributed to variations in degree of warm-up prior to the test. There was no standard conditioning procedure for these tests.

After the 4,000-mile accumulation, emissions tests were conducted in triplicate with full speciation of exhaust and evaporative emissions. The results for the regulated emissions and fuel economy are given in table 5. As in the low mileage tests, CO and NO_x emissions were well below the TLEV emissions standards. Test repeatability was good.

The summary of results derived from the speciation data are given in table 6. The average specific reactivity was about 2.3 gO3/gNMOG. This corresponds to a value of 0.68 for the RAF. The repeatability of the RAF fell well within the Air Resources Board requirements for all four vehicles taken singly and as a fleet total. These requirements are ±15% for the individual vehicles and ±30% for the fleet. The coefficient of variation for the RAF was about 5% for the individual vehicles and 7% for the entire fleet. Applying the RAF to the measured NMOG gives values of less than the TLEV standard of 0.125 gNMOG/mile.

Four exhaust species contributed more than 80% of the total reactivity. These species are ethanol, ethylene, formaldehyde, and acetaldehyde. Although the specific reactivity of ethanol is low (1.3 gO3/g), it is a major contributor to the total reactivity because it constitutes about 60% of the total mass of NMOG. The reactivity values for the other four major contributors range from 5.5 to 7.3 gO3/g.

The toxic compounds in automotive exhaust are defined as formaldehyde, acetaldehyde, 1,3-butadiene, and benzene. With the E85 fuel, emission levels of the toxics were quite low, except for acetaldehyde. Acetaldehyde emissions are significantly higher for ethanol fuels than for other fuels because acetaldehyde is produced by the partial oxidation of ethanol. The acetaldehyde and total toxics emission rate averaged 19 and 25 milligrams per mile, respectively. If the toxic emissions were weighted by toxicity, the total for E85 would be reduced significantly. On the basis of allowable exposures (threshold limit values), acetaldehyde has a much lower toxicity than the other three toxics.

Summary and Conclusions

Emissions tests of E85 fuel were conducted using four identical model variable fuel vehicles that were calibrated for ethanol. Emissions and performance were comparable for the four vehicles. Detailed speciation of the exhaust was performed in order to determine the photochemical reactivity potential relative to that of gasoline. The ratio of the reactivities, the reactivity adjustment factor, was 0.68. With the application of the RAF to the NMOG emissions, the exhaust emissions were less than the California Transitional Low-Emission Vehicle standards. The repeatability of the results was well within the requirements for inclusion in the data base for establishing a generic reactivity adjustment factor for ethanol.

References

1. V. R. Burns, et al., "Description of Auto/Oil Air Quality Improvement Research Program," SAE Paper 912320, October, 1991.

2. W. P. L. Carter, "Development of Ozone Reactivity Scales for Volatile Organic Compounds," Statewide Air Pollution Research Center, Riverside, CA, U. S. EPA Contract CR-814396-01-0, April, 1990.

Table 1. Properties of E85 Fuels

Designation	A	B	C
Components, volume %			
Fuel grade ethanol	-	84%	84%
E85	100%	-	-
isopentane	-	7%	7%
EPA Cert	-	9%	-
Industry average gasoline	-	-	9%
Sp. Grav.	0.758	0.776	0.776
H/C, mole/mole	2.860	2.765	2.767
O/C, mole/mole	0.380	0.372	0.372
Molecular weight/C-atom	20.97	20.75	20.75
RVP, psi	7.8	7.8	7.8
EtOH, vol%	80.5	81.0	81.0
EtOH, wt%	84.3	82.9	82.9
MIR, gO3/gFuel	1.36	1.46	1.50
Composition, wt%			
n-Paraffins	5.7	1.4	2.0
i-Paraffins	5.9	10.7	9.4
Olefins	0.1	0.7	0.9
Naphthenes	3.2	1.1	1.5
Aromatics	0.8	3.2	3.3
Oxygenates	84.3	82.9	82.9
Oxygen, wt%	29.0	28.7	28.7
Benzene, wt%	0.37	0.11	0.26
Benzene, vol%	0.32	0.10	0.23

Table 2. Low Mileage Emissions Test Results

			(mass as HCE = CH1.85)						
			HC	NMHC	NMOG	CO	NOx	CO2	FE
Car	Fuel	Mileage	gpm	gpm	gpm	gpm	gpm	gpm	mpg
EPA standards			0.41			3.4	1.0		
TLEV standards					0.125	3.4	0.4		
215	Cert	57	0.373	0.333	0.333	2.76	0.12	499.6	17.6
215	C	603	0.115	0.067	0.206	1.33	0.11	469.0	13.2
216	Cert	40	0.343	0.298	0.298	2.45	0.13	521.5	16.9
216	A	91	0.068	0.030	0.143	0.49	0.15	467.2	12.9
217	Cert	42	0.378	0.332	0.332	2.07	0.15	532.3	16.6
217	A	80	0.164	0.115	0.163	1.04	0.10	466.5	12.9
218	Cert	50	0.318	0.280	0.280	2.15	0.13	518.4	17.0
218	B	95	0.096	0.050	0.207	1.07	0.11	479.5	12.9

HC = Hydrocarbons
NMOG = Non-methane Organic Gases
CO = Carbon Monoxide
NOx = Nitrogen Oxides
CO2 = Carbon Dioxide
FE = Fuel Economy

Table 3. Low Mileage Speciated Emissions

Car	Fuel	Mileage	GC NMOG gpm	MIR gO3/ gNMOG	RAF	GC NMOG gpm	Adj NMOG gpm	ETOH mgpm	HCHO mgpm	Acet mgpm	13But mgpm	Benz mgpm	ΣToxics mgpm
TLEV standards							0.125						
215	C	603	0.325	2.00	0.58	0.219	0.128	209	1.8	21.0	0.2	0.2	23.2
216	A	91	0.252	1.93	0.56	0.161	0.091	158	3.4	16.3	0.0	0.9	20.6
217	A	80	0.181	2.18	0.64	0.151	0.096	46	3.1	16.4	0.2	1.9	21.6
218	B	95	0.408	1.73	0.51	0.257	0.130	239	3.2	21.3	0.0	0.2	24.7

Adj = Reactivity Adjusted
ETOH = Ethanol
HCHO = Formaldehyde
Acet = Acetaldehyde
13But = 1,3-Butadiene
Benz = Benzene

Table 4. Hot Start Emissions Over Mileage Accumulation Period

			Hot Transient Phase of LA4				
Car	Fuel	Mileage	HC gpm	CO gpm	NOx gpm	CO2 gpm	FE mpg
215	C	603	0.20	1.19	0.05	407.0	15.3
215	A	1648	0.13	1.36	0.08	413.4	14.6
215	A	2783	0.08	0.95	0.07	421.7	14.2
215	A	3912	0.05	1.90	0.08	398.0	15.0
216	A	91	0.09	0.17	0.12	403.0	15.0
216	A	1129	0.12	0.84	0.13	398.6	15.1
216	A	2152	0.07	0.86	0.13	399.2	15.0
216	A	3137	0.06	0.70	0.12	408.7	14.8
217	A	80	0.18	1.10	0.04	420.6	14.3
217	A	1134	0.16	0.68	0.14	376.4	16.0
217	A	2173	0.06	0.37	0.07	429.4	14.0
217	A	3197	0.09	0.75	0.12	396.3	15.1
218	B	95	0.18	0.93	0.03	417.2	14.9
218	A	1137	0.18	1.37	0.03	422.0	14.2
218	A	2172	0.14	2.23	0.08	420.6	14.2
218	A	3300	0.11	1.37	0.06	418.1	14.4

HC = Hydrocarbons
CO = Carbon Monoxide
NOx = Nitrogen Oxides
CO2 = Carbon Dioxide
FE = Fuel Economy

Table 5. Regulated Emissions and Fuel Economy, Fuel A

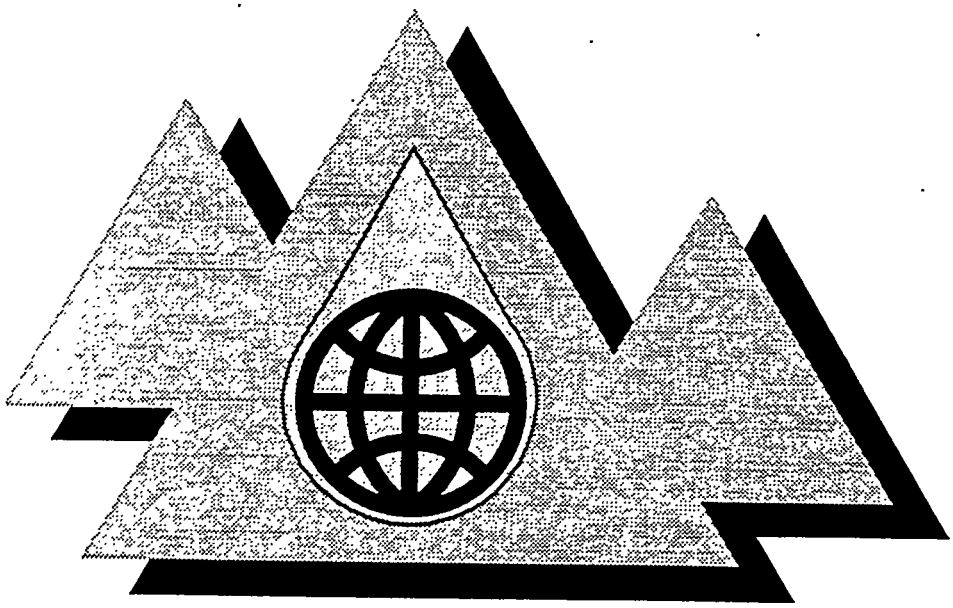
		(mass as HCE = CH1.85)						
Car#	Odom	HC gpm	NMHC gpm	NMOG gpm	CO gpm	NOx gpm	CO2 gpm	FE mpg
EPA standards			0.41		3.4	1.0		
TLEV standards				0.125	3.4	0.4		
215	4956	0.089	0.049	0.134	1.15	0.15	463.0	13.0
215	4983	0.087	0.052	0.121	1.26	0.15	468.3	12.8
215	4994	0.093	0.056	0.153	1.24	0.18	450.8	13.3
216	4230	0.073	0.037	0.142	1.04	0.21	455.8	13.2
216	4242	0.079	0.049	0.132	0.82	0.19	452.6	13.3
216	4253	0.094	0.061	0.166	1.01	0.21	457.7	13.1
217	4243	0.102	0.057	0.137	1.95	0.24	466.9	12.8
217	4255	0.106	0.067	0.157	1.29	0.20	463.5	12.9
217	4266	0.082	0.049	0.129	1.39	0.25	467.1	12.8
218	4341	0.071	0.037	0.139	1.01	0.21	467.9	12.8
218	4368	0.079	0.042	0.100	0.90	0.15	467.4	12.8
218	4380	0.086	0.051	0.121	1.20	0.16	464.0	12.9

HC = Hydrocarbons
NMHC = Non-methane Hydrocarbons
NMOG = Non-methane Organic Gases
CO = Carbon Monoxide
NOx = Nitrogen Oxides
CO2 = Carbon Dioxides
FE = Fuel Economy

Table 6. Speciated Emissions Tests Results

					HCE = CH1.85							
Car#	Odom	GC NMOG gpm	MIR gO3/ gNMOG	RAF	GC NMOG gpm	Adj NMOG gpm	ETOH mgpm	HCHO mgpm	Acet mgpm	13But mgpm	Benz mgpm	ΣToxics mgpm
TLEV standards						0.125						
215	4956	0.245	2.33	0.68	0.168	0.114	159	6.0	25.9	0.2	1.3	33.4
215	4983	0.161	2.44	0.71	0.114	0.081	97	3.0	17.9	0.2	1.0	22.1
215	4994	0.210	2.24	0.65	0.145	0.095	136	3.0	22.1	0.2	1.3	26.6
216	4230	0.230	2.20	0.64	0.157	0.101	155	4.2	18.7	0.2	1.2	24.3
216	4242	0.197	2.27	0.66	0.138	0.092	121	5.1	15.9	0.3	1.0	22.3
216	4253	0.244	2.08	0.61	0.172	0.104	157	5.0	15.0	0.3	1.4	21.7
217	4243	0.187	2.37	0.69	0.131	0.091	115	5.0	17.8	0.1	1.4	24.3
217	4255	0.201	2.21	0.65	0.139	0.090	133	3.8	15.8	0.2	1.2	21.0
217	4266	0.193	2.29	0.67	0.133	0.089	112	4.1	19.0	0.2	1.3	24.6
218	4341	0.275	2.22	0.65	0.192	0.125	172	6.0	25.9	0.3	1.3	33.5
218	4368	0.133	2.69	0.79	0.092	0.072	76	5.0	18.7	0.1	0.8	24.6
218	4380	0.163	2.53	0.74	0.115	0.085	94	4.5	20.0	0.3	1.0	25.8

Adj = Reactivity Adjusted
ETOH = Ethanol
HCHO = Formaldehyde
Acet = Acetaldehyde
13But = 1,3-Butadiene
Benz = Benzene



Heavy Duty Truck Technology and Trials

THE ETHANOL HEAVY DUTY TRUCK FLEET DEMONSTRATION PROGRAM

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ABSTRACT

The purpose of this project is to determine the performance, reliability, cost of operation and emissions from over-the-road trucks operating on high percentages of ethanol fuel and represents the first information collected on these types of vehicles.

The first fleet of four ethanol trucks, owned and operated by ADM, are 1992 White-GMC WIM64T models powered by Detroit Diesel Corporation (DDC) 300 horsepower, dedicated ethanol 6V-92TA engines with 9-speed manual transmissions. Initially, the trucks are being operated on short routings, allowing them to return to the terminal each night. Eventually, interstate routings will be included as part of the operating routine.

The emissions testing data for this program has been performed by the U.S. DOE \ University of West Virginia Transportable Emissions Testing Center and from transient emissions tests by Detroit Diesel Corporation.

THE ETHANOL FUEL HEAVY-DUTY TRUCK FLEET DEMONSTRATION PROGRAM

Introduction

The State of Illinois, through the Illinois Department of Energy and Natural Resources (ENR), is testing and evaluating the use of high percentages of anhydrous ethanol as an alternative transportation fuel. ENR has been working for several years with original equipment manufacturers (OEM) on the production of vehicles optimized for ethanol fuel to be used for test and demonstration purposes. One such demonstration program is the Ethanol Fuel Heavy-Duty Fleet Demonstration Program where ethanol substitutes for diesel fuel in heavy-duty, over-the-road trucks.

The Detroit Diesel Corporation (DDC) Model 6V-92TA is the first commercially available heavy-duty truck, urban transit, touring, and school bus engine optimized for alcohol fuels. The first DDC 6V-92TA pre-production methanol engine was put into service in 1983 in an urban transit bus fleet in California. Currently, fifty-seven (57) pre-production and several hundred production 6V-92TA methanol engines are in service. This engine was USEPA and CARB emissions certified in mid-1991.

In 1991, the first two DDC 6V-92TA pre-production ethanol engines were installed in urban transit buses in Canada. Each bus logged over 30,000 miles in the first year of operation with very little down time. By late 1992, the engine was USEPA and CARB emissions certified. The first and largest U.S. fleet of fourteen (14) 6V-92TA 253 horsepower, ethanol fuel urban transit buses began operations in Peoria, Illinois in 1992. Also in 1992, the first and largest American ethanol fuel, heavy-duty truck fleet demonstration program was put into service in Illinois. This fleet of four (4) White-GMC over-the-road trucks is owned and operated by Archer Daniels Midland (ADM) of Decatur, Illinois and is powered by DDC 6V-92TA dedicated ethanol engines. The ethanol truck engines differ somewhat from the engines used in the Peoria buses in that they have been factory-programmed to deliver 300 horsepower, rather than 253 horsepower.

Participants in the program include Archer Daniels Midland, Detroit Diesel Corporation, USDOE, and the Illinois Department of Energy and Natural Resources (ENR). The USDOE / University of West Virginia Transportable Emissions Testing Laboratory is also a major contributor to the project by performing the emission tests on the ethanol and diesel control trucks.

The Project

In 1991, USDOE requested the State of Illinois Department of Energy and Natural Resources (ENR) to develop a test and demonstration program for over-the-road trucks operating on ethanol fuel. This heavy-duty, over-the-road truck program received financial support under the Alternative Motor Fuels Act (AMFA) of 1988. Based on this request, ENR, in partnership with ADM, and DDC, initiated this comprehensive test and demonstration effort with a fleet of the first ethanol powered, over-the-road trucks in the nation.

Goals and Objectives

Unlike methanol and natural gas, the use of high percentage ethanol fuel blends for transportation purposes has been limited to only a few localized demonstration projects. Trucks, buses, and passenger cars optimized for ethanol fuels have simply not been available from the original equipment manufacturers due, primarily, to a lack of demand for such vehicles. A lack of established refueling facilities is a second factor. The performance and reliability of ethanol vehicles under actual field conditions has not been adequately documented. Further, until recently, very little emissions data on high

percentage ethanol fuel vehicles has been available.

Ethanol is currently one of the only cost-effective, renewable transportation fuels on the market. Ethanol is made primarily from corn, a crop grown in great abundance every year throughout the Midwest. . Illinois is the leading producer of ethanol in the country. Annually, over 500 million gallons of gasoline-quality, anhydrous ethanol is produced in Illinois using almost 200 million bushels of Illinois corn. Illinois is also the leading user of 10% blended ethanol gasoline in the nation. Over 150 million gallons of ethanol is used to substitute for gasoline every year and a full 30% of all the gasoline sold in Illinois contains ethanol.

Because it has a higher BTU content per unit volume relative to methanol, anhydrous ethanol (76,000 BTU's per gallon) can be compared more favorably to diesel fuel than anhydrous methanol (57,000 BTU's per gallon). Most of ethanol's other chemical properties are also closer to diesel fuel than methanol fuel. Ethanol is also considerably less toxic and less corrosive than methanol.

The Ethanol Fuel Heavy-Duty Truck Fleet Demonstration Program is assessing the performance, reliability, durability and emission characteristics of heavy-duty, over-the-road trucks operating on ethanol as the primary fuel and the potential role of ethanol fuel in meeting the regulations imposed by the Clean Air Act (CAA) of 1990. These trucks are being used under normal field conditions where the real world operating environment can attest to the commercial viability of the fuel and engine design. The ethanol trucks have also been emission tested by the USDOE / University of West Virginia Transportable Emissions Testing Laboratory.

The Fleet Operator

The first fleet of heavy-duty, over-the-road ethanol trucks is owned and operated by Archer Daniels Midland (ADM) of Decatur, Illinois. ADM is the largest producer of gasoline-quality (less than 1% water content by volume), anhydrous ethanol in the nation and operates a fleet of over 800 vehicles. The ADM Trucking, Incorporated subsidiary operates the fleet trucks for the company and will be required to conform to the regulations established for truck fleet operators under the Clean Air Act. It would only make sense, then, that ADM be a logical choice as the first fleet operator for this program.

The ethanol truck fleet is operated out of the ADM Trucking facility in Decatur, Illinois. ADM Trucking services its vehicles both in-house and through local dealerships. The ethanol trucks are used to deliver shipments of liquefied carbon dioxide (CO2) to destinations in Illinois, Indiana and Wisconsin where the trucks can leave the facility each morning and return to the Decatur facility each evening, without the requirement of remote refueling facilities.

The Fuel

The DDC 6V-92TA dedicated ethanol engines used in this program operate on "E-95" ethanol fuel. The "E-95" fuel is essentially a mixture of 95% 200-proof, anhydrous ethanol and 5% light hydrocarbon denaturant (Figure 1). A very small amount (less than 0.1%) of a special lubricating agent, Lubrizol, is added to the fuel mixture to provide upper cylinder lubrication. ADM Corn Processing produces the ethanol fuel on-site at the Decatur facility. The fuel is delivered to the ADM Trucking facility where it is stored and dispensed from a 5,000 gallon aboveground storage tank. The 5% light hydrocarbon denaturant, called "natural gasoline", is a mixture of C5 and C6 (pentane and hexane) hydrocarbons and is purchased from the various oil refineries in the Midwest. The energy content of the E-95 ethanol fuel (including the 5% natural gasoline energy content) is approximately 78,000 BTU's per gallon, compared to a value of about 128,000 BTU's per gallon for #2 diesel fuel. Based on this, the ethanol fuel used in this test and demonstration project contains about 61% of the energy per gallon as the #2 diesel fuel used in

conventional diesel trucks.

The Vehicles

The ADM ethanol fleet is composed of four ethanol powered trucks and one identical truck equipped with a conventional 300 horsepower, 6V-92TA diesel engine that serves as a control unit for the program. ADM selected 1992 White-GMC WIM64T trucks because the Detroit Diesel 6V-92TA engines could be installed easily without chassis or frame modifications. The trucks can be easily identified by the words "Ethanol 95" and a ring of corn kernels on each fuel tank.

The four ethanol trucks are powered by DDC 6V-92TA ethanol engines. These are dedicated engines that have been optimized for the E-95 ethanol fuel previously mentioned. The engines are six cylinder, 552 cubic inch, vee-configuration engines that have been factory programmed for 300 brake horsepower. The development of the ethanol 6V-92TA was based on DDC's previous experiences with the methanol version of this engine. Numerous engine modifications were necessary to optimize the engines for ethanol fuel. Because of the lower energy content of ethanol (compared to diesel fuel), ethanol-tolerant high capacity fuel injectors and fuel pumps were installed. Special glow plugs were installed in redesigned piston heads to enhance compression ignition, especially in cold weather. The glow plugs operate for one minute before the engine can be started and remain on until normal engine operating temperatures are attained. A Detroit Diesel Electronic Control (DDEC), which is an electronic unit fuel injector and engine management control system, has been installed on each engine. A catalytic converter has been added to further reduce emissions. A five minute "kill" switch has been installed that shuts the engines off automatically after five minutes of low-idling time. Additional modifications include ethanol tolerant fuel lines and an increased engine compression ratio of 23.0 : 1.0. Except for the increased horsepower and torque, the 6V-92TA ethanol engines are identical to the engines used in the Peoria Ethanol Bus Project. The control truck uses a conventional DDC 6V-92 diesel engine (without a catalytic converter) with electronics and specifications identical to the ethanol engines. The transmissions used in all of the trucks is the Fuller Model RTX-12609B, which has nine (9) forward speeds plus a reverse gear. The rear axle is a Rockwell RT40-140, with a final ratio of 4.56 : 1.00. The wheelbase for the trucks is 206 inches and they are equipped with cruise control and block heaters.

The trucks were built at the White-GMC factory in Virginia. Conventional DDC 6V-92TA engines were installed at the factory. One of the trucks was shipped to ADM in Decatur directly as the control truck for the program. The other four trucks were shipped to DDC in Detroit, Michigan where the engines were modified for ethanol fuel usage. After the ethanol engine modifications were completed (approximately six weeks), the trucks were shipped to ADM.

The curb weight of each tractor truck is about 17,400 pounds and the gross vehicle weight of the truck with an empty CO2 tanker trailer is about 33,000 pounds. The maximum gross vehicle weight is approximately 78,000 pounds.

Each of the four ethanol trucks and the control diesel truck have two 120 gallon, side-mounted fuel tanks. The range on the ethanol truck is approximately 800 miles while the range on the diesel control truck is about 1,100 miles between refuelings. Because of the this differential in mileage and the limited availability of E-95 fuel, the ethanol trucks are currently being operated on routes that will allow them to leave the ADM facility every morning and return to Decatur every evening. Eventually, it is being planned that E-95 refueling facilities will be located at ADM truck terminals in Iowa and Missouri to increase the range of the vehicles and demonstrate the truck fleet in other parts of the Midwest.

Routes and Duty Cycles

An important part of this program is to evaluate the performance of a heavy-duty, ethanol powered truck fleet under actual field conditions. Except when one of the vehicles is pulled from service for a promotional event or mechanical servicing, the trucks are operated every working day delivering products from the ADM plant in Decatur, Illinois. One driver has been assigned to each of the four ethanol trucks and the control diesel truck so that the results obtained from each vehicle will remain consistent throughout the tests. The driver of each vehicle will be accustomed to the operation of that specific vehicle and will be able to discern a malfunction or operating problem simply by the way it performs on the road.

The control diesel and the four ethanol trucks are being used to transport liquefied CO2 from Decatur to cities like Chicago, Indianapolis and St. Louis. Each truck runs to different delivery points to vary the operation times and conditions. Eventually, it is planned that additional E-95 refueling facilities will be established in Iowa and Missouri to increase the range of the vehicles and expand the program to other areas of the Midwest. At this time, a typical duty cycle would be a few minutes of low to moderate speed (ADM is located on the outskirts of Decatur), several hours of highway driving, followed by one to two hours of low speed, stop-and-go driving in the major cities to make the delivery, several more hours of highway speed driving, and then a few more minutes of low to moderate speed driving in Decatur. Idling time is generally kept to a minimum because of the 5 minute kill switches installed in the trucks. If the truck is left unattended on low idle for five minutes, the engine will automatically be turned off. Overall, the ethanol trucks are averaging over 6,000 miles per vehicle per month. Because of the considerable amount of highway driving being done, the average speed of the vehicles often exceeds 45 miles per hour. The average load of a full CO2 trailer is about 37,000 pounds for a gross vehicle weight of approximately 54,400 pounds.

Results from Operations

A considerable amount of data is being generated and collected as a result of this project. Several tests and demonstrations on the operation of heavy-duty truck fleets using methanol and compressed natural gas fuels are currently underway in this country. By contrast, this project is the first application of heavy-duty, dedicated ethanol engines in an over-the-road truck fleet.

Vehicle Performance

The primary sources of vehicular performance data are; in-use data from ADM's fleet operations records, engine dynamometer test data from DDC's engine certification run at Southwest Research Institute (Table 1), and test data from the USDOE / University of West Virginia transportable heavy-duty chassis dynamometer (Table 2).

Fuel Economy

Fuel economy is an important part of vehicle performance. From earlier discussion, recall that the E-95 ethanol fuel contains about 78,000 BTUs per gallon compared to 128,000 BTUs per gallon for diesel fuel. On an energy basis, we would expect the comparably loaded and operated E-95 trucks to produce only 61% of the miles per gallon fuel economy of the diesel powered control truck. However, the in-use fuel economy data from the diesel truck shows an average fuel economy of 5.3 miles per gallon versus an average of 4.0 miles per gallon for the four E-95 ethanol trucks.

The greater than 24% increase in energy economy (BTU's of fuel consumed per mile traveled) is an unexpected result and can be attributed to a number of factors. The compression ratio of the E-95 engines is 23 to 1 relative to the 17 to 1 ratio for the diesel powered unit. Although it is well established in both practice and theory that compression ratio

increases translate to increased peak engine thermal efficiency; increased peak engine thermal efficiency does not have a direct one-for-one correspondence with improved vehicle fuel economy. This is due, in large part, to the fact that most vehicle duty cycles do not require maximum engine power for a significant percentage of the time of operation, and the differential efficiency gains at partial load operations are not as pronounced. Obviously, the engine's idle fuel consumption rate is also an important contributing factor in the determination of vehicle fuel economy, and is not directly related to peak engine efficiency. However, engine performance tests on the DDC 6V-92TA engine do not show an increase in thermal efficiency for the E-95 engine relative to the diesel unit. Figures 2 and 3 show engine performance curves supplied by Detroit Diesel Corporation for the diesel powered and E-95 powered engines, respectively. These curves are for engines calibrated to give a peak power output of 277 brake horsepower. (Note that the engines used to power the ADM trucks are calibrated to deliver 300 brake horsepower, but the fuel consumption characteristics for the 277 bhp and 300 bhp calibrations should be similar.) The power and torque output for these engines is identical; only the brake specific fuel consumption rates are different. This information indicates that the full load performance of the E-95 engine, over the 1,000 to 2,100 RPM operating range, equates to an average thermal efficiency of about 35%, compared to a figure of approximately 40% for the diesel engine. Therefore, we have to conclude that the potential inherent benefits from the higher compression ratio and the accompanying increased engine efficiency do not explain the in-use fuel economy measurements.

The most significant remaining factor which may explain the increase in energy-based fuel economy would be dissimilar duty cycles between the E-95 and diesel powered vehicles. Although the introduction of such a bias is clearly unintentional, it is the most likely remaining factor and could be a significant contributing factor. Detailed analysis of the vehicles' operating cycles has yet to be conducted.

The in-use fuel economy data for the E-95 powered vehicles should also be tempered with the data from the heavy-duty chassis dynamometer tests (Table 2) operated by the University of West Virginia, which shows a 21% decrease in fuel economy relative to the predicted E-95 mileage of the 2.76 miles per gallon (equivalent) obtained from the diesel engine truck. These tests were run with the vehicle operating over the Central Business District Cycle (top speed of 20 miles hour, stop and go operations, with a significant amount of idle time). This is a significantly different operating cycle from the in-use operating cycle which shows an average speed of approximately 45 miles per hour.

Emissions testing is another integral part of this test and demonstration project. Detroit Diesel Corporation performed an engine calibration and transient emissions test in a factory testing cell. The transient emissions test data obtained from the test cell is displayed in Table 1. Briefly, the emissions from the pre-production 6V-92TA ethanol engine easily pass the 1994 CAA standards for this type of engine. Since the ethanol engines used in this program were built, the DDC 6V-92TA ethanol engine has been USEPA and CARB emission certified and is now considered a regular production Detroit Diesel engine.

The USDOE / University of West Virginia Transportable Emissions Testing Center first tested the control diesel truck and one of the ethanol trucks in July 1992. The ethanol trucks did not perform as well as predicted (please refer to Table 2). There are two potential mitigating factors which may have a bearing on this. First, because the sixteen tandem wheel tires were badly worn on the two trucks as a result of the testing, it is likely that the truck was not properly aligned on the dynomometer rollers, or the load on the truck was not properly applied. Secondly, the emissions testing duty cycle used by West Virginia was primarily designed for buses with

automatic transmissions. Basically, the duty cycle calls for steady acceleration to a given speed in a predetermined amount of time, level off at that speed, then decelerate and stop. It is relatively easy for a bus to meet this type of duty cycle since the automatic transmission does not require manual gear shifting during the testing process. Unfortunately, a truck with a 9-speed manual transmission requires several gear shifts to accelerate to the target speed. This may lead to erroneous reading in the emission levels because of the gear shifts and the attempt to meet the acceleration time requirements. A new emissions testing duty cycle program is currently being developed by West Virginia to account for the shifting of transmission gears during acceleration. In the meantime, a second set of emissions tests were performed by the West Virginia in June at the Peoria bus maintenance facility. The results of these emissions tests are not yet available for publication.

ADM has been keeping computerized maintenance and cost of operation records on all five of the trucks. DDC has also provided considerable engineering and field support for this program. A DDC representative was scheduled to be on-site two days per week for the first two months, once every week for the next ten months and once every two weeks for the next year. Complete site visit reports have been prepared by DDC describing the nature of the visit and any work required on the vehicles.

In the past, fuel injectors on these engines represented a potential problem. The pre-production methanol 6V-92TA engines encountered serious plugging problems after only a few thousand miles and had to be replaced after only 3,000 miles. This problem seems to have been nearly eliminated in the ethanol truck fleet. Fuel injectors on the four 6V-92TA ethanol engines have lasted between 75,000 and 85,000 miles before replacement was necessary.

To this point, the reliability of the 6V-92TA ethanol engine is as good or slightly better than its diesel counterpart. Two of the four vehicles have already accumulated over 100,000 miles each with minimal downtime. The other two vehicles will pass the 100,000 mile marker by mid-summer of 1993. The drivers of the trucks have also been very pleased with their performance.

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TABLES AND FIGURES

Table 1 - Detroit Diesel Corporation Model Year 1992 E-95 6V-92TA Emissions Certification Numbers

	ENGINE ID	TEST LOC.	PROJECT EXHAUST EMISSIONS SMOKE % ACCEL	LUG	PEAK	(GRAMS PER HORSEPOWER-HOUR) OMCHE	CO	NOx	PART.
TEST ENGINE (Includes Deterioration Factor)	6VF103279	SWRI	1.2	2.2	5.0	0.73	1.71	4.15	0.04
1994 EMISSIONS STANDARDS						1.30	15.50	5.00	0.10

Table 2 - University of West Virginia Emissions Testing Results Average Emissions (Grams/Mile)

UNIT	FUEL	CO	NOx	HC	PM	CO_2	MI/GAL	BTU/MILE
92006	Ethanol	17.76	21.066	7.78	0.25	3408.9	2.18	59,118
92010	#2 Diesel	9.35	24.142	3.59	2.07	3668.9	2.76	47,204

Figure 1 - E-95 Ethanol Fuel Specifications

Chemical Composition:	C_2H_5OH - Ethyl Alcohol
Fuel Composition:	95% 200 Proof, Anhydrous Ethyl Alcohol (Ethanol)
	5% Natural Gasoline (C5 and C6 Hydrocarbons) or Unleaded Gasoline Denaturant
	Trace (less than 0.1%) Lubrizol Upper Cylinder Lubricant
Energy Content:	Approximately 78,000 BTU's Per Gallon Volume. Based on 76,000 BTU's Per Gallon of Anhydrous Ethanol and 118,000 BTU's Per Gallon of Unleaded Gasoline.
Boiling Point:	78 to 79 Degrees C
DOT Designation:	Flammable Liquid.
Harmful Effects:	Local - Mild Irritation of Nose and Eyes Occurs at Very High Concentrations. The Liquid Can Defat the Skin.
	Systemic - Prolonged Inhalation of High Concentrations, Besides the Local Effect on the Eyes and Upper Respiratory System, May Produce Headache, Drowsiness, Tremors and Fatigue.
First Aid:	Irrigate With Water.

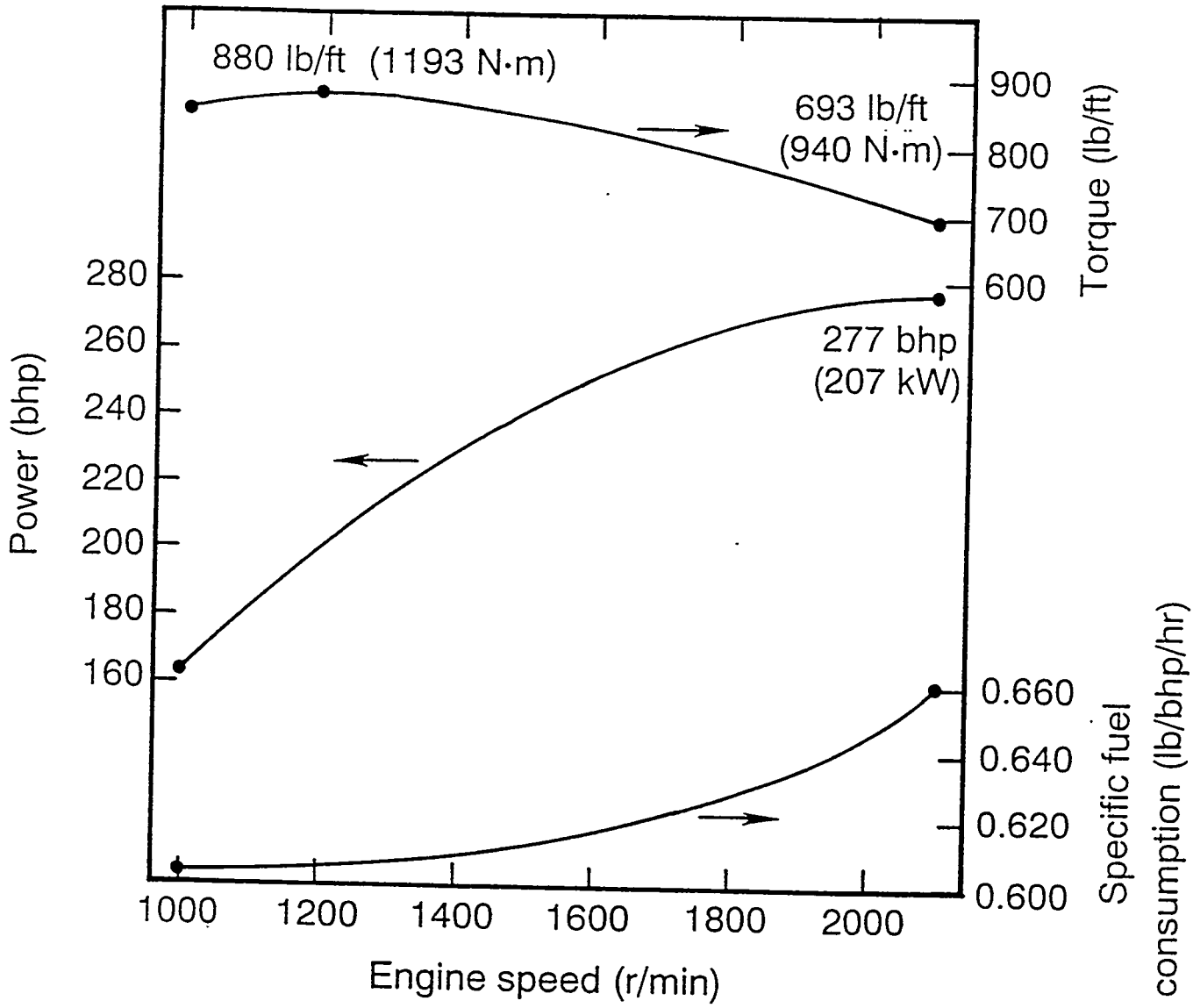

Figure 2. Engine performance curves for the DDC 6V92 TA engine model operating on #2 diesel fuel; 277 bhp calibration

(courtesy of Detroit Diesel Corporation)

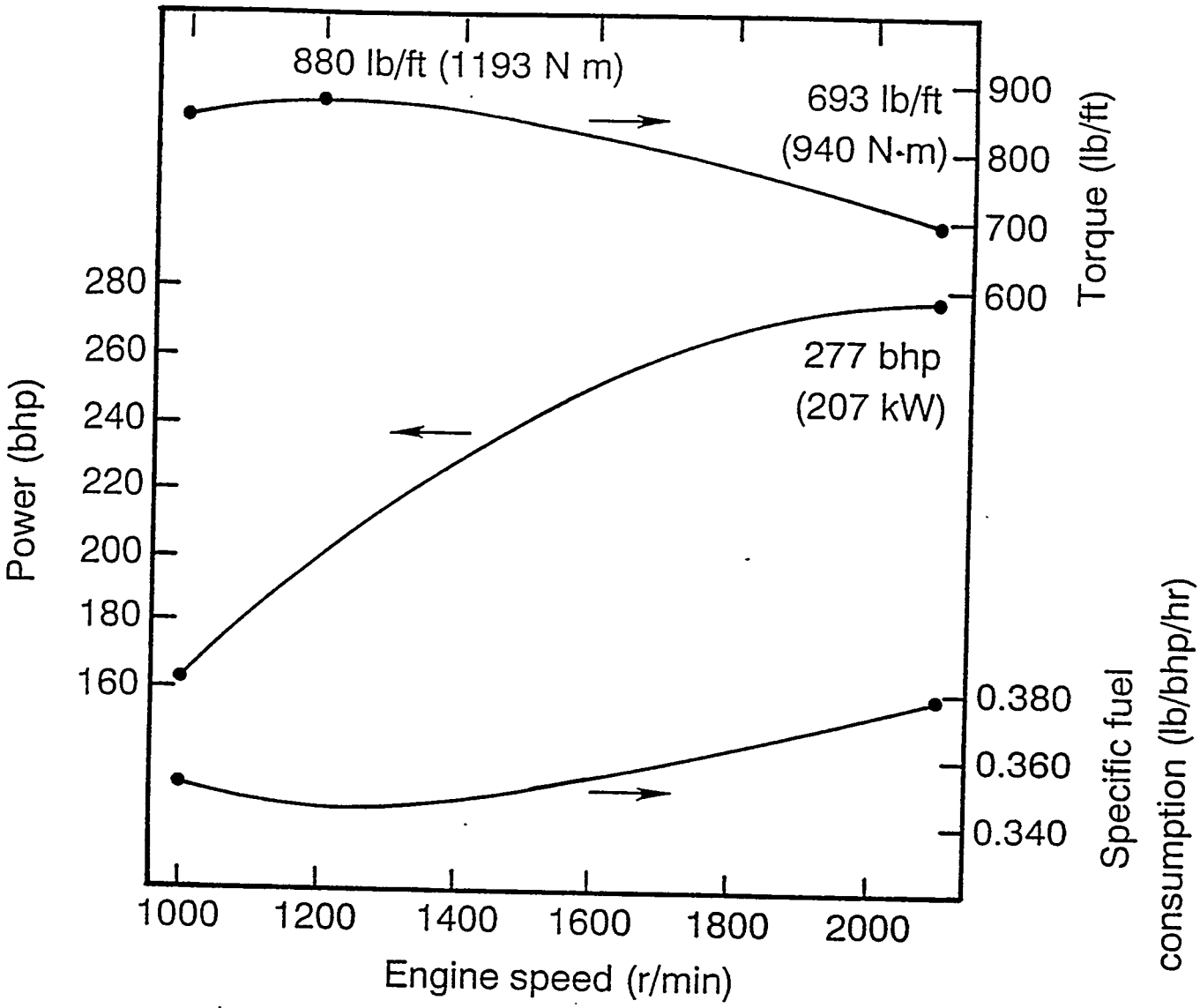

Figure 3. Engine performance curves for the DDC 6V92 TA engine model, operating on E95, 277 bhp calibration

(courtesy of Detroit Diesel Corporation)

DEMONSTRATION PROGRAM FOR HEAVY-DUTY VEHICLES EQUIPPED WITH ETHANOL POWERED DIESEL ENGINES

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Abstract

The Swedish government and other entities such as the Swedish Ethanol Foundation and SAAB SCANIA are engaged in a number of projects to determine the technical feasibility and economic viability of meeting a portion of Sweden's transportation fuel needs with ethanol. All aspects of substituting ethanol for conventional petroleum derived fuels are being studied. Laws and regulations which may restrict the use of alcohols as a motor fuel are being examined. Infrastructure issues are being defined. Fuel formulation issues are being investigated and demonstration projects are being initiated. The work with the largest visibility are the demonstration projects, many of which involve ethanol powered buses. Emission tests are being conducted on a number of these demonstration vehicles. This paper describes the variety of projects that are underway. In instances where results are available, summary data is presented.

DEMONSTRATION PROGRAM FOR HEAVY-DUTY VEHICLES EQUIPPED WITH ETHANOL POWERED DIESEL ENGINES

INTRODUCTION

Since the mid 1980s I have had the opportunity to work with alternative fuel vehicles, first as technical manager of Stockholm Transport and then as a consulting engieer. During my time in Stockholm Transport we started a development project for buses running on pure ethanol. This project has become a part of a national program for ethanol as a motorfuel. The details of the program will be presented by Mr. Sören Bucksch from the Swedish Communication Research Board. Our objective is to determine the circumstances under which a large-scale system for use of alcohol and alcohol blends as motor fuels is possible. This paper presents an overview of projects within.

Projects

A strategum where different scenarios on the use, production and distribution of motor alcohols are analyzed is about to start and is supposed to be completed during 1994.

In addition a study on Swedish laws and regulations concerning the use of alcohols as motor fuel was completed during the beginning of this year. The results demonstrated that:

- There is no current need for new rules or regulations.
- Rules and regulations are not a hinderance for the use of alcohols as motor fuels.

Ethanol Buses in Stockholm

Stockholm has the world's largest fleet of ethanol-powered buses. This year there will be another 20 buses in service, bringing the total fleet number to 52 vehicles.

Stockholm Transport (SL) is conducting a program of fleet tests on ethanol-driven buses. It is probably the world's largest and most advanced fleet test of heavy duty vehicles fueled by pure ethanol. The tests, which began in April 1990, are being conducted by SL along with SAAB-SCANIA and the Swedish Ethanol Foundation.

Infrastructure

Refueling Station

In order to conduct the tests, a special Refueling Station was built. This station was constructed in compliance with Swedish laws on the use of alcohol as fuel provisions for security regulations can be observed at the station. Each bus has a sensor which identifies the bus at the station in order to prevent unauthorized refueling. Refueling is automatically registered on a computer that records the designation of the vehicle, the date in question and the volume of fuel transferred. The connection between the refueling pump and the bus comprise an entirely closed system, and the gases from the refueling operation are returned to the underground tank through a special line.

Fuel Supply

The ethanol used for the test fleet is produced at a paper mill in the northern Sweden. It is made from the waste liquor from the production of paper. The fuel is manufactured and blended at the mill, which is also responsible for quality control and composition.

A specially equipped truck has been developed for the project. It is used to make regular deliveries from the mill to the bus depot, a distance of some 700 km.

Fuel

The fuel has to be altered to suit the engine, minimize emissions, guarantee good performance (under cold conditions) and minimize costs. It is comprised of 95% E 95, 3% denaturating agent and 2% ignition enhancer, as shown in Table 1. As your can see from the data in the table, we have reduced the ignition improver considerably and can still satisfy these engines.

Table 1. Ethanol Fuel Composition

95 % E95 (95% ethanol, 5% water)
3% MTBE, Isobutanol
2% ICI AVOCET

Maintenance Facility

A maintenance facility, capable of inspecting, overhauling or repairing two buses at a time has been established on our premises. A few modifications have been made to the ventilation system and tools for the fuel system, but all other respects it is a normal maintenance facility.

Testing Facilities

An exhaust emission test laboratory was built to study emissions from the fleet. This laboratory has the facilities necessary to measure the regulated components in the exhaust. The plan is to test each vehicle each year. Test results will establish the condition of the engine, fuel system, and catalyst system. The laboratory is located in the bus depot adjacent to the garage. A chassis dynamometer has been installed, complete with equipment to measure the regulated exhaust constituents.

Vehicles

The buses in the project are all manufactured by SCANIA-BUS. They are equipped with a DSI 11E Scania diesel engine rated at 184 kW at 2,000 rpm. These engines have a compression ratio of 24:1. This enabes a reduction in required concentration of ignition improver in the fuel, thereby reducing fuel costs considerably.

The engine is charge-air cooled. The shape of its combustion chamber and its compression ratio, injection pressure and injection timing, have been modified to accommodate the ethanol fuel, which has significantly different combustion properties compared to diesel fuel. The injection pump has a lubrication system separate from the fuel system.

Ethanol has improved combustion characteristics over diesel fuel with regard to nitrogen oxides (NO O_x) and particulate emissions. The engine is equipped with an oxidizing catalyst, enabling equally low particle values as those obtained when using a particle filter. At the same time, the catalyst reduces hydrocarbon and carbon monoxide values to a minimum. This gives the engine an emission performance level 75 percent lower than ECE R49, which is the European standard for emission measurement.

The test buses use two different catalysts: an Englehard, Ceramic monolith, 15.4 liter and a Degussa, Metallic monolith, 10 liter.

Test Results

Fuel Consumption

After about 3 years we have driven more than 2 million km on the ethanol fuel we now know a little about fuel and consumption characteristics. This information is presented in Table 2.

Table 2. Fuel Consumption History

	Diesel fuel (l/km)	Ethanol l/km
The worst bus	0.625	1,077
The best bus	0.529	0.892
The average bus	0.574	1.013

Reliability

During this period we have had only one fuel-related fault, a leaking fuel liner connection. This means that the average ethanol bus uses 1.xxx times as many liters of fuel as a diesel-operated bus. The smell of vinegar has been noticed in the exhaust fumes of certain buses and investigations showed that the fuel injectors were leaking. During January they were replaced on all the buses in question. We have also discovered that something in the fuel forms a coating on the surfaces of the injector needles.

Exhaust Emissions

An extensive program of exhaust emission tests has been set up. The program is divided into three parts:

1.All 32 buses will be tested in our own laboratory for regulated emissions. We have used the ECE R49 13 mode cycle for our tests.

2. Six (6) buses have been tested completely for regulated and unregulated emissions. In these tests we used the ECE R 49 cycle, as well as a special bus cycle. Analyses have been made of CO/CO_2, HC(FID), NO_3/NO_2, aldehydes, ethylene, ethylene oxide, ethylene nitrite, ethanol and PAC. The tests are being carried out by the Swedish Motor Testing Center. A summary of the results are presented in Table 4.

Table 3. Emission Standards, Goals and Results

Emissions (g/kWh)	1994 law	Ethanol Goals	Achieved Values
Nitrogen oxides NO_x	9.0	4.5	3.2
Carbonmonoxide CO	5.0	0.1	0.28
Hydrocarbon HC	1.2	0.2	0.09
Particulates	0.4	0.05	---

Table 4

Exhaust component	Scania DSC 1104	Scania DSI 11E
Formaldehydes (mg/km)	68 - 290	9 -12
Acetaldehydes (mg/km)	19 - 80	24 - 62
Methanol (mg/km)	---	41 - 54
Ethanol (mg/km)	---	83 - 154
Methylnitrate (micro g/km)	---	6 - 9
Ethylnitrate	---	5 - 13
Ethene (mg/km)	36 - 110	---
Propylene (mg/km)	8 - 12	---

Table 5. Measurements for Poly-Aromatic Hydrocarbons

Exhaust component	Dieselbus (microgram/km)	Scania DSI 11E (microgram/km)
PAH, particulate phase	40 - 330	4 - 7
PAH, gas phase	---	3 - 7
Nitro-PAH, particulate phase	0.2 - 1.1	0.2
Nitro-PAH, gas phase	---	0.01 - 0.08

Table 6. Toxicity Measurements

	Particulate phase (rev/m)	Semivolatile phase (rev/m)
TA 98-S9	12 - 82	5- 12
TA 98+S9	2	34 - 130
TA 100-S9	16 - 34	10 - 20
TA 100+S9	0 - 18	24 - 42

3.Special tests and analyses of samples have been made by medical institutions (TCDD receptor affinity tests).

Buses on Ethanol in the City of Örnsköldsvik

The purpose of this project is to determine the reliability of the design and to evaluate different ignition improvers. Two buses are now running for the fourth year in a nordic area of Sweden. This year another four buses will be added to the fleet. This is first, of all a reliability test and secondly, a test of different ignition improvers. So far there are no published results from these tests. Currently there are no published results from these tests.

Buses on Ethanol in the Cities of Skövde and Mariestad

A fleet of ten retrofitted and five new buses are being operated on ethanol in the western part of Sweden. The objectives of this project are to gain experience and ascertain the possibilities of alleviating pollution problems, especially in cities, by using clean fuels, and in particular oxygenated fuels.

The Second Biggest Test in the World with Bio-Ethanol Driven Buses Containing Diesel Engines

Länstrafiken in Skaraborg is conducting a fleet test with 15 ethanol-fueled buses starting this year. The tests are conducted by Länstrafiken, with SAAB-SCANIA and

the Swedish Ethanol Foundation. Financial support for this project is provided by the Transport Research Board.

The goals of this project are to:

1. Establish the real costs for operating a bus fleet on Bio-Ethanol, and evaluate new techniques and infrastructure requirements.

2. Determine the exhaust emissions of ethanol relative to diesel (unregulated and regulated).

3. Develop the engine system and fuel specification.

During a three year test period that started on June 1, 1993, Länstrafiken is conducting a series of tests and evaluations. As a fulfillment of their responsibility to the funding agencies, Länstrafiken will report on the test results.

To conduct the tests and support the operation of these buses, two special refueling stations have been built. A tanker is also in service to transport fuel from a factory in the northern part of Sweden. Fuel consumption rates and operating costs are being tracked. This data will be analyzed and compared with diesel-powered operations.

To study the emissions we are going to make tests on a chassis dynamometer to allow for continuous evaluation. Special tests will be made on both unregulated and regulate emissions. These tests are performed by Swedish Automobile Testing Laboratories. Evaluations medically will take place at the Karolinska Institutet. The first emission tests in this project were carried out in August, 1993.

Garbage Trucks on Ethanol in the City of Stockholm

A study of how ethanol-powered garbage trucks will lead to the construction of at least one vehicle with an engine that uses the fuel in place of diesel. The study is being conducted by the Cania dealer in Stockholm along with SKAFAB, the company responsible for all transports of garbage in the city. Construction of the truck has just begun. We anticipate that it will be in service by the beginning of 1994.

Ethanol-Emulsion Diesel

Diesel Fuels Blended with 15% of Ethanol Tested in Fleets of Trucks, Buses and Lorries.

Wider use of biofuels for passenger cars, trucks and buses is an important method for reduction of vehicle emissions. This is especially true of carbon dioxide, but other pollutants in automotive exhaust can be affected as well. The use of biofuels for this purpose would increase considerably by the introduction of ethanol into diesel oil and a technique for producing such fuels is available. There is a possibility of introducing a 15% mixture of ethanol into diesel and marketing the fuel after completion of a series of introductry studies and field tests.

The objective of this project is to investigate regulated and unregulated emissions, including PAH and the mutagenicity when using the mixed fuel. Emissions resulting from using the mixture of ethanol and diesel oil will be compared with the emissions of the same diesel oil without ethanol.

The Swedish Communication Research Board assigned the Swedish Ethanol Foundation to develop a large program on mixed fuel and Ethanol-Emulsion Diesel. The program is divided into three parts. We have just started part one.

Laboratory Tests

Laboratory tests will be coordinated with the universities of Sweden. The characteristics of different concentrations of diesel, ethanol and emulsion will be studied. A one cylinder engine will be used to research ignition delay, fuel consumption and emissions from different mixtures. To ensure adequate lubrication in the fuel system tests will be made with injection pumps and injectors.

Vehicles

Vehicles will be tested on a chassis dynamometer to evaluate drivability while running on mixed fuel. At the same time, emission tests will be performed. A small fleet of test vehicles will be placed in service to evaluate infrastructure, refueling, maintenance and so on. After results of the first part of the program become available, a decision will be made whether to continue with later phases, which include large scale fleet tests, optimizing

the mixture and emission testing with the optimized mixture.

Summary

Sweden has established a large scale evaluation program. All aspects of substituting ethanol for petroleum-derived fuels are being examined, including exhaust emissions, economics, required maintenance, infrastructure requirements and fuel economy. A special program to provide information on these projects has also been established.

THE DEVELOPMENT OF A HEAVY-DUTY METHANOL ENGINE FOR LOW NOx EMISSIONS

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Abstract

A global deterioration in air quality, particularly in urban areas is occuring despite more restrictive emissions standards. Additionally, a general increase in emissions of green house gases may compound this problem. The need for mitigation of these concerns has become a driving force in support of lean burn methanol combustion technology due to the anticipated beneficial environmental impact associated with the use of this fuel and combustion technology.

The feasibility and potential for low HC, CO, particulate and aldehyde emissions of a diesel derived, hot surface ignition (HSI) methanol engine has previously been demonstrated. The operational behavior of the Navistar DT-466 methanol engine demonstrated that the stringent 1994 U.S. emissions standards can be easily achieved with this alternative engine technology.

This publication presents the latest results in the engine development program and outlines the potential of the HSI methanol engine concept to meet future emissions standards. In particular, the influence of the application of EGR on the performance and emissions of the methanol engine are presented and discussed. The development of an EGR strategy is outlined and the importance and influence of the fuel specification are considered. An assessment of the impact of these development steps is attempted through the use of a computer based transient test simulation procedure.

Introduction

Methanol has long been considered a promising alternative fuel for use in heavy-duty applications. Diesel derived. DI methanol combustion concepts. in particular. have demonstrated a high potential for compliance with future heavy-duty emissions standards. Due to the comparably high oxygen content in combination with the relatively low C/H ratio of methanol. the combustion process is. in general. sootfree and the combustion temperatures are comparably low. Combustion concepts which use neat methanol are able to take advantage of the benefits · associated with the specific properties of the methanol fuel, especially with respect to particulate and NOx emissions /1/.

In view of future emissions standards as well as the previsions of the Clean Air Act /2/. it is clear that engine manufacturers are being legislatively induced towards the development of advanced engine concepts which are capable of meeting the more restrictive standards. This is especially true with regard to the influence of vehicular exhaust gas constituents on the formation of ozone in urban areas. FEV's initial development effort with the Navistar DT-466 HSI methanol combustion concept indicated a clear potential for compliance with the 1994 California emissions standards. These encouraging results were obtained without the application of electronic injection system control /3/. In consideration of the level of development effort that will be necessary to produce advanced diesel engine technologies which are capable of meeting the new emission standards, methanol engines represent a significant potential for emissions reduction.

DI HSI Methanol Engine

FEV has reported on the development of a hot surface ignition (HSI) methanol concept for heavy-duty application that is based on the Navistar DT-466 DI diesel engine. The HSI combustion system was configured and optimized for the lowest possible exhaust emissions. The resulting FEV DI HSI combustion concept configuration is illustrated in Figure 1 and pertinent engine data are provided in Table I. The goal of the initial development effort was the introduction of this engine technology into the California heavy-duty truck demonstration program for alternative fueled engines. Accordingly, the development program included appropriate optimization with respect to several important engine parameters:

- o Mixture Formation
  - Injection System
  - Combustion Chamber Shape
  - Air Swirl Intensity
- o Ignition System and Controls
- o Exhaust Gas Aftertreatment
- o Engine Durability Testing (500 hours)

DI HSI Methanol Engine (Navistar DT-466)	
Number of Cylinders	Inline-6
Bore	109.2 mm
Stroke	135.9 mm
Displacement	7.64 liters
Rated Power	157 kW
Rated Torque at Engine Speed	696 Nm 1600 rpm
Compression Ratio	18.6 : 1
Air Swirl Intensity	c_u/c_a = 2.5
Oxidation Catalyst Substrate Volume Loading	 Metal 5.5 liters 100 g/sq.ft.

Table I : Methanol Engine Data

(g/hp-hr)	1994 California	Navistar DT-466	
		Diesel Engine (Cert. 1993)	Methanol Engine
NO_x	5.0	4.7	3.52
HC/OMHCE	1.3	0.3	0.057
CO	15.5	1.4	0.061
PM	0.10	0.25	0.049
CH_2O	0.05	n/a	0.011

Table II : Transient Test Emissions

Upon completion of the development program, an engine was configured for installation into an International Model 4800 truck. The truck has been used for cinder spreading in the winter and general road repair and maintenance in the summer at a test site in South Lake Tahoe, California /4,5/. Most recently, the engine has been removed from the Lake Tahoe vehicle and will be installed in a vehicle in Sacramento. This step was taken as a means of allowing the engine to accumulate operating hours at a faster rate.

Emissions testing under transient test conditions confirmed the exemplary results of the steady-state testing that was conducted throughout the development program. As indicated by the data in Table II, the methanol engine concept should comply with the 1994 standards for all regulated emissions components. In particular, the emissions levels for critical exhaust gas components, such as unburned fuel and aldehyde emissions are very low.

Since the engine is a lean burn engine, using an oxidation catalyst, NOx reduction was not possible, other than by use of injection timing adjustment. Consequently, a decision was made to conduct additional optimization, aimed at reducing NOx emissions through the application of an EGR system, while attempting to maintain the levels of HC and CO emissions that were obtained during the earlier development work. An additional goal was to avoid any significant efficiency losses.

These goals represent the framework for the development testing with the Navistar DT-466 methanol engine that is reported and discussed in this paper.

EGR System Configuration

As discussed above, the baseline methanol engine has already demonstrated excellent unburned fuel, aldehyde and CO emissions characteristics. Therefore, the introduction of exhaust gas recirculation is a suitable means of obtaining low NOx emissions. Investigations that have been conducted with smaller displacement DI HSI combustion concepts have demonstrated the beneficial influence of EGR on methanol combustion. At low engine loads, in particular, the increase of intake air temperature, with the addition of hot EGR, supports mixture formation and results in accelerated combustion, leading to improved engine efficiency as well as lower HC and CO emissions /6/.

The prototype EGR system configuration used in the heavy-duty methanol engine test program is shown schematically in Figure 2. The EGR system features two EGR valves, which are vacuum controlled. Hot exhaust gas is taken

from the exhaust gas manifold and recycled to the intake system upstream of the compressor. Since, prior to the application of EGR, it was not possible to conduct any turbocharger matching according the requirements for EGR, this system configuration ensured an optimum pressure ratio across the EGR pipe with respect to obtaining the maximum possible EGR rates under both part and high load conditions. One significant benefit associated with the use of methanol in a diesel engine is the realization of EGR without problems related to particulate deposits in the intake air system, especially with regard to influences on the turbocharger.

Exhaust Gas Recirculation

FEV developed a test plan to investigate the operational behavior of the DI HSI heavy-duty methanol concept under high EGR rate conditions. During the performance of these investigations, FEV attempted to determine the combustion limits with EGR. This point was defined as the operating condition at which additional recirculated exhaust gas resulted in unstable engine operation.

The influence of EGR on the fuel consumption, emissions, intake air temperature and the relative air/fuel ratio is shown in Figures 3 and 4 for 800 and 2400 rpm at very low engine load (BMEP = 0.1 bar). Several different injection timing settings were evaluated over a range of EGR rates. The investigations were carried out with a constant glow plug power setting of 65 watts. EGR was applied until the engine could no longer be operated at a stable load and speed point.

The results indicate that, at 800 rpm, EGR rates as high as 45% could be applied before unstable combustion was encountered. Depending on the injection timing setting, NOx emissions could be reduced by 80%. Advanced injection timing results in lower unburned fuel and CO emissions in combination with an improvement in fuel consumption. Although very high EGR rates were possible, the exhaust gas temperatures at these low loads, remained relatively low. As a result, the light-off temperature for the oxidation catalyst was not reached and the conversion rate for unburned fuel and CO emissions was negligible. The fuel consumption behavior (identified as FE in the figure) indicates no significant influence at low load. Only a slight improvement in fuel consumption was observed with increasing EGR rate. Fuel consumption data are shown on a energy equivalent basis in terms of kilograms diesel fuel per hour.

At high engine speed (2400 rpm), the tendencies are the same, but due to the generally higher exhaust gas temperature level, the conversion of methanol and CO is supported by an increase in the hot EGR fraction. Although the engine-out unburned methanol and CO emissions level increase with increasingly retarded BOI, the emissions at retarded timing settings (downstream catalyst) are significantly lower compared to operation at advanced BOI. Above the light-off limit, the higher mass flow of unburned fuel and CO results in better catalyst efficiency. At this operational point, operation of the methanol engine is limited to a maximum EGR rate of about 30%.

With regard to the fuel economy, accelerated combustion at higher EGR rates results in an improvement in fuel consumption for all of the timing settings that were investigated.

The influence of EGR on the cylinder pressure characteristics, fuel consumption and exhaust emissions is shown in Figure 5 for a part load operational point (BMEP = 3 bar) at medium speed (1600 rpm). Up to an EGR rate of between 10 and 12%, the engine can be operated without any disadvantages in fuel consumption. Above this level, the engine efficiency deteriorates significantly. Due to the reduction in turbocharging effects that occurs with increasing EGR rates, the peak cylinder pressure decreases. However, for more advanced injection timing, the maximum rate of pressure rise begins to increase at high EGR rate because of a longer ignition delay. With regard to the emissions behavior, the level of NOx can be reduced up to 95% when maximum EGR is supplied.

However, in consideration of the unburned fuel emissions, the EGR rate should be limited to about 20%, as a means of ensuring good overall emission levels.

As indicated above, the DT-466 DI HSI Methanol engine can be operated with very high EGR rates. In order to obtain maximum NOx reduction, compromises with regard to unburned fuel and CO emissions as well as fuel consumption must be considered, especially at high part load. The maximum achievable EGR rates for the methanol engine are shown in Figure 6 as an engine map. At low engine loads, EGR rates as high as 45% can be obtained, however, combustion instability limits the maximum EGR rate to lower levels as load is increased.

As a result of this effect, the EGR rate must be reduced nearly linearly with increasing engine load. Above BMEP levels of 7.5 to 9 bar in the low speed range and 9.0 bar to 10.5 bar under medium and high speed conditions, even a very small amount of EGR results in unstable engine operation.

Part Load Operational Behavior

Figures 7 through 9 indicate the part load characteristics of the DT-466 methanol engine both with and without EGR at three different engine speeds. The engine data, indicated in the figures, represent engine operation with optimized injection timing and glow plug power settings. The emissions data were acquired downstream of the oxidation catalyst. The figures highlight only the part load range up to the point where EGR can no longer be effectively applied.

At low engine speed (800 rpm, Figure 7), operation at the maximum EGR rate results in an increase in fuel consumption of about 8% for loads above a BMEP of 4 bar. This influence is combined with a significant decrease in the maximum rate of cylinder pressure rise (referred to as $(dp/d\alpha)_{max}$). The introduction of EGR causes a higher residual gas fraction in the charge air. This, in turn, leads to deceleration of the combustion process as the result of a lower burning velocity. Depending upon the particular EGR rate and the corresponding turbocharger performance, the intake air temperature can be significantly increased, without increasing NOx emissions.

The reduction in NOx emissions is about 95% in the low load range and, despite a relatively low EGR rate, about 50-60% in the upper load range. In combination with the high inert gas fraction, an overall richer mixture at high engine loads results in a more significant influence with regard to NOx emissions. Exhaust gas temperatures remain below the light-off temperature of the oxidation catalyst at low loads and, therefore, the HC emissions are relatively high under these conditions. Above a BMEP of 4.5 bar, the level of HC are very low for both operational modes.

Figures 8 and 9 indicate that the operating characteristics of the methanol engine with EGR are similar in tendency as the data for low engine speed. The influence of the application of EGR on fuel consumption is less significant than at low speed. Due to the higher overall intake air temperature that can be achieved, the oxidation catalyst lights off at a lower BMEP. Although not insignificant, the differences in NOx emissions between engine operation with and without EGR at higher engine speeds are less dramatic. This is particularly evident at mid to upper part load.

Based upon the data indicated above, the NOx reduction potential is dependent on the operational point. Although the influence of EGR for NOx reduction is more significant at higher engine loads, the maximum possible EGR rate obtainable at these operational points is limited due to the richer air/fuel ratio and the different exhaust gas composition. As a result, the most significant NOx reduction potential exists in the medium and low load range.

The resulting NOx emissions behavior with and without EGR is given in Figure 10 and 11. Since the operational range representing idle as well as higher speeds is of essential importance for the transient test cycle, it is very important to realize an EGR strategy which responds to the EPA transient test cycle requirements.

Transient Test Simulation

As a means of evaluating the program results, a transient test simulation, based on the steady state results from the development program, was conducted to compare the methanol engine during operation with EGR to the baseline methanol engine.

The transient simulation is based upon a modal analysis of the transient cycle. A pseudo-transient cycle, consisting of a sequence of particular steady state modes that are present during the performance of an actual transient test is built up. The simulation relates second by second movement through the series of steady state modes and directly relates acceleration and deceleration processes to the steady state modes. This simulation has been successfully adapted to the heavy-duty transient test cycle, especially with regard to accurate prediction of NOx values. Previous bench-marking of the transient test simulation has indicated that NOx emissions in the transient test can be accurately predicted and only negligible differences between actual and simulated transient test data exist. Due to the fact that the transient characteristics of the catalyst are not currently evaluated in the model, the simulation of CO, methanol, particulate and formaldehyde emissions levels cannot currently be reliably predicted for comparison with actual transient test cycle test data.

A comparison between the engine configurations with and without EGR indicates substantial improvements in NOx emissions through the application of an EGR system (Figure 12). A reduction in NOx emissions of about 45%, to a level slightly below the envisioned future standard for NOx, is predicted by the simulation. In parallel, the transient test cycle fuel consumption, only increased by about 3.5% with the application of EGR. This result was achieved despite the fact that, during the engine development program, no development efforts were undertaken to rematch the turbocharger for the modified flow conditions with hot EGR.

The influence of the characteristics of the methanol fuel on exhaust emissions, especially with regard to NOx emissions reduction, have been evaluated in previous engine development programs /1/. The use of M85 with 15% (by volume) gasoline has consistently resulted in NOx emissions which were in a range between 0-40% higher compared with neat methanol operation. The degree of NOx emissions deterioration with M85 fuel is dependent on engine load and speed.

For operation of the DI HSI methanol engine with M85 fuel and without EGR, the NOx emissions were at about 38% higher compared to neat methanol utilization. Operation of the methanol engine with M85 fuel and EGR resulted in NOx emissions which were about 44% higher than the corresponding results, obtained during operation with neat methanol (M100).

Summary and Conclusion

Based upon the results of the engine development program that is reported in this paper, several conclusions can be drawn with respect to the success with which EGR can be adapted to a methanol fueled engine, derived from a diesel engine.

- Integration of an EGR system into the engine concept, resulted in considerable reductions in NOx emissions over the entire engine load and speed range. Some additional advantages with respect to unburned fuel and CO emissions were also achieved through the application of EGR.

- The application of EGR did not lead to significant disadvantages in fuel consumption. A transient test simulation indicated a 3.5% fuel consumption increase during operation with EGR. It is likely that the fuel consumption increase would be smaller if the turbocharger was adapted for the changes in flow conditions that are encountered when hot EGR is applied.

- The Navistar DT-466 methanol engine, when operated with neat methanol, has an excellent potential to reach the NOx emissions of 2 g/hp-hr or lower.

- The use of M85, instead of neat methanol, led to an increase in NOx emission in the transient test cycle. The fuel consumption is not influenced by the change of the fuel.

Future Development

Future development goals for the heavy-duty DI HSI methanol engine include optimization of the prototype EGR concept, the application of charge air and recirculated exhaust gas cooling and matching of the turbocharger to the modified flow characteristics under EGR operational conditions.

Additionally, the introduction of electronically controlled injection and closed-loop EGR may be necessary to successfully transfer the operational behavior presented above to an engine concept that operated in a dynamic cycle. These development steps will be sufficient to allow direct, accurate control of the air/fuel ratio in the combustion chamber.

Because of the excellent ignition behavior that is typical of the HSI combustion system, it is possible to consider additional measures involving the introduction of a certain percentage of water in the neat methanol. Avoiding the final distillation step during methanol production would result in an advantage with regard to the fuel costs. For this reason, the methanol/water blend can be effectively used, either to obtain further reductions in NOx emissions or to reduce EGR rates with improved engine efficiency.

Acknowledgements

The authors would like to thank the California Air Resources Board (CARB) for their support of the research work presented in this publication. In addition, gratitude is extended to Navistar International for their co-operation and hardware support.

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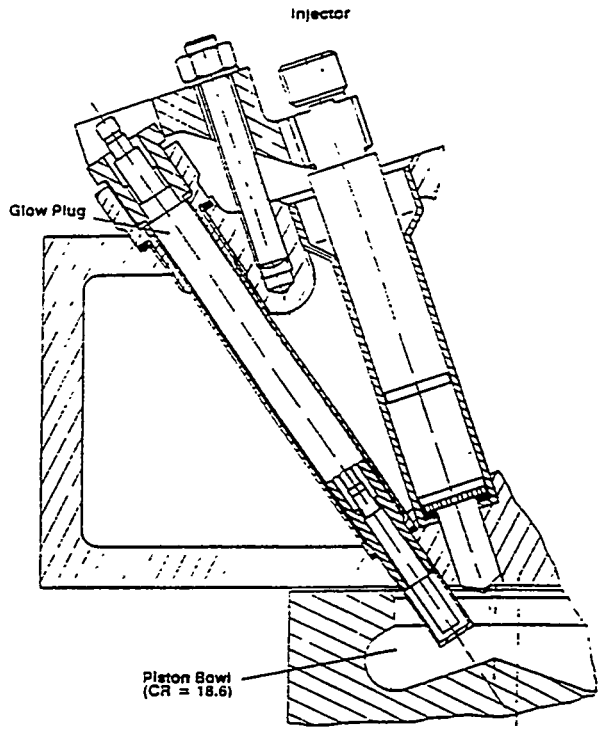

Figure 1: Hot Surface Ignition Combustion System

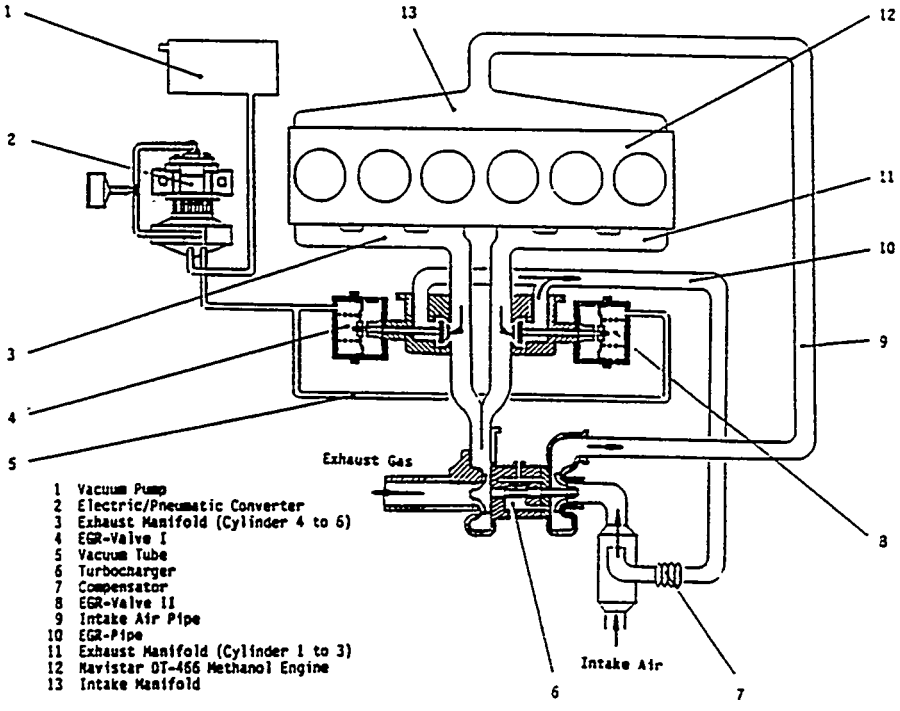

Figure 2 : EGR System Configuration

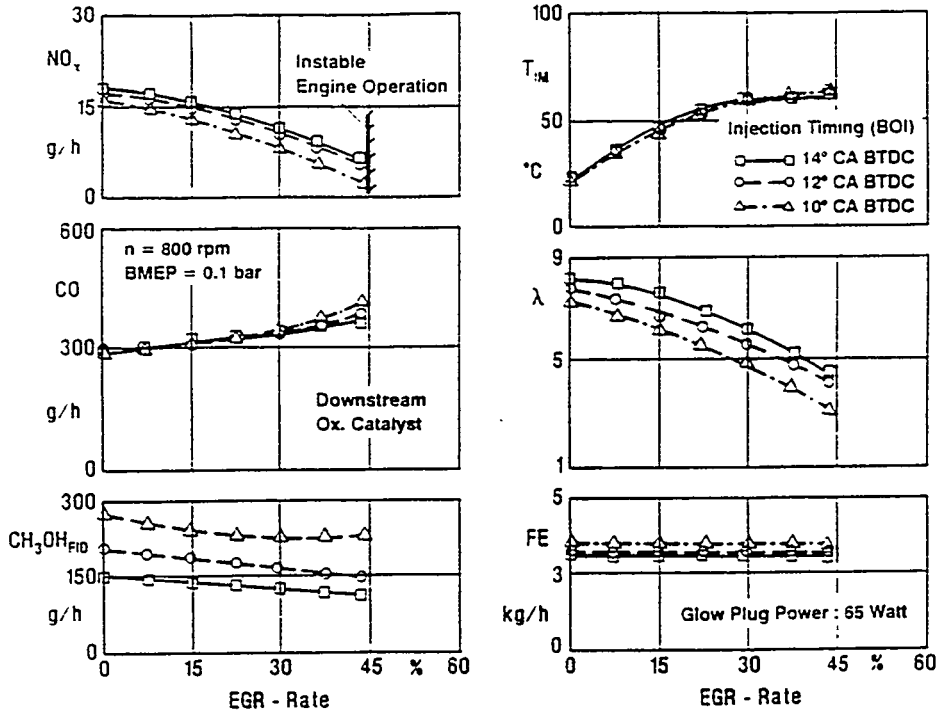

Figure 3 : Influence of EGR Rate on the Operational Behavior at 800 rpm Engine Speed and an Engine Load of BMEP = 0.1 bar

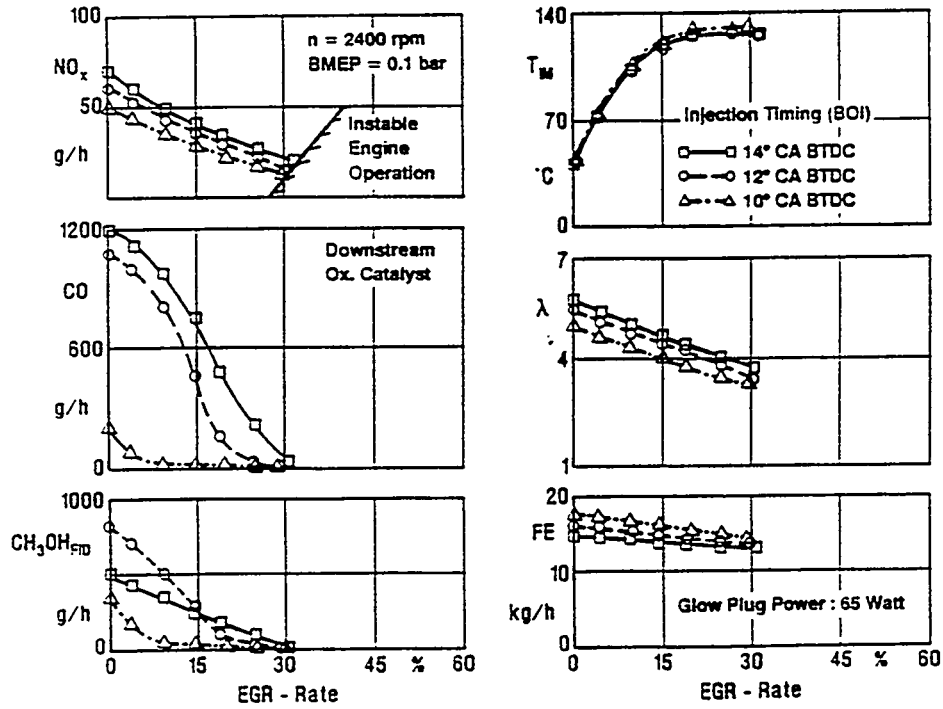

Figure 4 : Influence of EGR Rate on the Operational Behavior at 2400 rpm Engine Speed and an Engine Load of BMEP = 0.1 bar

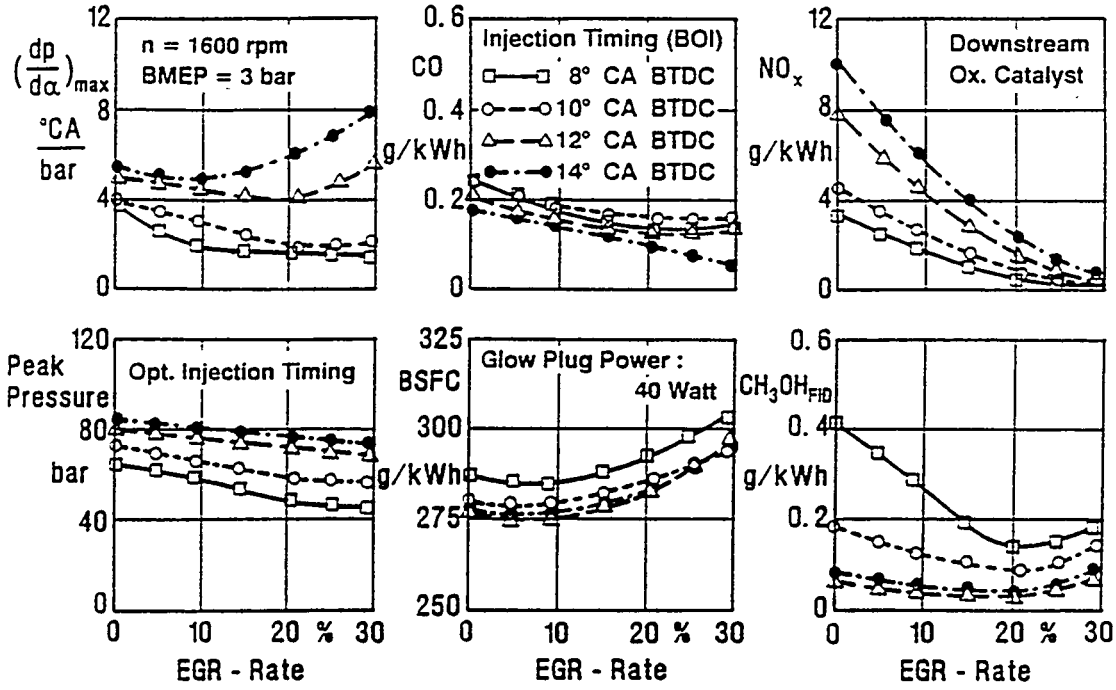

Figure 5 : Influence of EGR Rate on the Operational Behavior at 1600 rpm Engine Speed and an Engine Load of BMEP = 3.0 bar

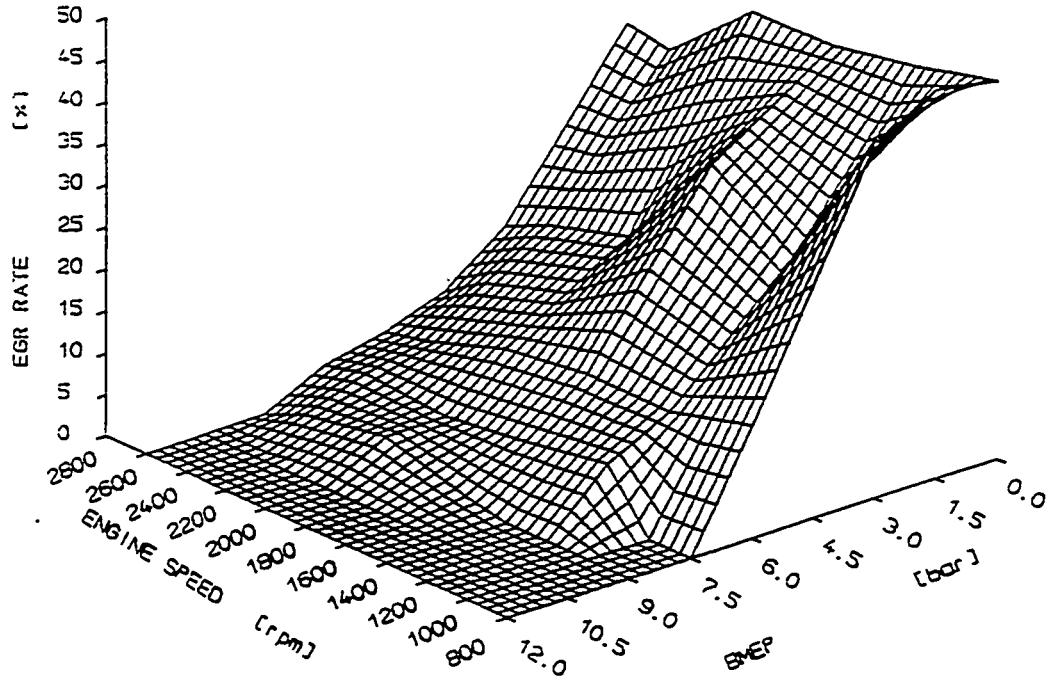

Figure 6 : EGR Strategy for the DI HSI Methanol Engine

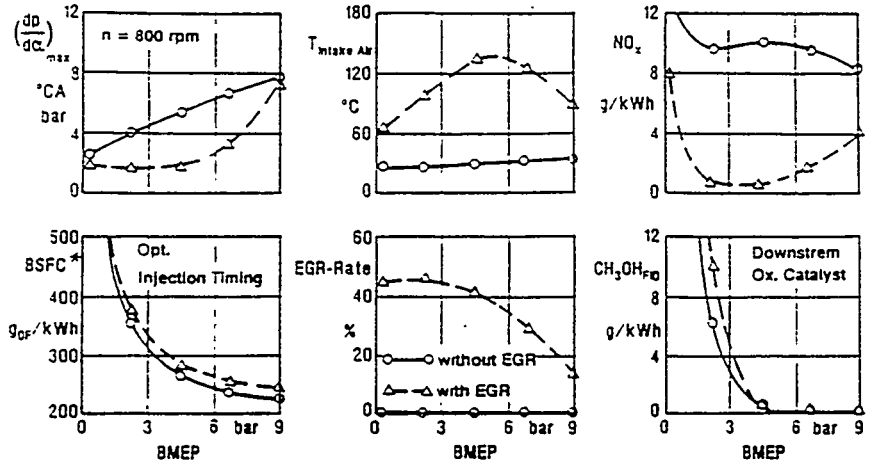

Figure 7: Part Load Performance of the DT-466 DI HSI Methanol Engine with and without EGR for an Engine Speed of 800 rpm

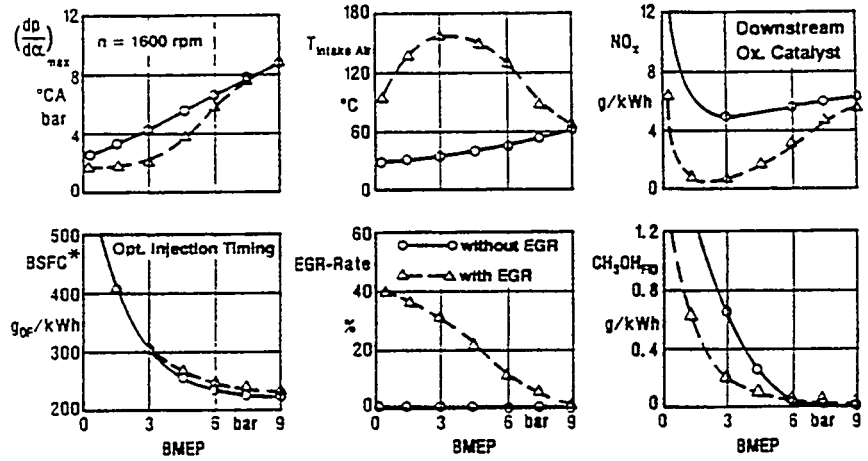

Figure 8: Part Load Performance of the DT-466 DI HSI Methanol Engine with and without EGR for an Engine Speed of 1600 rpm

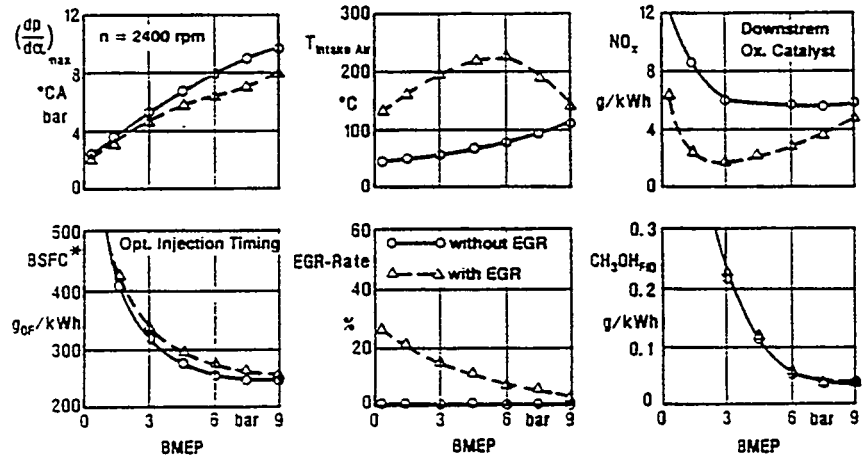

Figure 9: Part Load Performance of the DT-466 DI HSI Methanol Engine with and without EGR for an Engine Speed of 2400 rpm

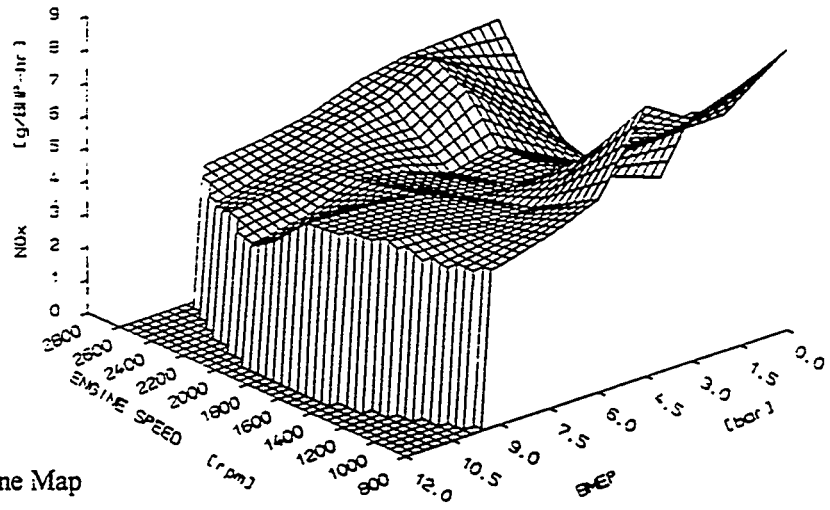

Figure 10: NOx Emissions Engine Map (without EGR)

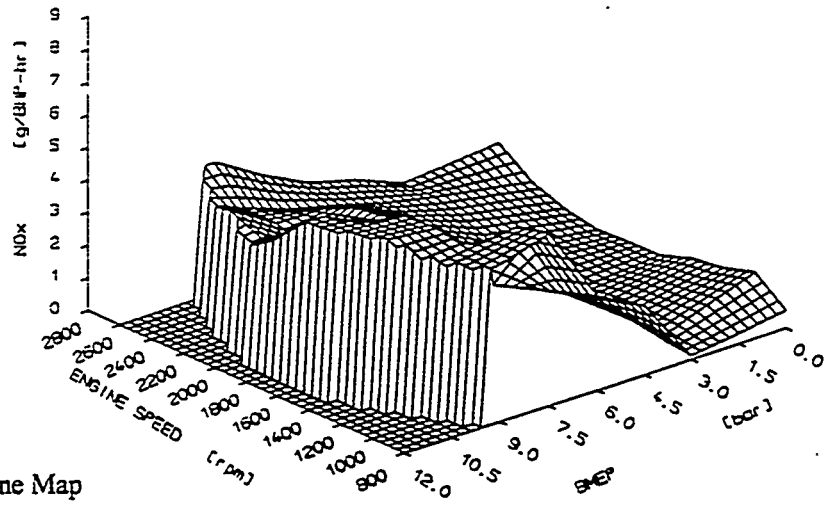

Figure 11: NOx Emissions Engine Map (with EGR)

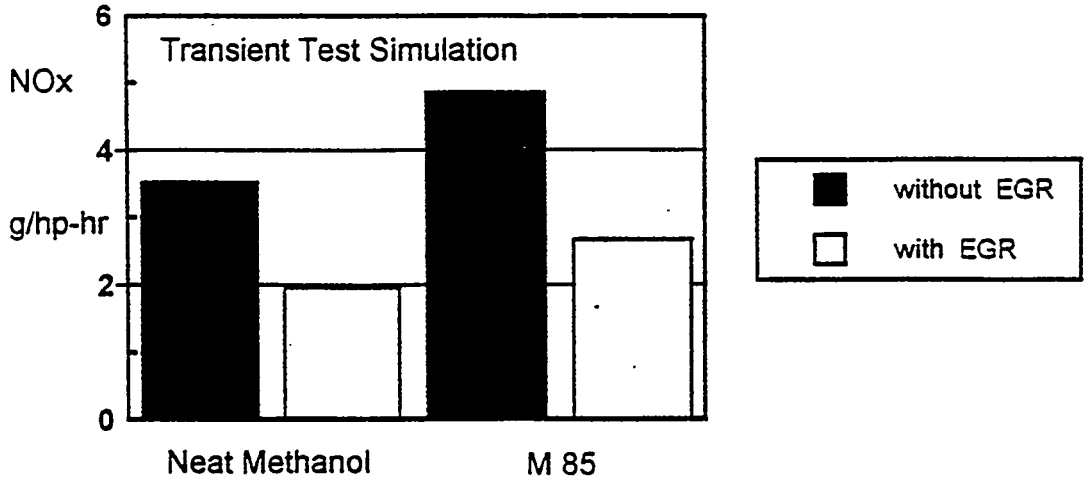

Figure 12: Results of the Transient Test Simulation Calculation

M85 VEHICLES IN THE SCAQMD CLEANFLEET DEMONSTRATION

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Abstract

The CleanFleet demonstration now has 111 alternative fuels vans in daily package delivery service with Federal Express. This includes 20 vehicles running on M85 methanol. The vehicles have been in service about a year, and have accumulated over 400,000 kilometers. On the whole, they have been very successful and reliable. The bulk fuel storage and dispensing system was the source of some fuel contamination, and was fixed. The vehicle fuel tank pickup tube/fuel pump assembly had a design problem, and the fleet has been updated to an improved design par. The trucks have been emissions tested, and will continue in service through October 1994.

M85 VEHICLES IN THE SCAQMD CLEANFLEET DEMONSTRATION

Introduction

Planning efforts began in 1990 for the South Coast Alternative Fuels Demonstration Project (also called CleanFleet), and the vehicles began operating on April 17, 1992. During the next eight months 111 alternative fuels vehicles began normal package delivery service for Federal Express. This fleet includes 20 vehicles running on M85.

CleanFleet is funded by a diverse consortium of government and industry sponsors, listed below in Table 1. The South Coast Air Quality Management District (SCAQMD) is the host organization; Battelle Memorial Institute is the technical support contractor. Chevrolet, Dodge, and Ford provided the vehicles.

CleanFleet's objective is:

> To demonstrate and document the emissions, operations, and economic status of alternative fuel commercial delivery vans in the early 1990s for meeting air quality regulations in the late 1990s.

CleanFleet was designed as a head-to-head comparison of similar vehicles, operating in actual revenue service using alternative fuels. The fuels being tested are M85 methanol, compressed natural gas (CNG), propane, reformulated gasoline, and electricity. Unleaded gasoline is used as a control fuel.

The design goal for the experiment was to have seven vans from each manufacturer using each of the five fuels (totaling 105 alternative fuel vehicles), plus three control vehicles for each combination of manufacturer & fuel (totaling 45 control vehicles). This design goal was substantially achieved, although not every combination was available. Table 2 shows the vehicles that CleanFleet was able to obtain.

Table 1. CleanFleet Sponsors

South Coast Air Quality Management District	Chevrolet Motor Division
California Air Resources Board	American Methanol Institute
California Energy Commission	Southern California Gas Company
Mobile Source Air Pollution Reduction Review Committee	LP Gas Clean Fuels Coalition
U.S. Department of Energy	National Propane Gas Association
U.S. Environmental Protection Agency	Western Liquid Gas Association
Federal Express Corporation	Gas Processors Association
Ford Motor Company	ARCO Products Company
Chrysler Corporation	Chevron USA Products Company
	Southern California Edison

Table 2. Number of CleanFleet Vans

Vehicle Manufacturer	M-85	Propane Gas	Compressed Natural Gas	Phase 2 Reformulated Gasoline	Electric	Control
Ford	20	13	7	7	1	12
Chrysler	0	0	7	7	0	6
Chevrolet	0	7	7	7	0	9
Vehma	0	0	0	0	2	0
	20	20	21	21	3	27

Each fuel was placed at a different Federal Express business location, as shown in Figure 1.

The M85 Demonstration

The M85 vehicles are based at Santa Ana, California. The fleet is made up of 20 Ford Econoline M85 vans plus 3 standard gasoline Ford Econolines using standard unleaded gasoline for experimental control. The first of the 23 vehicles began service on October 6, 1992, with the last beginning service one week later on October 12. The Federal Express employees at the station received training on the M85 vehicles themselves; safe practices for handling M85; and the special CleanFleet data recording requirements. A fuel storage and dispensing system was installed at the Federal Express site. The vehicles are scheduled to remain in service for 2 full years, to October 1994.

The Service Conditions

The M85 vehicles are used for package pickup and delivery in urban and suburban traffic conditions. The service is characterized by an extremely high number of engine shut-offs and restarts, with short trips between starts. The average mileage is about 40 miles per day. Within these 40 miles, the engine is shut off and restarted between 50 and 100 times. All the trucks are used every weekday, with a few of the trucks in service on Saturdays. All the trucks are idle on Sundays.

The Vehicles

The M85 trucks are 1992, full size Ford Econoline E-250 vans and are not equipped with air conditioning. They are flexible fuel vehicles (FFVs). As such, they are not optimized for either emissions or performance. The catalytic convertor is a standard gasoline unit, and the compression ratio is not as high as it could be. The overall vehicle dimensions are shown in Table 3.

The engines are 4.9 liter in-line 6 cylinder types with electronic fuel injection and a compression ratio of 8.8. The engine is equipped with a 7th fuel injector for assisting with cold starts. The high wear engine components have been hardened.

The Fuel

The fuel is a blend of 85 percent methanol with 15 percent gasoline produced specially for CleanFleet by Arco and Chevron. The gasoline component is a special phase 2 reformulated gasoline that is being tested in the CleanFleet.

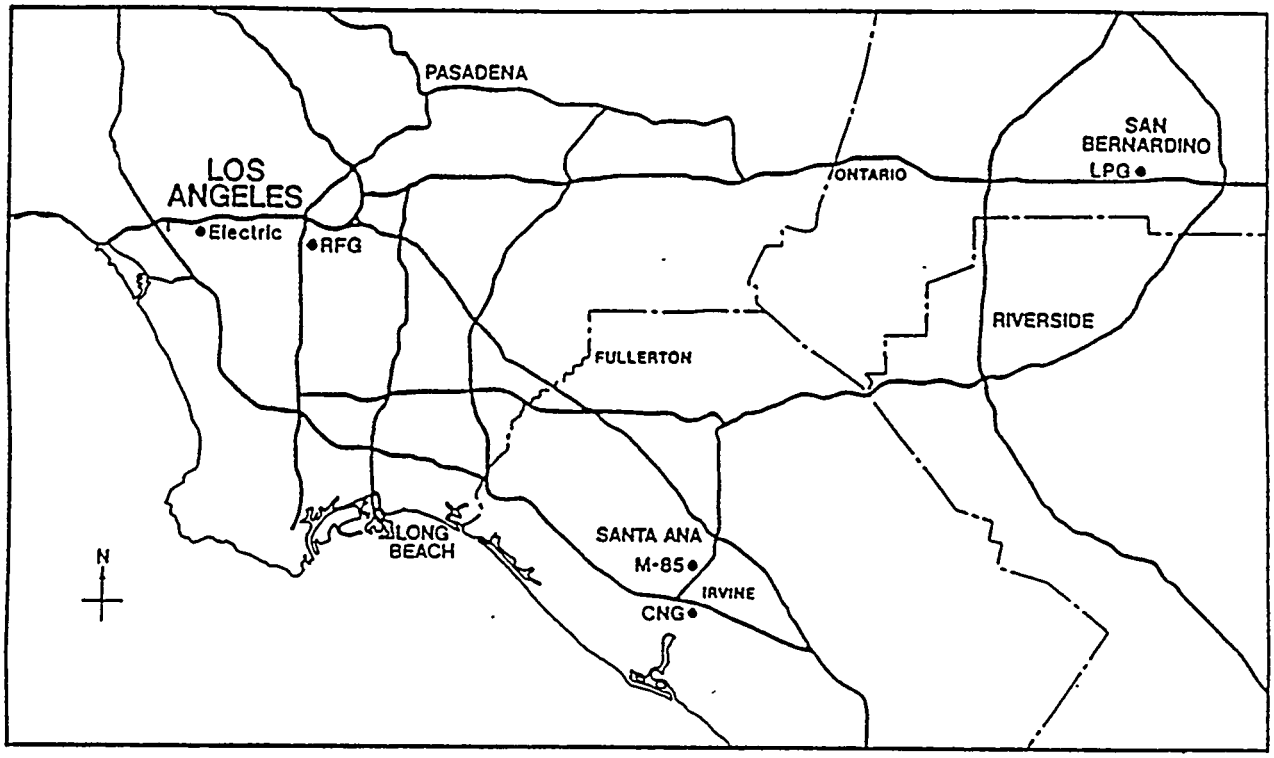

Figure 1. Location of Demonstration Sites

It has a low aromatic content and uses MTBE as an oxygenate. The M85 is splash blended for the project in the delivery tank truck, then hauled to the Federal Express station at Santa Ana.

The fuel is stored on-site in a 15,000 liter above-ground tank. It is dispensed through a conventional design pump and hose. The system is equipped for California stage 2 vapor recovery and is fully methanol compatible.

Status of M85 Demonstration

The M85 and control vehicles have been used in daily service for nearly a full year. Even though they are FFVs, the trucks are never fueled with gasoline or with retail M85. They are refueled every night with the special M85. As of August 1993, the M85 and control vehicles at Santa Ana have accumulated over 400,000 kilometers with an average of more than 18,000 kilometers per vehicle. Their performance is fully satisfactory at this time. Three of the M85 vehicles have recently been tested for exhaust emissions (both regulated and speciated) at the California Air Resources Board.

Table 3. Overall Vehicle Dimensions

Vehicle Specifications	Methanol (M-85)
Manufacturer	Ford Motor Company
Vehicle model name/number	Econoline, E-250
Assembly plant name/city/state	Lorain Assembly Plant, Lorain, Ohio
Modifications/conversions	Ford Motor Company
General description of modifications — fuel supply, storage, engine, chassis	Flexible fuel vehicle (FFV), changes to fuel supply, storage and engine
Notes About Vehicle — Use of Powerplant and/or Components not yet available on the commercial market	FFV Econoline not currently available on the commercial market
Functional Equipment — Powertrain	
Engine	Displacement and type: 4.9 L1-6 EFI BHP @ RPM: N/A Ft/Lb torque @ RPM: N/A CR: 8.8:1
Transmission	Ford 4-speed E40D
Battery	Maintenance-free, 12 volt, 72 amp/hr.
Functional Equipment — Chassis	
Frame	Type of construction. Single channel, five cross members
Front suspension	Type: Coil Springs: Coil 4" ID Axle capacity: 3,700 lb.
Rear suspension	Type: Multi-leaf/2 stage Springs: 55" x 3.0", 5 leaves Axle capacity: 5,345 lb.
Steering	Type: Recirculating ball, XR-50 gear Ratio: 17.0:1 15.5"
Brakes	Front, type: Disc, self-adjusting, hydraulic Front, size: 12.56 Rear, type: Drum and shoe type, self adjusting Power-assist booster, size: 13.46" effective diameter, dual diaphragm type

Table 3. Overall Vehicle Dimensions (Continued)

Vehicle Specifications	Methanol (M-85)
Wheels	Type and size: 8-hole disc, 16" x 7.0"
Body	Construction: Cargo Van Doors: Side and rear
Dimensions	Overall length: 211.8 (in.) Wheelbase: 138 (in.) Overall width: 79.5 (in.) Cargo volume: 255 (cu. ft.) Curb weight: N/A (lb.) Maximum load weight: 2.245 (lb.)
Fueling Systems	
Description of the system components and design used for delivery of the fuels to the combustion chambers (as opposed, if so, to standard carburetion or fuel injection) as it differs from the unleaded gasoline or diesel type considered "normal" for the engine	Fuel sensor in-line for percentage methanol. Methanol compatible fuel lines. Larger fuel injectors plus 7th cold start injector.
Fuel storage	Tank type: Methanol-compatible, plated steel with insulator Capacity: 35 gallons Tank location: Mid-ship
Other significant modifications	Engine combustion chamber components: Hardened block for improved wear Emissions control system components/design: Mass air/SEFI

Significant Results To Date

The M85 fuel storage and dispensing system proved to be a challenge. The vendors were unaware of the requirements for methanol compatibility, despite their claims to the contrary. The system was initially equipped with galvanized steel pipe fittings, some aluminum tank components, a pump, and a dispensing hose that were not methanol compatible, and a nozzle that had aluminum components. These were discovered when the in-tank fuel filters on two of the M85 vans plugged with materials from the dispenser hose. This occurred in November, after about a month of service. Subsequent analysis revealed the presence of aluminum. The offending parts were replaced with appropriate materials, and in June the tank was emptied and cleaned to remove any residual contamination. There

has been no further indication of materials incompatibility in this system.

The fuel economy of the M85 vehicles, calculated on an energy basis, is somewhat less than for the control vehicles. The heating values used for this calculation are from actual sample analyses of the fuel in the CleanFleet. For a given amount of fuel energy, the M85 vehicles are traveling an average of 92 percent of the distance that the Ford unleaded gasoline vehicles are traveling.

The vehicles have had problems with the in-tank fuel supply pump and filter assemblies. The fuel pickup was a few millimeters too long, and it rubbed against the inside surface of the fuel tank. This created debris that plugged the filter, in turn causing failure of the fuel pump. Nine of the 20 vehicles stopped running in service because of this problem. All 20 vehicles have now had this unit replaced with an improved version.

Two safety incidents have occurred at Santa Ana, both engine compartment fires for M85 vehicles. In the first incident, the driver extinguished the fire at its onset, and only very minor damage resulted. In the second case, the fire caused extensive damage to the front of the vehicle. Both cases are still under investigation, though preliminary results point to the extra cold start injector. As a precaution, Ford has disconnected the cold start injectors for all the M85 trucks.

In general, the M85 vehicles are well liked by the drivers and other staff. The vehicles have provided a fully acceptable level of service and reliability.

Future Activities and Results

The M85 vehicles will continue to operate through October of 1994 with careful observation. Quantitative analyses will be performed on the maintenance burdens of the test and control vehicles. Surveys of employee attitudes will be taken. Emissions tests will be repeated at the midpoint and the end of the demonstration. The engines will be disassembled and measured for wear. A comprehensive economic analysis will be performed, as well as statistical analyses to assess the significance of any observed differences.

The results of the entire CleanFleet of 111 vehicles are released through quarterly data reports, quarterly statistical reports, and the project final report in late 1994.

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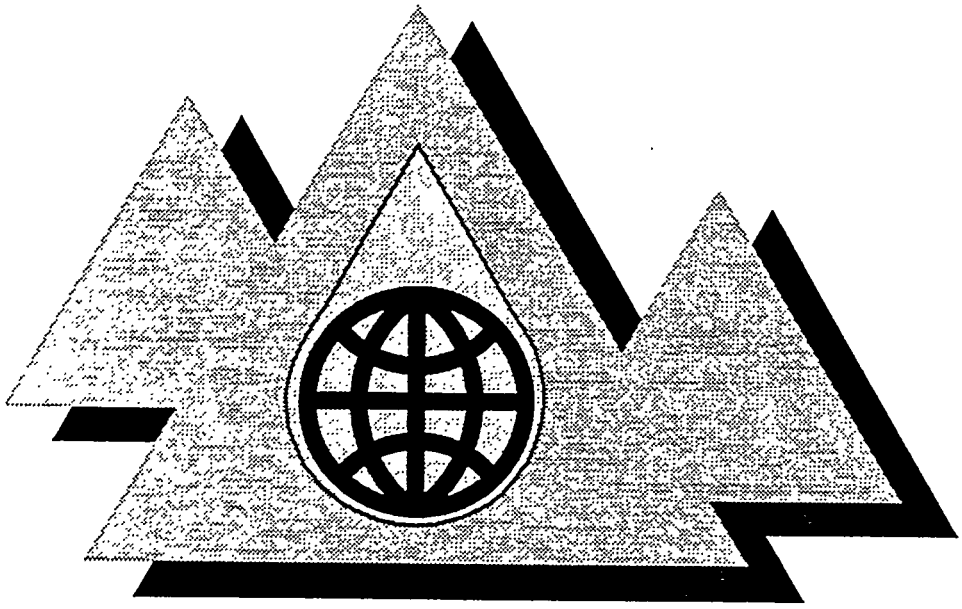

Alcohol and Oxygenate Fuel Safety/ Toxicity

POTENTIAL HEALTH RISKS OF GASOLINE OXYGENATED WITH METHYL TERTIARY BUTYL ETHER

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Abstract

The 1990 Clean Air Act Amendments mandated the use of oxygenated gasoline during the winter months, beginning November 1, 1992, in areas of the United States that did not attain the carbon monoxide health standards. Methyl tertiary butyl ether (MTBE) at about 15% by volume was the predominant oxygenate used to meet this mandate. Individuals in a few areas of the country reported health symptoms (e.g., headaches, eye irritation, nose irritation) that they associated with MTBE oxyfuel use. These reports prompted a large, rapid-response research program to investigate certain issues related to the potential health risks of MTBE. All of the available health effects and exposure data were assessed by the Office of Research and Development of the U.S. Environmental Protection Agency. This paper briefly describes the results of that assessment, focusing on the potential for acute exposure risks, chronic noncancer risks, and chronic cancer risks.

Introduction

To protect the public health, the U.S. Environmental Protection Agency (EPA) has set National Ambient Air Quality Standards for carbon monoxide (CO) at 9 ppm for an 8-h average and 35 ppm for a 1-h average; neither is to be exceeded more than once per year. These levels were set to protect susceptible subpopulations, especially people with coronary artery disease (e.g., angina). However, because millions of people in the United States live in areas that exceed these standards, Congress (in the Clean Air Act Amendments of 1990) mandated the use of oxygenated fuels (about 2.7% oxygen by weight) during the winter months (beginning November 1, 1992) in areas where the CO standard is not attained. Oxygenated fuels were designated for this purpose because almost all of the CO problem results from vehicular emissions, especially in the winter months. Several types of oxygenated fuels may be used, but methyl tertiary butyl ether (MTBE) has achieved, by far, the greatest market penetration. To meet the oxygenate standard, MTBE is used at 15% by volume. Lesser amounts are commonly used year-round for octane enhancement in certain fuels, but the focus of this paper is on the 15% MTBE oxyfuel because of the higher exposure concentrations that result from its use.

Soon after MTBE oxyfuel was introduced, residents in a few areas of the United States reported experiencing acute symptoms (e.g., headaches, eye and throat irritation) while refueling or driving. The complaints were primarily made in Fairbanks and Anchorage, AK, Missoula, MT, and, to a lesser extent in New Jersey. Very few or no complaints came from other areas. Although these self-reported symptoms did not provide a sufficient scientific basis for determining the existence of health effects, they did prompt EPA to develop a rapid-response research program encompassing EPA, other federal agencies (e.g., the Centers for Disease Control and Prevention [CDC]), industry (especially the American Petroleum Institute and the Oxygenated Fuels Association), and academia. From about December 1992 to July 1993, hundreds of scientists investigated exposures to and various health effects of MTBE. The results of these and some prior studies were presented at a conference held in July 1993 at Falls Church, Virginia. Using this and other information, the EPA Office of Research and Development (ORD) prepared a comprehensive risk assessment of acute and chronic health effects of MTBE (U.S. Environmental Protection Agency, 1993). This paper summarizes that assessment. Because EPA needed the ORD assessment for the 1993/1994 MTBE oxyfuel season, data that had not yet been published were used in the assessment. Such information is subject to change.

The ORD risk assessment is for exposure of the general public to MTBE oxyfuels, not occupationally exposed persons. However, studies of occupational groups were used in the assessment to gain understanding of relatively high-level MTBE effects as a rough guide to what might be considered the high-level boundary of risks to the public from lower, less frequent exposures.

The following discussion is divided into sections on short-term and long-term health effects, an exposure assessment, and acute and chronic health risk assessments, followed by a summary.

Health Effects

Interpreting the health effects of MTBE oxyfuels is difficult, not only because of the limited number of studies, but because exposures are to a complex mixture of evaporative and combustion emissions that contain hundreds of components, many of which are known to be toxic (e.g., formaldehyde, benzene, 1,3-butadiene). Given that compounds in mixtures can have additive, synergistic, or antagonistic effects, it is important to consider the mixture as a whole and not just the individual compounds. In this respect, the data base for MTBE consists mostly of controlled human and animal studies of "pure" MTBE,

with some acute epidemiologic studies involving uncharacterized mixtures. Another source of difficulty in interpreting the health effects of MTBE is that, even if there were substantial data on "average" people, some subpopulations are likely to be more susceptible, due either to differences in exposures or to inherent differences in susceptibility. Also, effects from short-term and long-term exposures could be profoundly different.

Short-Term Exposure Effects

Epidemiological Studies. The CDC, in association with the states of Alaska, Connecticut, and New York, the EPA, and other agencies, conducted epidemiologic studies of symptom complaint prevalence in Fairbanks, AK, Stamford, CT, and Albany, NY (CDC, 1993a,b,c). In Fairbanks, symptom complaint surveys were taken while MTBE oxyfuels were in use and subsequently, after they had been discontinued. In Stamford, MTBE oxyfuels were in use during the study; Albany was chosen to serve as a comparison city that was not part of the oxyfuel program. Additional information on Fairbanks while MTBE oxyfuels were being used was gathered by Beller and Middaugh (1992), who noted that the symptoms reported were mild and transient and did not appear to increase hospital admissions.

Although there were several significant differences between the study elements in each city, the basic approach was to administer a health symptoms questionnaire to commuters and persons in occupational groups with varying degrees of exposure to vehicle emissions. Individuals were asked whether they had symptoms similar to the earlier complaints reported by the public, namely, headache, eye irritation, burning of nose/throat, cough, nausea, dizziness, or spaciness. All participants were questioned about the occurrence of these symptoms over the previous month; also, occupationally exposed participants were questioned about the occurrence of symptoms on the day of the interview. In Fairbanks (but not the other cities), a telephone survey with similar questions was conducted. Those surveyed were asked not to report on symptoms that they associated with a cold or flu. Some of the individuals interviewed in person had blood drawn for measurement of MTBE and its primary metabolite, tertiary butyl alcohol (TBA). In Fairbanks (but not Stamford or Albany), there was significant adverse publicity about the use of MTBE oxyfuels when the initial study was conducted. This confounds interpretation of symptom reporting to an unknown degree.

In Fairbanks, there was a clear decrease in symptom report prevalence of occupationally exposed persons and others reached by telephone after MTBE oxyfuels were removed. For example, 72% of occupationally exposed persons reported headaches while these fuels were in use; only 4% reported headaches after MTBE was removed. At the same time public concern about health symptoms and the higher price of gasoline (14¢ per gallon) also decreased. Thus, the study was confounded.

Results from Stamford could not be directly compared to those from Albany, primarily because people in Albany had an apparently high incidence of symptoms from flu, colds, or allergies that confounded the results. When symptom reports across four groups (commuter, professional driver, car repair or gas station attendant, and "other" [e.g., meter readers]) in Stamford are compared, there are no major differences. For example, 42% of commuters questioned had one or more health symptoms, compared to 35% of professional drivers, who would be expected to have higher exposures to MTBE oxyfuels.

Investigators at the Environmental and Occupational Health Sciences Institute performed two studies in New Jersey. The first study concerned garage workers from the New Jersey Departments of Transportation and Treasury (Mohr et al., 1993). Questionnaires of health symptoms were administered to workers in northern New Jersey (while MTBE oxyfuels were in use) and southern New Jersey (while

MTBE oxyfuels were not being used). No statistically significant difference between the two groups was found, although the study had adequate statistical power to detect effects if they had occurred. Fieldler et al. (1993) attempted to determine whether persons reporting multiple chemical sensitivity were also more sensitive to MTBE oxyfuels. Results of a symptom questionnaire showed a trend towards enhanced response in such persons, but it was not statistically significant, possibly because of small sample sizes.

Human Clinical Studies. Investigators at both EPA (Gerrity et al., 1993) and Yale University (Cain et al., 1993) exposed young (about 18 to 35 years old), healthy men and women to "pure" MTBE for 1 h at room temperature. Gerrity et al. used 5 mg/m^3 MTBE; Cain et al. used 6 mg/m^3 MTBE. Protocols for the two studies were very similar and included subjective tests (e.g., symptom questionnaires) and objective tests for behavior, indicators of upper airway inflammation, and indicators of eye inflammation. Blood samples were drawn from a very small number of subjects for MTBE and TBA determinations. No statistically significant effects were observed in either study, although the studies had adequate statistical power to detect effects if they had been present. Pharmacokinetic measurements on six subjects suggested that the half-life of MTBE was about 1 h; for TBA the half-life could not be determined because of its slow clearance, but is likely to be greater than 1 day.

Human Blood Studies. There has been substantial interest in understanding whether there is a relationship between health symptoms and blood levels of MTBE and/or TBA, but most of the recent human studies have not been very enlightening. Because no symptoms were reported in the human clinical studies, there was no basis for measuring an association in those studies. In Fairbanks, the association between the highest quartile of blood MTBE levels and symptom reports was not statistically significant, but sample sizes were small. In Stamford, the association between MTBE blood levels and symptoms was statistically significant. These findings indicate that exposure to MTBE occurred, but blood levels of MTBE cannot be used yet as a quantitative biomarker of effects. For example, blood levels of MTBE were slightly higher in the negative human clinical studies, compared to the epidemiologic studies. Although TBA was slightly higher in the epidemiologic studies compared to the human clinical studies, there were no significant associations between higher levels of TBA and symptoms. One reason for this lack of clear relationship may be that MTBE has a relatively short half-life in the blood (roughly 1 h), so a single blood measurement at the end of a work shift would not quantitatively reflect the total pattern of exposure. Also, samples sizes in these studies were small, and thus the statistical power to detect an association was limited. In addition the temporal relationship between exposure and symptoms, if any, is not known.

Animal Studies. Tests of respiratory irritancy due to acute exposure to MTBE did not produce noteworthy results in mice (Tepper et al., 1993) or in rats (IRIS, 1993). However, certain effects in reproductive and developmental toxicity studies of MTBE have garnered attention. A developmental toxicity study in mice showed that MTBE levels $\geq$14,400 mg/m^3 could reduce pup viability; no adverse effect was observed at 3,600 mg/m^3 (Tyl and Neeper-Bradley, 1989). In a two-generation reproduction study (Neeper-Bradley, 1991) in rats exposed to $\geq$10,800 mg/m^3, rat pups had reduced body weights at birth and reduced weight gains during postnatal development; there were no effects at 1,440 mg/m^3. From these data, a preliminary assessment (with an uncertainty spanning at least an order of magnitude) of an MTBE level at which no adverse developmental toxicity is likely to occur in humans, including sensitive subpopulations, was 48 mg/m^3 (Clegg, 1993). No exposure duration is assigned to this assessment because of the uncertainty as to whether or not there is a narrow window (e.g., minutes or hours) of vulnerability during specific periods of organogenesis.

Long-Term Exposure Effects

Chronic studies were performed with male and female rats (Burleigh-Flayer et al., 1992) and mice (Chun et al., 1992). Animals were exposed for 6 h/day, 5 days/week for 18 mo (mice) or 24 mo (rats). Male rats in the two higher concentration groups were autopsied early due to excessive mortality. Based on the rat data (Burleigh-Flayer et al., 1992), EPA developed an inhalation reference concentration (RfC). An RfC is defined as an inhaled concentration, with an uncertainty spanning about an order of magnitude, that can be inhaled continuously over a lifetime by humans (including sensitive subpopulations) and is thought not to pose any appreciable deleterious noncancer hazard. The RfC for MTBE is 3 mg/m^3 (IRIS, 1993). The lowest observed adverse effect level in the rats was 10,800 mg/m^3, at which there were increased liver and kidney weights, increased severity of spontaneous kidney lesions, and increased incidence of extreme exhaustion in female rats; also, swollen periocular tissue was observed in both male and female rats. In addition, male rats had kidney effects.

There are no human data on the potential carcinogenicity of MTBE. Parker et al. (1993) have developed a preliminary cancer assessment based on the rat and mouse studies described above. This assessment will remain preliminary until other cancer studies in progress are completed and the final draft assessment is reviewed and verified by an EPA-wide Work Group. Because of several aspects of the rat and mouse bioassays (e.g., reduced survival, less-than-lifetime exposures, inadequate data on potential mechanisms), there is considerable uncertainty in the assessment, and it was only possible to develop a weight-of-evidence classification, not a potency estimate. In brief summary, there was an increase in kidney tumors in male and female rats (at $\geq$10,800 mg/m^3), testicular tumors (at $\geq$10,800 mg/m^3) in male rats, and liver tumors in male and female mice (at 28,800 mg/m^3). Interpretation of these data, especially for male rat kidney tumors, is difficult for several reasons. Some chemicals cause tumors in male rats due to the accumulation of a species- and sex-specific protein ($alpha_{2u}$ globulin). This mechanism of tumor generation does not occur in humans. At present, available reports do not permit a definitive conclusion but are currently suggesting that $alpha_{2u}$ globulin was not involved in the MTBE-induced tumors; if it was not, then the male rat kidney data would be relevant to humans. Other findings are also difficult to interpret (e.g., the significance of the mouse liver tumors). Separate mutagenicity studies of MTBE were negative. At the present time, the data suggest that a tentative Group "C" weight-of-evidence classification (possible human carcinogen, based on limited animal evidence) is appropriate. Further evaluation, with even more uncertainties, suggests that if MTBE is a carcinogen, it has a relatively low potency compared to numerous other air pollutants with carcinogenic activity.

Exposure Assessment

Both an acute and chronic MTBE exposure assessment (Huber, 1993; U.S. Environmental Protection Agency, 1993) were developed, based primarily on data from studies of commuters (Lioy et al., 1993), gas-station-measurements (Johnson, 1993; Clayton Environmental Consultants), and a few field measurements (Zweidinger, 1993). The basic approach was to take activity pattern data (i.e., time spent in different microenvironments), estimate "typical" high and low exposures in those microenvironments, apply various assumptions, and then develop a time weighted average exposure concentration. It must be emphasized that because of the limited data, the exposure assessments have considerable uncertainty.

Using this approach, an annual exposure estimate was calculated for four scenarios: a 4-mo oxyfuel season and a 6-mo oxyfuel season, each using the high and low concentration estimates for microenvironments used in the model. A concentration of 1.5% MTBE was assumed for the nonoxyfuel season, because

some MTBE is present throughout the year as an octane enhancer and 1.5% is thought to represent (or even overestimate) the very high end of an average concentration of MTBE in fuel. The resulting four annual exposure estimates are in a range from 0.03 to 0.07 mg/m^3.

Acute exposures are highest during a 2-to 3-min gasoline fill-up. Measured values have ranged from 0.32 to 137 mg/m^3. These low and high values were measured on different days at the same gas station, illustrating the large variability involved. The concentration for a typical high-end exposure for a fill-up was 36 mg/m^3. For other typical high-end scenarios the concentrations were 0.36 mg/m^3 inside a vehicle during commuting, 0.036 mg/m^3 inside public buildings or homes, and 1.8 mg/m^3 inside a public garage. Using these values, 1-h time-weighted averages were calculated for two scenarios. For the first scenario, using the highest measured values for a fill-up and a commute, the average exposure level was 5.6 mg/m^3. For the second scenario, using typical worst-case levels (not the highest measured on rare occasions) for refueling, personal and public garages, commuting, and a public building, the average exposure level was 1.8 mg/m^3 MTBE.

Health Risk Estimates

Acute Risks

Human clinical studies (1-h exposures to 5 or 6 mg/m^3 MTBE) did not demonstrate significant effects in terms of symptoms (e.g., headaches) or objective measures of eye/nose inflammation or neurobehavioral changes. Based on the exposure conditions of these studies, it does not appear that healthy members of the public exposed under temperate conditions are likely to experience symptoms at MTBE concentrations that would be commonly encountered. However, the influence of dose-rate or cumulative dose on symptoms, if any, has not been investigated. For example, brief high-level exposures (e.g., during a fill-up) have not been compared to longer term low-level exposures such as those in the human clinical studies. Also, studies have not adequately addressed persons who may have enhanced sensitivity, nor have studies investigated exposures to MTBE oxyfuel mixtures. These data gaps constitute additional uncertainties.

The epidemiological studies conducted thus far have investigated associations between MTBE oxyfuels exposures and symptoms, but they do not provide adequate evidence of cause-effect relationships because confounding variables may have been involved. Workers in northern New Jersey (while MTBE oxyfuel was in use) spent most of their day around vehicles (e.g., pumping gas, driving, repairing cars) and would be expected to have a higher exposure than members of the general public. However, there was no statistically significant difference in symptoms between these workers and similar workers in southern New Jersey when MTBE oxyfuels were not in use. In Stamford, there was not a large difference in symptom prevalence between commuters and persons who worked in close proximity to vehicular emissions. Study participants in Stamford with the highest blood levels of MTBE did have significantly more symptoms, but this association is difficult to interpret because blood MTBE concentrations cannot, as yet, be used as a quantitative biomarker of effects. The Albany epidemiologic study was confounded by an high incidence of flu and/or allergies and therefore cannot be interpreted relative to MTBE symptoms.

From the above human clinical and epidemiologic studies it does not appear that healthy young adults receiving high exposures typical for the general public are likely to experience health symptoms under temperate (i.e., not subarctic) conditions. However, for most chemicals, there are susceptible subpopulations, and there is no reason to assume that MTBE would be different, although such potential special-risk subpopulations have not yet been identified and studied. Thus, the question

of the effects of MTBE on susceptible subpopulations remains open.

The Fairbanks epidemiologic studies clearly show that after MTBE oxyfuels were withdrawn, reports of health symptoms substantially decreased. However, interpretation of this decline in complaints is confounded by other events, including a decrease in the price of fuel and a likely change in the public's perception of the problem. Thus, the influence of MTBE on symptom reports in Fairbanks is unknown. It is also recognized that Fairbanks has unique features of subarctic temperatures and a topography that can favor atmospheric inversions. These factors could influence results, and thus findings in other parts of the country cannot necessarily, at this time, be extrapolated to Fairbanks.

The risk of developmental toxicity is more difficult to assess because only animal data are available and minimally effective exposure durations have not been adequately characterized. Given that developmental toxicity was not observed in rats at 1,440 mg/m^3 MTBE, a reasonable preliminary estimate (with an uncertainty spanning about an order of magnitude) of an MTBE level at which no developmental toxicity is likely to occur in humans (including susceptible subpopulations) is 48 mg/m^3. Typically encountered acute and chronic exposures to MTBE are well below these levels. However, a 2- to 3-min gasoline fill-up can yield from 0.32 to 137 mg/m^3 MTBE. Thus, in a few instances, brief exposures exceeding 48 mg/m^3 could occur. Whether such brief exposures could actually cause developmental effects is unknown, largely because the likelihood of effects associated with such exposures cannot be estimated. However, concern increases as the concentration increases. When the animal no-adverse-effect level of 1,440 mg/m^3 is compared to the range of fill-up exposures, the exposures are from 10 to 4,500 times lower. Other more routine exposures of the general public are considerably lower and are not of concern. It should be noted that other compounds in gasoline (e.g., benzene) also are developmental toxicants. Thus, the data do not indicate a great difference in concerns between MTBE oxyfuels and gasoline without MTBE. However, it is important to investigate further the toxicity of both types of fuel.

Chronic Risks

A preliminary cancer assessment suggests that MTBE would be classified in the Group C weight-of-evidence category (i.e., possible human carcinogen, based on limited animal data). The data are not adequate to develop a quantitative cancer unit risk. However, if MTBE is carcinogenic, its potency is not likely to be greater than that of gasoline, which currently has a weight-of-evidence classification of "probable" human carcinogen.

There is not a significant concern about the chronic noncancer health risks of MTBE. When the RfC of 3 mg/m^3 (a level thought not likely to cause adverse effects, even in susceptible subpopulations) is compared to the highest annual exposure assessment of 0.07 mg/m^3, chronic noncancer risks would not be expected.

Conclusions

Healthy members of the general public receiving typical exposures to MTBE oxyfuels under temperate conditions are unlikely to experience symptoms such as headaches, eye irritation, nose irritation, or nausea. However, the data are not adequate to draw conclusions about potentially susceptible subpopulations. If acute symptoms are caused by MTBE, they are likely to be mild and transient. The impact of MTBE under subarctic conditions is not known. In Fairbanks, symptoms decreased substantially when MTBE oxyfuels were withdrawn, but so did public concern about MTBE. Even though the Fairbanks epidemiologic studies were confounded, the possibility of acute health symptoms being associated with exposure to MTBE oxyfuels in Fairbanks cannot be ruled out.

Developmental toxicity has been observed in laboratory animals exposed to high

concentrations of MTBE. Evaluation of these data suggests that typical public exposures are not of concern. If a risk of developmental toxicity does exist, it would be for some (not all) gasoline fill-up exposures. Other constituents of gasoline present throughout the year have developmental toxicity potential, so the presence of MTBE in gasoline is not the only reason for concern about some high-concentration fill-up scenarios.

Chronic exposures to low concentrations of MTBE alone do not appear to be a health risk concern, but there are no data on the effects of MTBE-gasoline mixtures. Chronic noncancer risks are not likely. The cancer assessment is preliminary, pending the completion and evaluation of additional laboratory studies, but the preliminary weight-of-evidence classification of MTBE is Group C (possible human carcinogen, based on limited animal evidence). However, because gasoline itself has a classification of a probable human carcinogen and has carcinogenic components, the addition of MTBE does not appear to increase the existing cancer risk.

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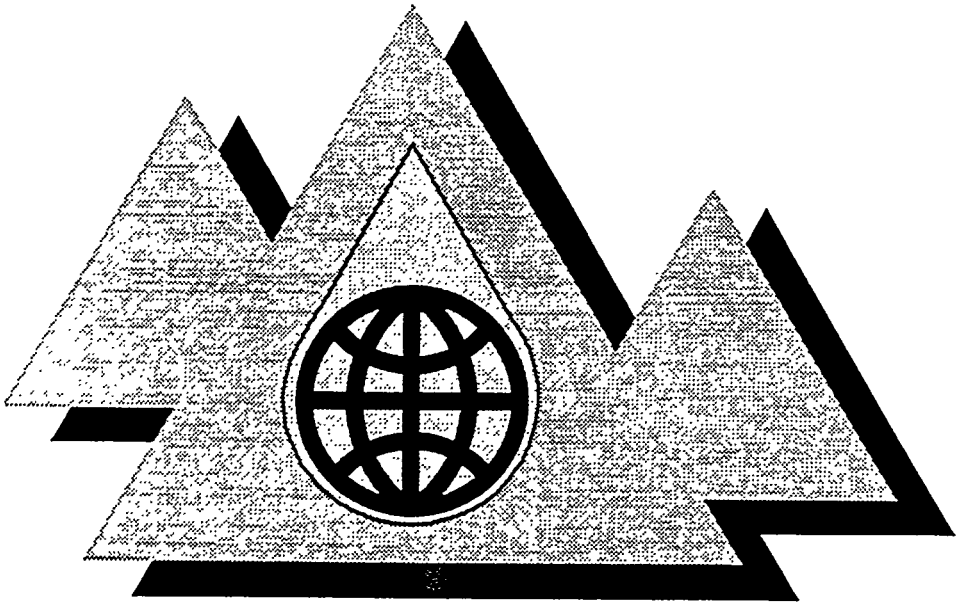

Vehicle/Engine Optimization and Emission Controls

DEVELOPMENT OF A SPARK IGNITED DI METHANOL ENGINE FOR PASSENGER CAR APPLICATION

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ABSTRACT

Methanol is regarded as a primary potential source of fuel for the transportation sector. A significant fraction of the effort which has been directed toward development of spark ignited methanol engines has been invested in conventional port injected, homogeneous, premixed charge, Otto cycle engines. These engines have been characterized by cold start difficulties and high cold start emissions.

Within a research program sponsored by the U.S. Environmental Protection Agency in co-operation with Volkswagen AG, a direct injected, spark ignited methanol engine has been developed. The baseline engine for this development was a high swirl, stratified charge, DI prototype gasoline engine for passenger car application. The engine features an EGR system as well as an oxidation catalyst. The methanol engine exhibits very low NOx emissions and a favorable fuel consumption behavior associated with higher compression ratio, DI concepts. The use of an oxidation catalyst allows comparably low levels for the tailpipe emissions.

The results of the engine/vehicle development program is presented and discussed. The influence of specific engine operational parameters on fuel consumption and emissions is demonstrated and a comparative assessment of this technology with other DI methanol concepts for passenger car engines is provided with regard to the U.S. FTP-75 test results.

Introduction

Considerable interest in alternative fuels has been generated by pending U.S. Federal and California emissions legislation. The desire for introduction of "clean fuels" has been a driving force in the development of new engine concepts for passenger car application. Emissions legislation has been initiated in order to achieve a reduction of those emissions components which have major impact on the smog situation in the larger US cities, due to their ozone forming potential. As a result of the emissions legislation that has been implemented in California, certain percentages of the fleet of vehicles which will be sold in California must comply with the restricted emissions limits (TLEV, LEV and ULEV). Moreover, beginning in 1998, a requirement for the sale of a number of zero emission vehicles (ZEV) exists.

In view of more restrictive standards, such as those adopted in California, alternative fuels such as CNG and methanol are gaining increasing interest. In comparison to CNG, methanol has significant advantages with regard to both handling and storage. An additional incentive for methanol vehicles exists when the efficiency requirements presented by the CAFE standards are considered. Compared to conventional gasoline engines, NOx emissions from a dedicated methanol engine are considerably lower. Moreover, the methanol related hydrocarbons result in a lower photo-chemical reactivity, in comparison with gasoline engines, due to different specific hydrocarbon compositions /1/. Conventional, homogeneous charge methanol Otto-cycle concepts which are available today tend to have a comparably increased formaldehyde level.

Because of its specific fuel properties, methanol has almost exclusively been used in the past as a fuel for Otto engine concepts. In addition to emissions benefits, optimized methanol Otto engine concepts exhibit a fuel consumption behavior which is, on the average, 10% lower compared with gasoline fuelled Otto engines /2/. In comparison with engine concepts that feature direct fuel injection under unthrottled conditions, the Otto engine presents more obvious disadvantages with regard to fuel consumption, especially in the operating range that corresponds to the FTP-75 test cycle. The disadvantages of the Otto engine can primarily be related to the relatively low compression ratio in combination with the mixture quality control for $\lambda = 1$.

Due to the typical sootfree engine operation that exists with pure methanol, very low particulate emissions are achieved. In combination with the substantial reductions in NOx emissions that are possible, methanol engine concepts with direct injection and unthrottled operation present a very high potential for meeting the very restrictive future emissions standards /3/.

This paper reports about the development of a spark ignition DI methanol concept sponsored by the US Environmental Protection Agency (EPA), conducted by *FEV* Motorentechnik, Aachen and supported by Volkswagen AG, Wolfsburg.

DI Methanol Concepts for Passenger Car Engines

Due to the poor auto-ignition behavior of neat methanol, additional measures for ensuring reliable ignition characteristics in a DI engine are absolutely necessary. Numerous concepts, involving modifications to the base engine concept, the fuel, or both have been developed in the past. Because of their beneficial NOx and particulate emissions behavior, engine concepts for utilization of neat methanol possess the best development potential for very low emission passenger car engines /4/. Although compression ignition of methanol is possible through the use of an ignition improving additive, this solution represents an incremental increase in the price of the fuel and results in an additional fuel blending/infrastructure problem. Among the different neat methanol concepts, forced ignition combustion concepts, such as hot surface ignition (HSI) and spark ignition (SI), present an advantage with respect to combustion of neat methanol fuel. Both of these concepts are able to efficiently and cleanly burn methanol without the requirement for an additional additive for improving the auto ignition behavior /5/.

In the case of the direct injected, spark ignition concept the ignition delay and combustion process is influenced by the adjustment of the beginning of injection and the ignition timing. Due to the limited energy that is available for ignition, both parameters have to be carefully adjusted in view of the need to ensure sufficient air/fuel mixture at the spark plug when ignition occurs. Additionally, the location of the spark plug with respect to the injection nozzle as well as the specific configuration of the spark plug itself are of critical importance with regard to their influence on ignition and combustion quality.

Test Configuration

The test engine which was used for the investigations that are presented in this paper, was derived from a prototype DI gasoline engine (Figure 1) that was initially developed at the research department of Volkswagen for use in the Futura concept vehicle /6/. The primary engine data are indicated in Table 1.

Methanol Engine Concept

The general configuration of the stratified charge combustion concept for the DI SI methanol engine is illustrated in Figure 2.

The combustion system that is used with the DI SI methanol engine is characterized by air/fuel mixture formation close to the wall of a centrally located semi-spherical combustion chamber. The mixture formation process is supported by a relatively high intake air swirl resulting in a mixture stratification which is an important precondition for the application of spark ignition in DI engines. The spark plug is located downstream of the injector, with respect to the swirl direction, near the combustion chamber wall. Consequently, as a result of the mixture stratification, an ignitable mixture is available at the spark plug under all operating conditions. For methanol operation, a methanol compatible distributor injection pump, manufactured by AMBAC International, is used. This pump is capable of supplying the relatively high fuel quantities required for methanol operation. Fuel injection is realized with a Stanadyne two-stage pintle nozzle. Relatively long spark duration, in combination with a spark plug with three electrodes, is necessary to obtain acceptable low load low emissions characteristics.

Displacement	1.716 liter
Bore	79.5 mm
Stroke	86.4 mm
Rated Power	66 kW
Rated Speed	4000 rpm
Rated Torque at Engine Speed	192 Nm 2500 rpm
Compression Ratio	16:1
Air Swirl	$c_u/c_a = 4.0$

Table 1 : Test Engine Data

Combustion System Development

The development of the DI SI methanol engine concept involved the optimization of the primary parameters influencing the mixture formation process, such as injection and ignition timing, compression ratio and swirl intensity.

Injection and Ignition Timing

The time interval between the start of injection and ignition (residence time) directly influences the degree of the homogeneity of the air/fuel mixture. Increasing the residence time between the start of injection and ignition, results in the formation of a greater fraction of homogeneous mixture.

To achieve acceptable light load HC emissions behavior as well as high engine efficiency in the higher load range it is necessary to control injection and ignition timing as a function of the operating point in the engine map.

Figures 3 and 4 depict the influence of injection and ignition timing on the operational behavior of the DI SI methanol engine at low and high engine load (BMEP = 2 bar and BMEP = 12 bar) for medium engine speed (2000 rpm). In addition to the fuel consumption behavior, the HC emissions at light load and NOx emissions at high load are important factors. In order to achieve a sufficiently intensive inflammation, it is necessary that ignition occurs during fuel injection. Ignition either before or after the time period for injection results in a deterioration of the combustion process or even misfiring (gray shaded areas in Figure 3). Fuel consumption data in the figures are presented on a diesel fuel equivalent energy basis (BSFC*).

At low load (BMEP = 2 bar), ignition should occur shortly after the start of injection or even concurrently. This is necessary because, only a short time after injection, at the downstream spark plug location, optimum air/fuel mixture conditions exist for ignition. A setting of injection and ignition timing at 15°CA BTDC results in lowest fuel consumption, whereas the lowest possible HC emissions occur at a 5 - 7 °CA earlier timing for both parameters. If ignition timing is substantially later than the start of injection, a large fraction of the injected fuel has already migrated into areas where, due to relatively low combustion chamber temperatures, quenching effects lead to a low combustion velocity and incomplete inflammation of the mixture.

At high engine load, however, low fuel consumption can be achieved with a relatively advanced injection timing (25°CA BTDC) and retarded ignition timing (6°CA BTDC), indicating a need for longer residence time under high load conditions. This selection of injection and ignition timing offers sufficient time for mixture formation. However, due to the higher degree of mixture homogenization under these conditions, a higher burning velocity and, consequently, increased rate of peak pressure rise and NOx emissions occur.

The influence of the internal homogenization on the combustion behavior is shown in Figure 5 for both low and high load points in terms of cylinder pressure (P_{Cyl}) and mass fraction burned (X_B). For low load, the combustion decelerates with a longer delay between injection and ignition. At the high load test point, combustion benefits from a longer residence time, resulting in accelerated burning characteristics.

In addition to injection and ignition timing, compression ratio and swirl level have a considerable influence on the operational behavior of the DI SI methanol engine.

Compression Ratio and Intake Air Swirl

The compression ratio was varied by reducing the bowl size while maintaining geometrical similarity. The spatial relationship between the injection nozzle, spark plug and combustion chamber wall was kept constant. The operational behavior of the DI SI methanol engine for different engine loads as a function of compression ratio at an engine speed of 2000 rpm is illustrated in Figure 6. Injection and ignition timing was optimized for each operational point.

The data indicate that an increase in compression ratio from 13:1 to 18:1 results in a slight improvement in engine thermal efficiency, especially at lower engine loads. In parallel, a significant increase in the peak cylinder pressure was detected.

Due to the increase in combustion chamber temperature, HC emissions are positively influenced by the higher compression ratio. However, a corresponding increase in NOx emissions also occur. For lower engine loads, the emissions behavior becomes more sensitive to changes in compression ratio. The reduction in piston bowl size at BMEP= 0.5 bar and compression ratio 18:1, appears to result in an increased fuel/wall impingement effect, causing higher unburned fuel emissions. The unique balance between combustion chamber shape and air swirl intensity may have been non-optimal under these operating conditions. In consideration of the overall operational behavior, a compression ratio of about 16:1 leads to a good combination of low emissions and good efficiency with the DI SI methanol engine.

An evaluation of the influence of air swirl intensity, shown in the Figures 7 and 8 for low swirl (c_u/c_a= 2.5) and high swirl (c_u/c_a= 4.0) cylinder head versions, indicates the potential advantage of lower swirl with the DI SI methanol combustion concept. The benefits of relatively low swirl are described by improvements in fuel consumption and combustion noise (rate of peak cylinder pressure rise) as well as a slight decrease in HC, CO and low part load NOx emissions. In addition, the low swirl version has a better potential for internal homogenization. At low and medium loads, a shorter delay time between BOI and ignition timing is required for optimum engine operation, whereas, at high loads, longer residence time results in better fuel consumption and full load torque behavior (see Figure 7, bottom left).

Exhaust Gas Recirculation

Another important goal of the DI SI combustion system development program was to reduce the NOx emissions, in particular, with regard to the low and mid part load operating range. A suitable measure for low load NOx emissions reduction is the application of exhaust gas recirculation (EGR). Figure 9 shows the influence of the EGR rate on emissions and fuel consumption for three different BMEP values across the part load range at medium engine speed (2000 rpm). Increasing the EGR rate to 45%, especially under low load conditions, results in a considerable reduction in NOx emissions (up to 85%). At the same time, the HC and CO mass flow emissions increase slightly. The fuel consumption remains essentially constant. At a BMEP of 6 bar, however, the maximum possible EGR rate is only 15% and is accompanied by a rapidly increasing HC mass flow. The DI SI combustion system is very sensitive with respect to high EGR rates. This is primarily due to the charge stratification as well as the limited ignition energy available with the current DI SI engine concept.

Figure 10 summarizes the results of the combustion system development by comparing the efficiency of various measures for emissions reduction at light load. The baseline combustion system version, optimized for operation without misfiring over the entire operating range, serves as the basis for comparison. Injection and ignition timing was optimized for each development step to realize the best HC emissions behavior. Through optimization of combustion system parameters, such as compression ratio, intake air swirl, injection nozzle geometry and spark plug, a HC emissions reduction of about 35% can be achieved. Concurrently, NOx emissions increase due to improved combustion conditions. Applying EGR results in a further 75% reduction in NOx emissions with only a minor increase in unburned fuel (HC) emissions. Finally, the additional application of an oxidation catalyst results in a considerable reduction in HC emissions of about 97%.

Part Load Operational Behavior

Figure 11 shows the thermal efficiency engine map for the DI SI methanol combustion concept. The data shown in the figure were obtained from the 16:1 compression ratio engine with the high swirl cylinder head. The shape of the full load BMEP curve reflects consideration of the steep increase in CO emissions that occurred near full load. Beyond the chosen limit of 1 Vol.-% CO, the combustion process deteriorates significantly due to the relatively rich local mixtures in areas of the combustion chamber. This limitation was used to define full load due to the smokefree combustion of methanol.

The DI SI methanol engine exhibits a maximum thermal efficiency of 37% at an engine speed of 2500 rpm. In the operating range below 2000 rpm, insufficient air swirl intensity results in a significantly lower full load torque level. Compared to other DI combustion concepts the thermal efficiency is low in this region. At high engine speeds, the efficiency of the spark ignition engine deteriorates due to the fact that the intake ports of the prototype cylinder head result in poorer volumetric efficiency. Cylinder head characteristics for stratified charge engine concepts, especially those which operate with locally concentrated injection, can only be optimized for a limited speed and load range when the design is limited to conventional swirl port technology.

The part load emissions behavior of this engine is illustrated for medium speed (2000 rpm) in Figure 12. Engine out emissions without EGR as well as the emissions with EGR, downstream of the catalyst, are shown. The oxidation catalyst that was used for these investigations was a metal substrate catalyst with a platinum coating (100 g/ft^3). Although the engine out HC and CO emissions appear to be relatively high, there is an excellent potential for emissions reduction when introducing EGR together with an appropriate oxidation catalyst configuration, especially at very low loads. Due to the comparably low compression ratio (16:1), the overall NOx emissions remain relatively low.

Status of Vehicle Development

The turbocharged, intercooled DI SI methanol engine was calibrated with the goal of demonstrating the potential of the DI methanol technology to comply with the very restrictive future US emission standards. The methanol engine was installed in a VW-Jetta vehicle, equipped with a methanol resistant fuel system. For the data indicated in Figure 13, a mechanical injection timing device and electronically controlled ignition timing were used. Exhaust gas recirculation was adjusted by a mechanically controlled actuator. For the purpose of comparison with the vehicle operational behavior of the DI SI combustion system, data for a DI hot surface ignition (HSI) methanol combustion system, which has been previously developed, is also included /7,8/.

For both concepts, an oxidation catalyst, which has been developed by Degussa AG, especially for methanol operation was utilized. In addition to the platinum coating (100 g/ft^3), the catalyst was configured with a washcoat that provides improved conversion efficiency for unburned methanol and formaldehyde. With regard to catalyst loading and space velocity, the oxidation catalyst was optimized for good light-off behavior, resulting in a beneficial conversion efficiency during the warm-up phase of the FTP-75 test cycle.

Since in-depth testing of the spark ignition engine in the vehicle has not been yet completed, a direct comparison to the more advanced development status of the hot surface ignition concept is difficult with regard to relative comparisons in the FTP-75 test cycle. Despite this inequity, Figure 13 shows a comparison of the gaseous exhaust emissions components for the DI methanol vehicles. Additionally, the California emissions standards for 1993 are plotted.

The OMHCE (Organic Material HydroCarbon Equivalent) emissions of the methanol vehicles were determined on the basis of the measurement for hydrocarbon, methanol and formaldehyde emissions. No deterioration factor has been applied to the emissions data shown in the figure.

Although the spark ignition concept is not fully optimized, reasonably low CO and OMHCE emissions were possible due to application of the optimized catalyst concept. The DI SI vehicle emissions levels are lower than the 1993 standards for CO and OMHCE, while the NOx emissions remain well above the requirements for 1993. A comparison of the tailpipe emissions from both vehicles operated without EGR indicates the potential for further improvements with the DI SI vehicle by advanced dynamic control of EGR. The DI HSI prototype methanol engine emissions levels remain well below the 1993 California standards for all regulated exhaust components.

With regard to fuel economy (diesel equivalent energy basis) in the FTP-75 test cycle, the hot surface ignition concept has a FTP fuel economy of about 38.3 mpg which, compared to the spark ignition concept (34.1 mpg), is about 12% better. This behavior is partially due to the range of adjustment possibilities for injection and spark timing with the current vehicle configuration as well as the specific characteristics of the high swirl, low compression ratio DI combustion concept.

Further improvements in the emissions behavior should be possible through the introduction of an electronic injection pump control system as well as closed-loop EGR control. Through these

means, better control of the mixture composition in the combustion chamber is possible especially for transient vehicle operation and can be corrected for air flow and temperature conditions. Through these developments, excellent potential for both DI methanol concepts to meet future NOx and HC emissions standards, is anticipated.

Summary and Conclusions

In comparison with conventional DI combustion systems, the DI SI methanol engine concept exhibits significantly lower NOx emissions in combination with good fuel consumption behavior. Application of hot EGR results in further improvements in the emissions behavior, especially with regard to NOx. The use of an oxidation catalyst allows comparably low levels of unburned fuel and CO emissions.

With respect to emissions in the FTP 75-test cycle, the DI methanol engine with hot surface ignition currently exhibits lower emissions compared to the spark ignition concept. However, the HSI engine is also at a more advanced development status.

Future Development

Future development goals for the DI SI methanol engine include the adaptation of a fully electronic injection system, including both ignition and EGR control. Achievement of these goals should provide a good potential for compliance with the restrictive California emissions standards, while maintaining the beneficial fuel consumption characteristics of DI engines.

In combination with the adaptation of electronic controls, the DI SI combustion concept may represent an interesting flexible fuel engine concept. The potential DI SI engine combustion noise and driveability characteristics make it an excellent candidate for such an application and introduce the potential for excellent emissions and fuel economy in a flex-fuel concept.

Acknowledgements

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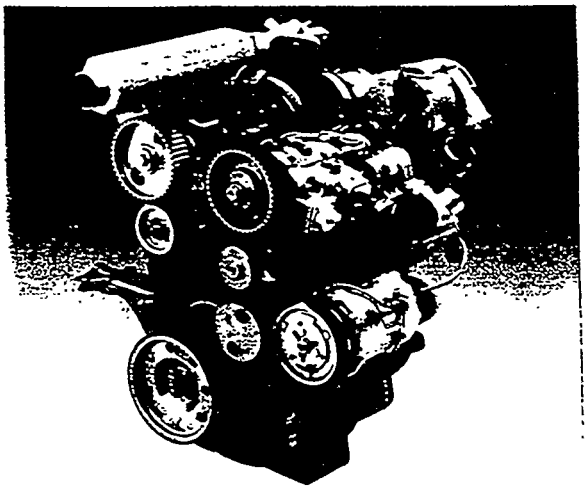

Figure 1 : Volkswagen 1.7 Liter DI Engine

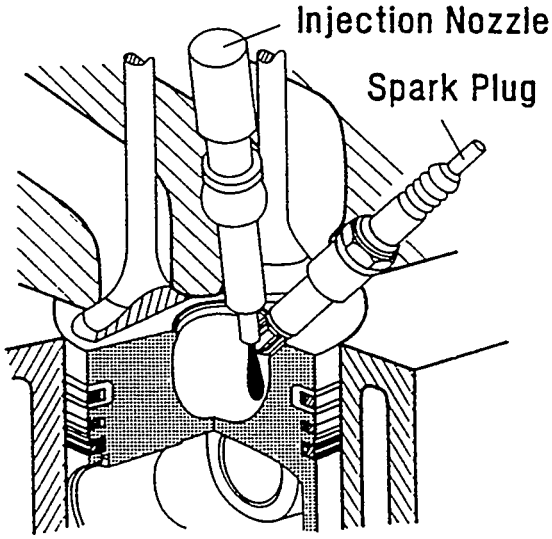

Figure 2 : DI Spark Ignition Methanol Concept

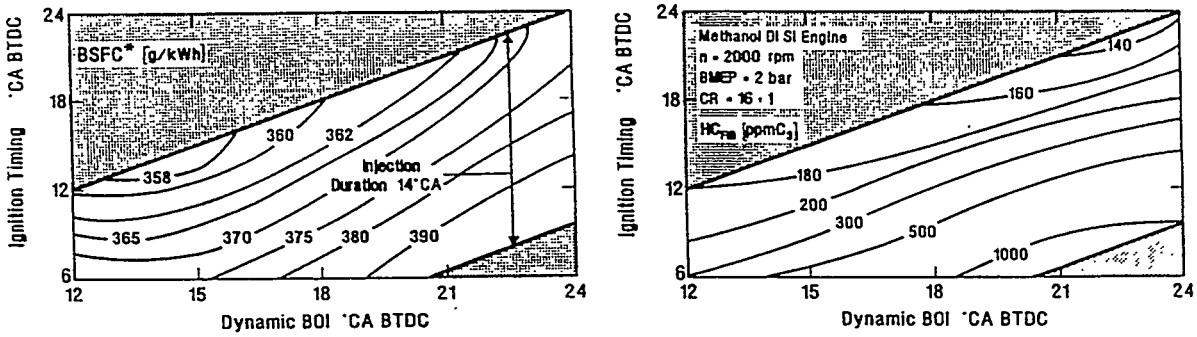

Figure 3 : Influence of Injection and Ignition Timing on the Fuel Consumption and HC Emissions Behavior for BMEP = 2 bar and 2000 rpm Engine Speed

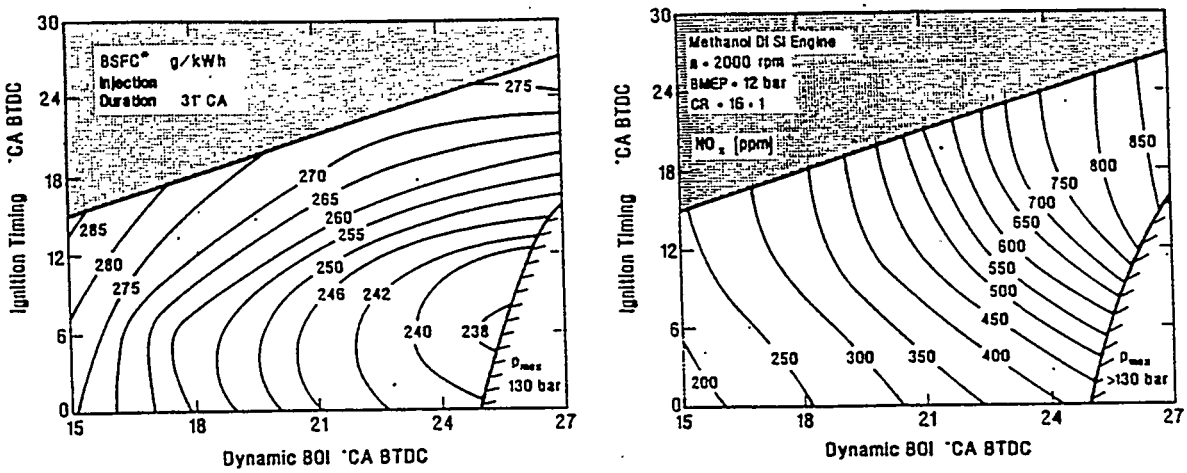

Figure 4 : Influence of Injection and Ignition Timing on the Fuel Consumption and NOx Emissions Behavior for BMEP = 12 bar and 2000 rpm Engine Speed

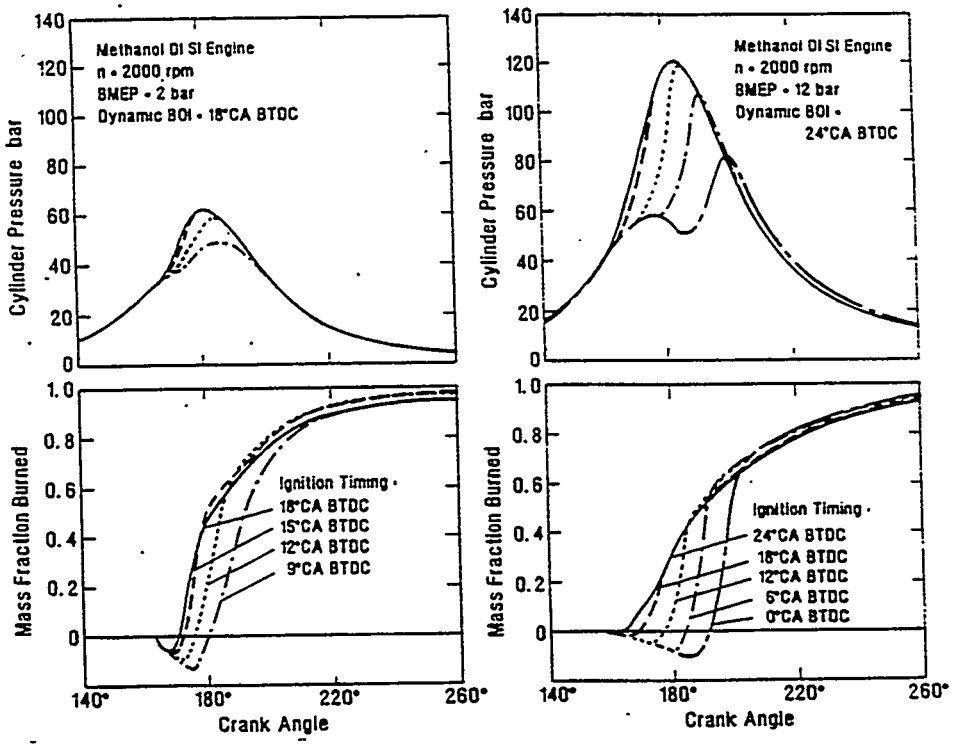

Figure 5 : Cylinder Pressure and Mass Fraction Burned Function at 2000 rpm Engine Speed and BMEP = 2 bar and BMEP = 12 bar for Different Ignition Timings

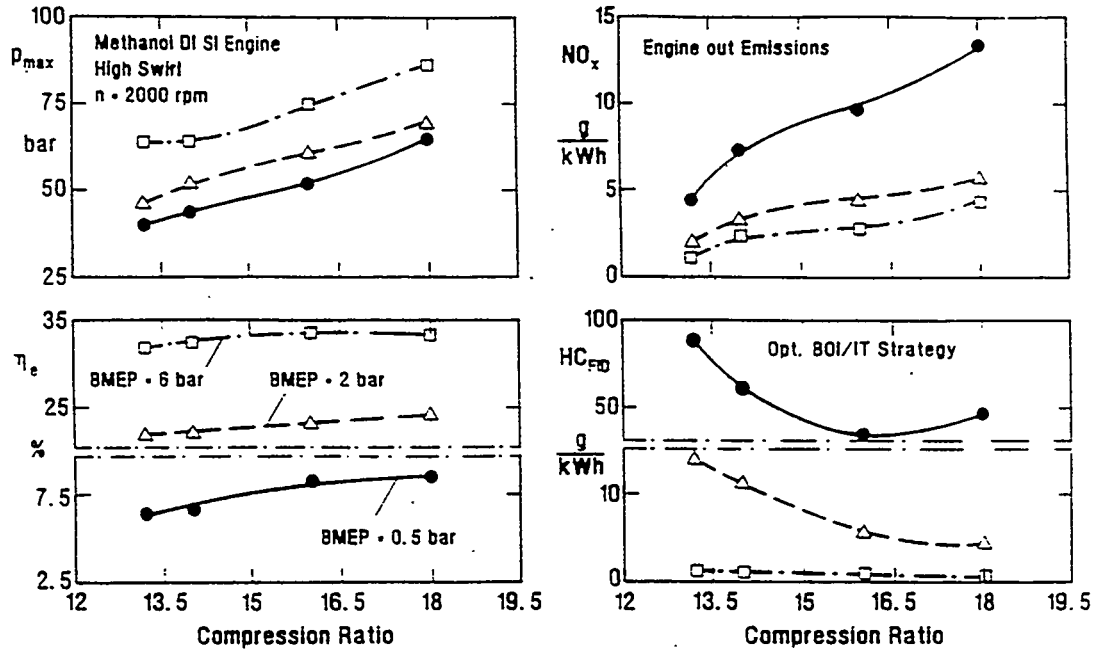

Figure 6 : Influence of Compression Ratio on the Operational Behavior for the DI SI Methanol Engine

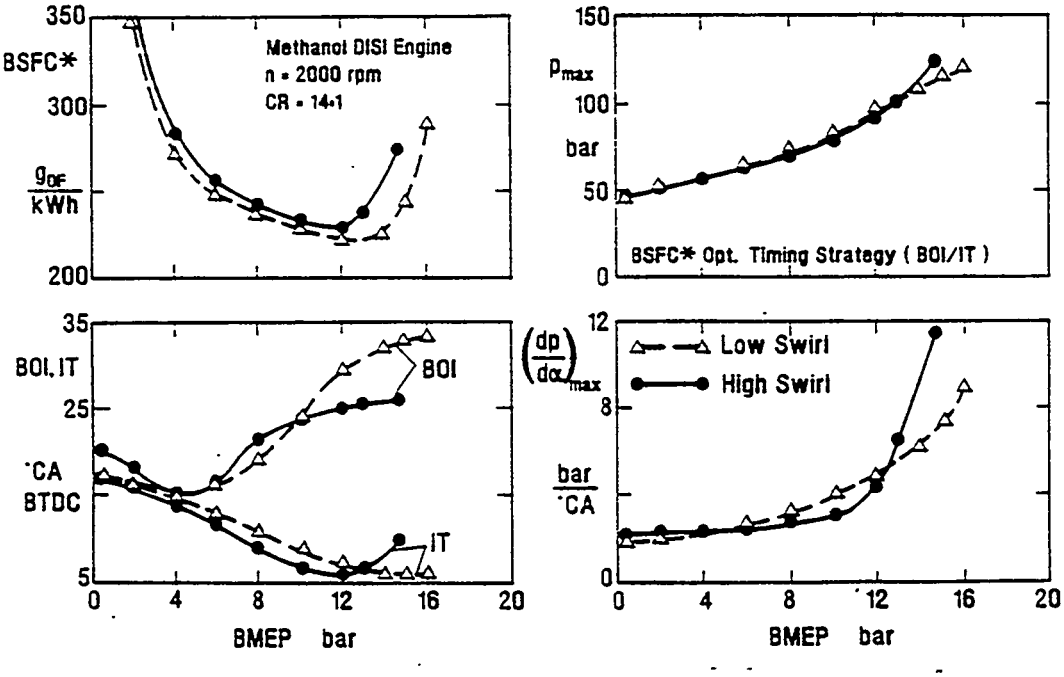

Figure 7 : Influence of Air Swirl on Fuel Consumption and Cylinder Pressure Characteristics as a Function for Engine Load at 2000 rpm Engine Speed

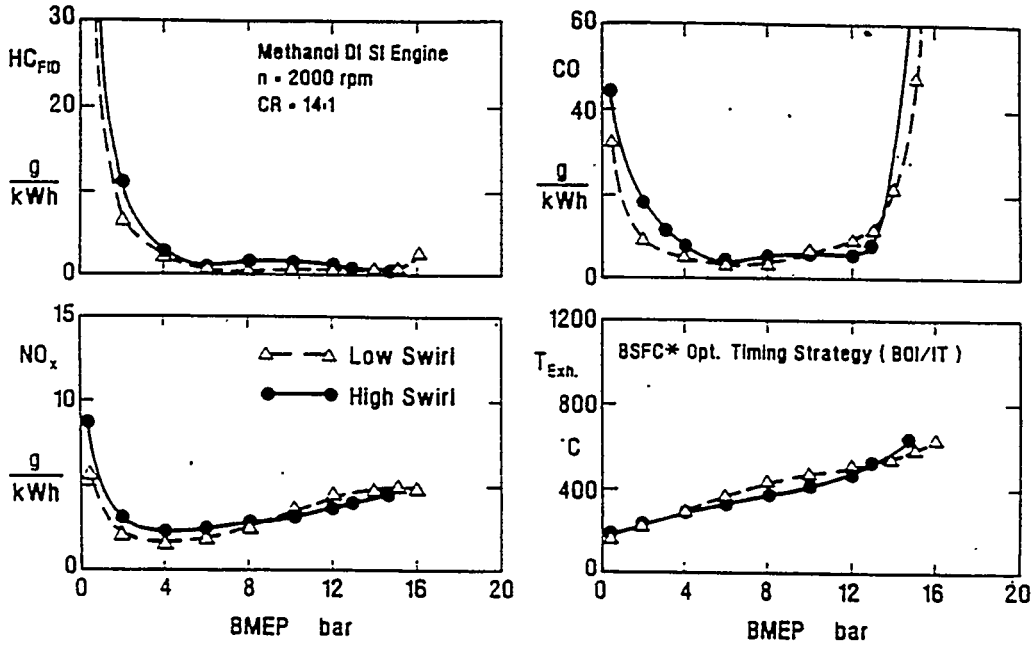

Figure 8 : Influence of Intake Air Swirl on the Emissions Behavior as a Function of Engine Load at 2000 rpm Engine Speed

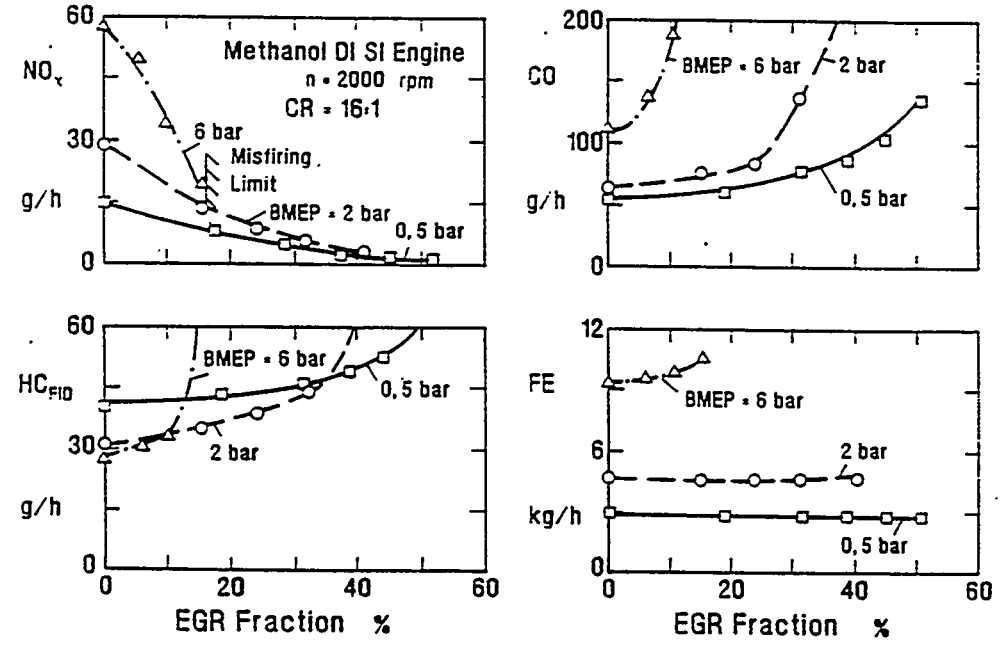

Figure 9 : Influence of Exhaust Gas Recirculation (EGR) on the Engine Operational Behavior

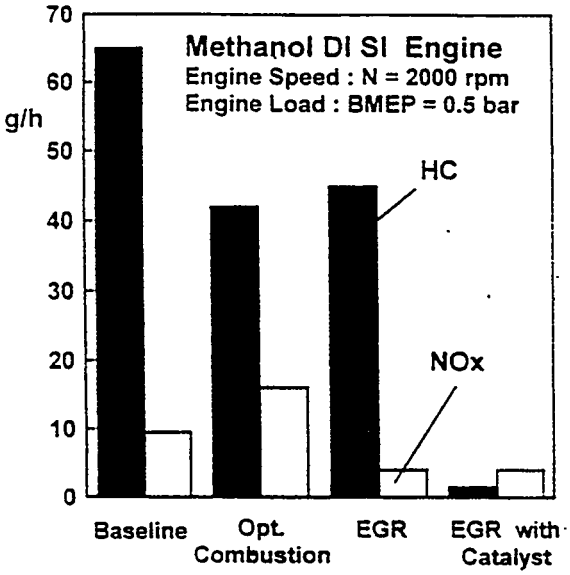

Figure 10 : Measures to Reduce the Low Load Emissions for the DI SI Methanol Engine

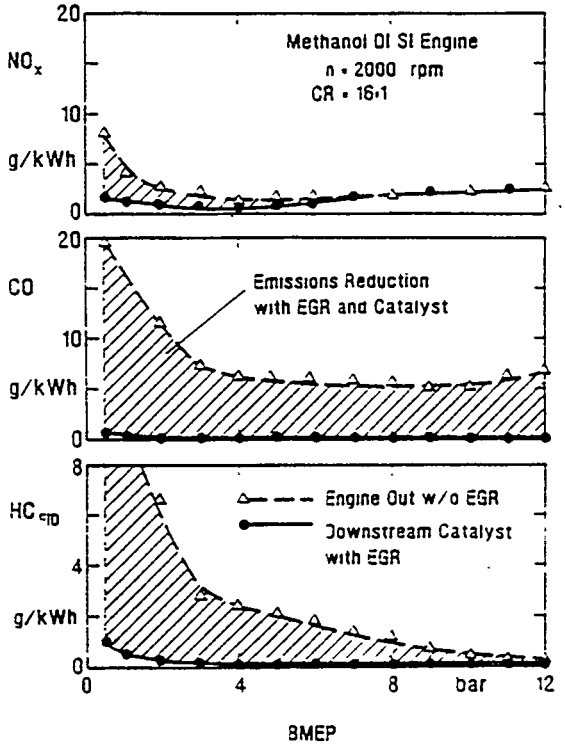

Figure 12 : Part Load Emissions Behavior for the DI SI Methanol Engine

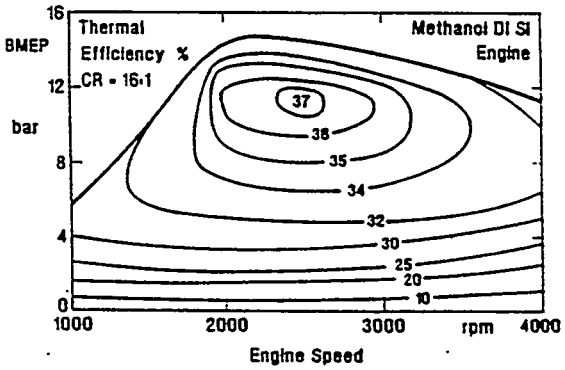

Figure 11: Thermal Efficiency Map for the DI SI Methanol Engine

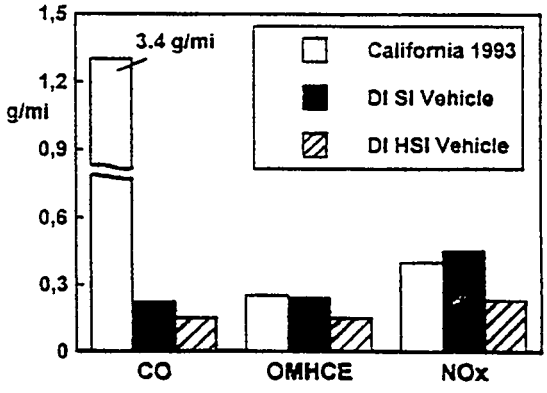

Figure 13 : FTP-75 Test Emissions

CATALYSIS FOR CONTROL OF AUTOMOTIVE EMISSIONS

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Abstract

This paper provides information on the purity of exhaust emissions from gasoline-fueled and methanol-fueled automobiles. As the use of alcohol-fueled vehicles grows, effective catalytic control of emissions from these vehicles is becoming increasingly important. The emissions from alcohol-fueled vehicles contain the unburned fuel and CO, but the number of partially oxidized fuel derivatives are much smaller compared to gasoline combustion. Since complex hydrocarbons, sulfur, and lead are absent from the exhaust, nonprecious transition metal oxide can offer an effective and inexpensive catalysis. This research examines the catalytic activity for oxidation of methanol, CO, and CH_4 over a series of transition metal (e.g., Cu, Mn, Co) oxide catalysts. These catalysts were prepared by the wet impregnation method and were all supported on transitional alumina. The BET surface area (BET) measurement and Scanning Electron Microscopy (SEM) were used to characterize the catalyst and support. The absorption and desorption behaviors of CO, CH_3OH, and O_2 on the catalysts were studied, and the reaction mechanism was suggested by using the transient response method.

CATALYSIS FOR CONTROL OF AUTOMOTIVE EMISSIONS

Introduction

In recent years it has been recognized that the exhaust gas discharged from internal combustion engines is a serious source of air pollution. Recent attempts to prevent such air pollution have concentrated on the destruction or elimination of noxious components by catalytic oxidation and catalytic reduction. This research focused on carbon monoxide, methane, and methanol oxidation over CuO, Cu-Mn, Cu-Mn-Co, Ag, Pd-Ag, and other catalysts. These active components are deposited on the transitional alumina. Since methanol is the principal organic constituent in methanol vehicle exhaust, its oxidation characteristics have not been widely examined under conditions characteristic of vehicle exhaust. The activities and selectivities of the catalysts were examined primarily as a function of temperature. Simplified feedstreams were employed. The added species greatly affected the activities and selectivities of some of the catalysts, while they hardly affected others. These observations indicate that laboratory catalyst comparisons must be made in the presence of key exhaust components to ensure that results reflect catalyst performance in vehicle exhaust (Goodrich, 1982). The nature and the behavior of the surface species on catalysts were studied in detail by means of the transient response method. The mechanism of the oxidation of carbon monoxide and methane over transition metal oxides was suggested.

Experimental Section

Catalyst Preparation

The catalytic metal salts may be those classed as metal-organic types,
such as the acetates, formates, and oxalates, or the heat-decomposable inorganic compounds, such as the carbonates or nitrates. The metals employed in the oxidation of carbon monoxide and methane are copper, cobalt, and manganese. The ratio of these metals, as well as the quantity in the final catalyst, is of the utmost importance. If the proper ratios are achieved these metals have a synergistic effect, while the right quantity ensures maximum activity and stability. Catalysts with improved and increased activity may be produced by multiple impregnation of the high surface area transitional alumina support with selective catalytic metal salts. These metal salts are dissolved in distilled water and the temperature raised to 80°C. The transitional alumina particles are placed in a suitable container, and the metal salts clear solution is poured over the particles. The impregnation is extended for at least 0.5 h, then cooled to approximately 25°C. The alumina particles are then removed from the solution, dried, and the catalyst is decomposed by heating the impregnated alumina to an optimum temperature for a definite period of time. After cooling the catalyst to room temperature, the impregnation procedure is repeated using the decanted liquor from the first treatment (Dwyer, 1972). The final dried and decomposed catalyst is reduced with hydrogen at 450°C for about 5 h. This constitutes the entire treatment and the catalyst is ready to be installed in an automobile exhaust device.

Catalyst Characterization

The surface areas of the support material and catalysts were measured by the BET method, and nitrogen was used as the absorbate. The transitional alumina is characterized by a porous structure and high surface area of 189.8 square meters per gram, with the said transitional alumina being prepared by heating a hydrated alumina to a temperature somewhat above 100°C and up to 150°C, so as to sense

partial dehydration without total conversion to alpha alumina. The surface areas of the supported catalysts were found to be fairly close to the surface area of the support material.

The catalysts were examined by using a scanning electron microscope (Cambridge). The accelerating voltage was 20kV, and the outside and inside surfaces were examined. Figure 1 shows electron micrographs of Cu-Mn/y-Al_2O_3 (14.4% wt% Cu and 0.8% Mn). The samples were coated with gold to prevent specimen charging.

Catalytic Oxidation Experimental Results

Figure 2 shows the feed and reactor systems used in the oxidation experiments. The reactor system utilized a fixed-bed tube reactor constructed from stainless steel. The reactor measured 4 mm id diameter and 280 mm in length.

Methane and carbon monoxide oxidation was studied over a series of transition metal oxides (Severino, 1986). The first series of experiments examined catalyst activity over Cu-Co-Mn/y-Al_2O_3 and Cu-Mn/y-Al_2O_3 catalysts for methane and carbon monoxide. Figure 3 presents the variation of CO conversion with temperature. It is evident that their rating of the catalysts according to activity was 13# > 14#>16#>15#. The weight composition of the catalysts is listed in Table 1. Figure 4 shows the comparison of CO conversion for some catalysts under the different reduction temperature. The methanol oxidation reaction will be studied at some length over a series of transition metal oxides such as Cu, Mn, CO and Cr supported on *y*-alumina. Metal nitrates were used to supply the metal. Each catalyst was prepared by a two-step wet impregnation of the support. The distilled water was used to dissolve the metal nitrate salt at each step. The metal nitrate solution and the support were contacted at 85 ~ 100°C for 8 h during the first step and 4 h during the second step. The mixture was dried at 125°C at each step. The catalysts were all calcined at 500°C for 5 h under an oxygen atmosphere.

The Nature and Behavior of Catalytic Oxidation of CO on CuO-MnO_2 Catalyst

The characterization of the catalytic oxidation of carbon monoxides and methane over CuO-MnO_2/*y*-Al_2O_3 catalysts was studied by a transient response method. There are several different methods that were applied to follow a nonsteady state of a reaction system. In the present study, a transient response to a step change in the concentration of reaction components was followed.

The total flow rate of the gas was kept constant at 110 ml/min. The intraparticle diffusion resistance of the catalyst was found to be negligible by examining the rate data for catalysts of different sizes 28-40 mesh, with the temperature between 70-120°C. The external mass transport effect was also found to be negligible at the same temperature range by examining the rate data with catalyst amounts of 526-1200 mg and flow rates of 50-120 ml/min.

A quartz tube reactor with 0.4-0.8g CuO-MnO_2 catalyst was used and the system was kept under a steady state with a constant flow rate at a given temperature. The response of the exit gas concentration is followed by
gas chromatographic analysis. The characteristic behavior of the response curve can provide information on the amount and the state of adsorbed species, and on the rates of several elementary steps. The concentrations of carbon monoxide, carbon dioxide, and oxygen were varied by changing the concentration of nitrogen as the diluent. Then the stream was suddenly changed to pure nitrogen and the O_2-O_2 response was followed. No appreciable amount of oxygen was

observed in the effluent stream. These results indicate that the surface of catalyst is fully covered with oxygen, which is adsorbed irreversibly and slowly. On the catalyst, four different responses, CO-CO, CO_2-CO_2, O_2-O_2, and CO-CO_2 were measured separately. In somes cases the responses were found to be instantaneous, indicating that carbon monoxide and carbon dioxide were fast and only a minor amount was adsorbed on the catalyst surface. Therefore, these steps were not kinetically significant. It was concluded that the reaction on the catalyst was controlled only by the oxygen adsorbed step. Figure 5 shows the response curves of CO, CO_2, and O_2, respectively. Figure 6 shows the response of CO and CO_2 after oxygen had been preadsorbed. Based on these results and conclusions, the possible mechanisms of carbon monoxide and methane oxidation over Cu-Mn oxide were represented by a sequence of steps:

$$O_2 + 2S \rightarrow O_2 \cdot 2S \text{ (R.D.S.)}$$
$$2CO + O_2 \cdot 2S \rightarrow 2CO_2 \cdot S$$
$$CO_2 \cdot S \rightleftarrows CO_2 + S$$

where S designates the site for activated adsorption of oxygen. The rate-determining step (R.D.S.) is the absorption of oxygen (Kobayashi, 1972).

Acknowledgments

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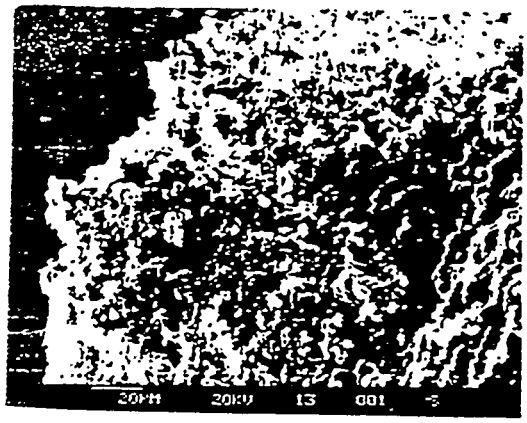


Figure 1. SEM micrograph of Cu-Mn/γ-Al_2O_3

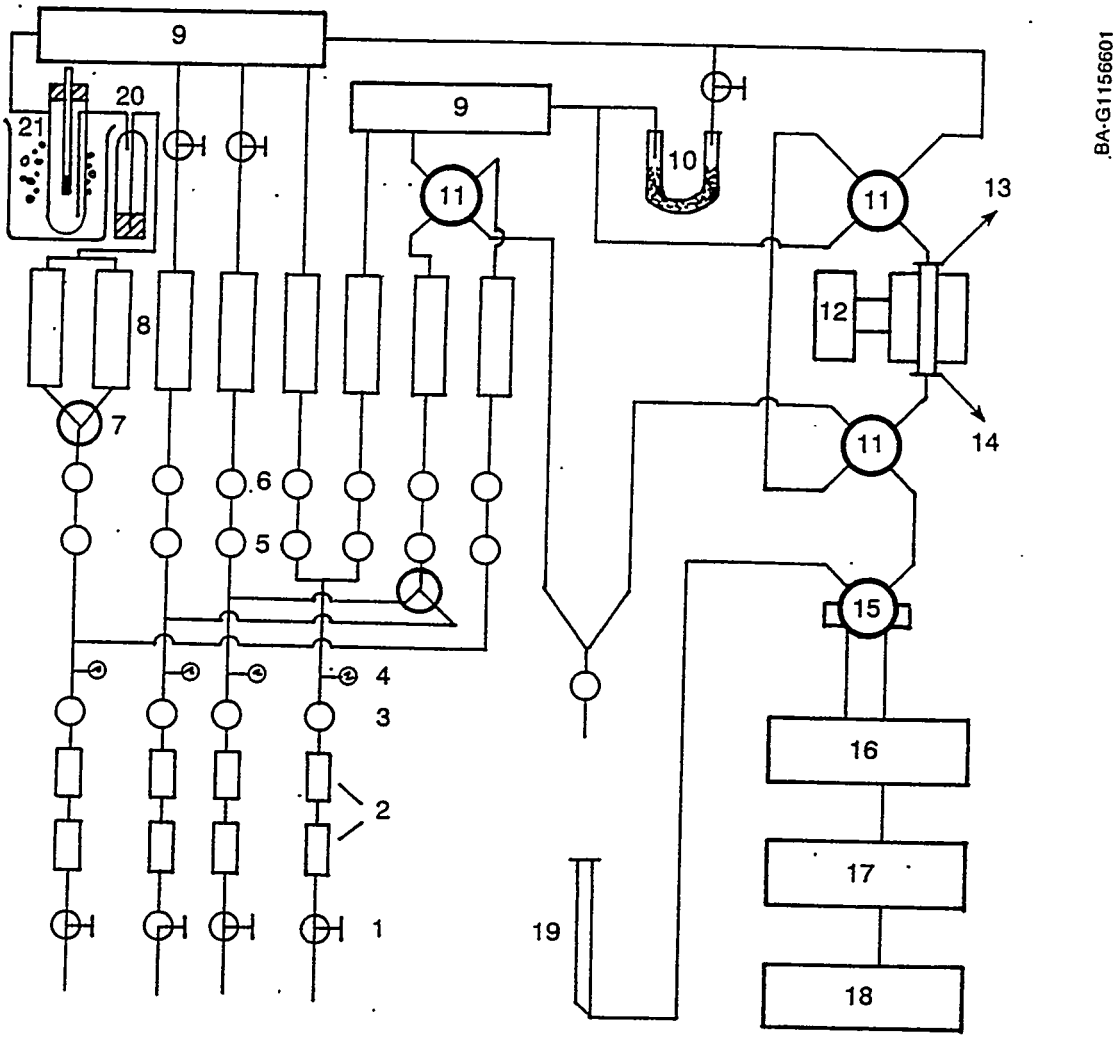


Figure 2. Feed and reactor systems
1. 3. 5. 6. 7. Valve 2. Purger 4. Manometer 8. Flowmeter 9. Mixer 10. U-type Pipe 11. Four-post Valve 12. Temmperature Controller 13. Reactor 14. Pipe Furnace 15. Six-port Valves 16. GAs Chromatograph 17. Recorder 18. Computer 19. Flowmeter 20. Feed System of Methanol 21. Methanol Condensor

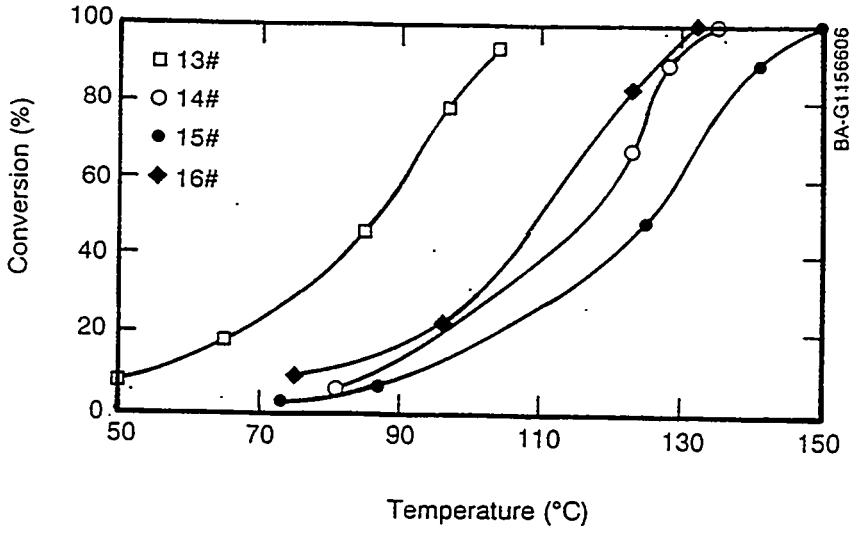


Figure 3. Variation of CO conversion with temperature

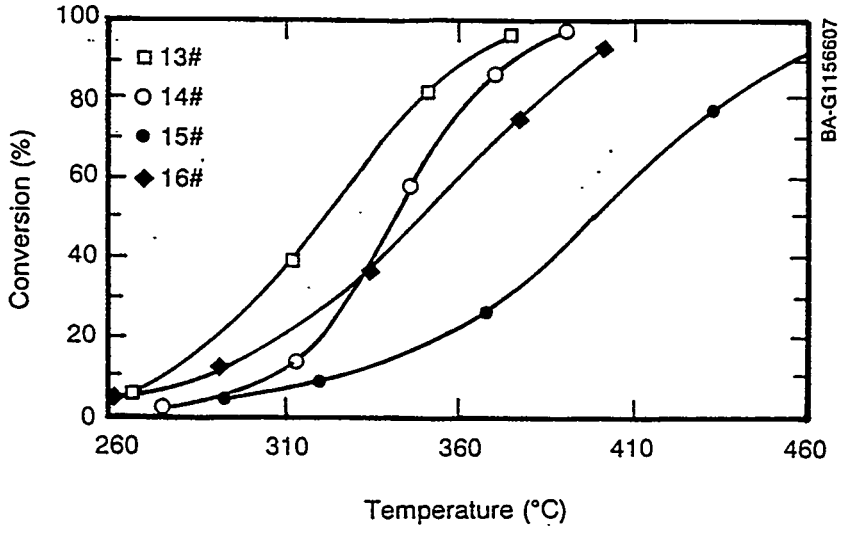


Figure 4. Variation of CH_4 conversion with temperature

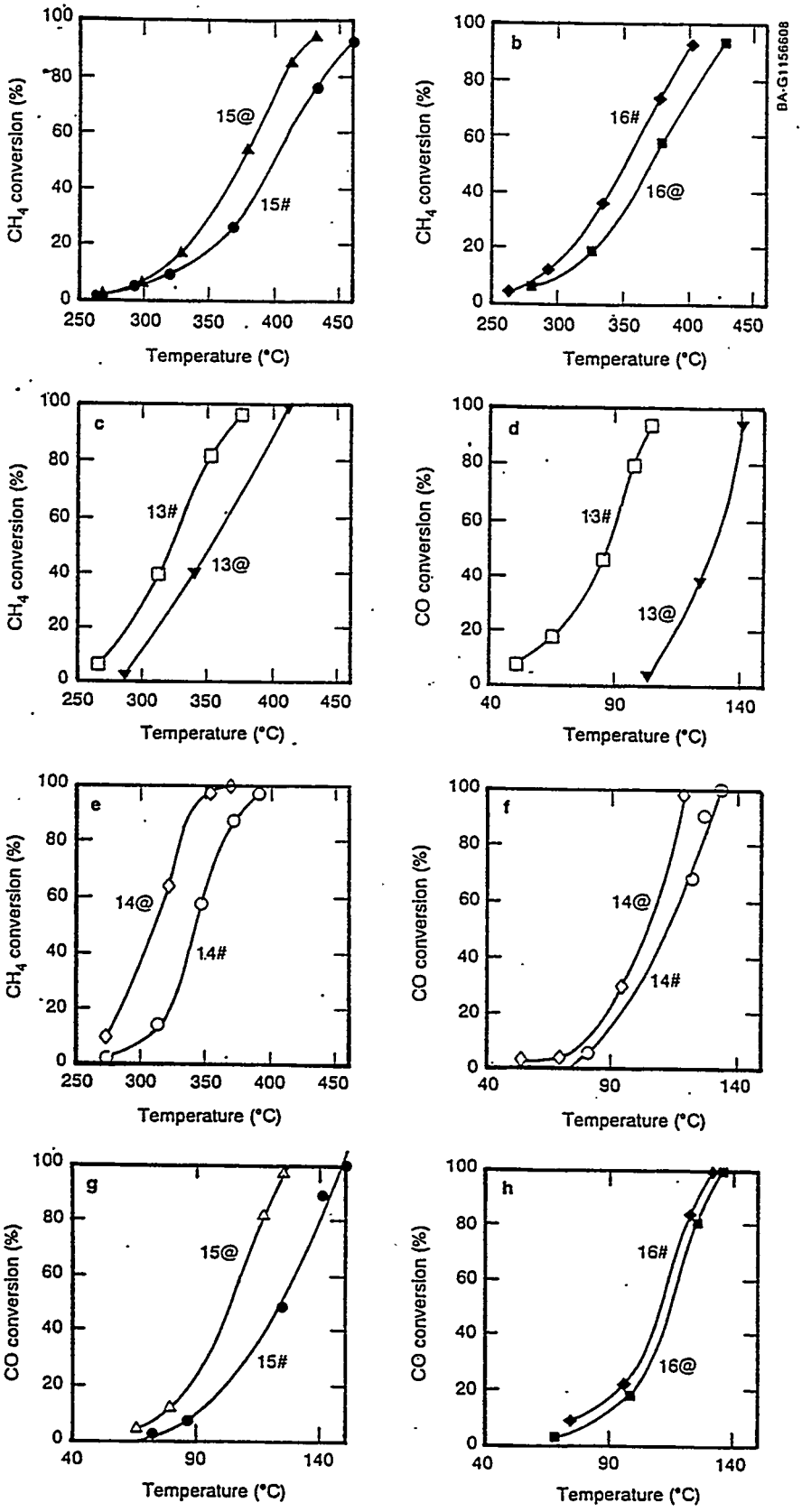


Figure 5. Variation of conversion with temperature over various catalysts

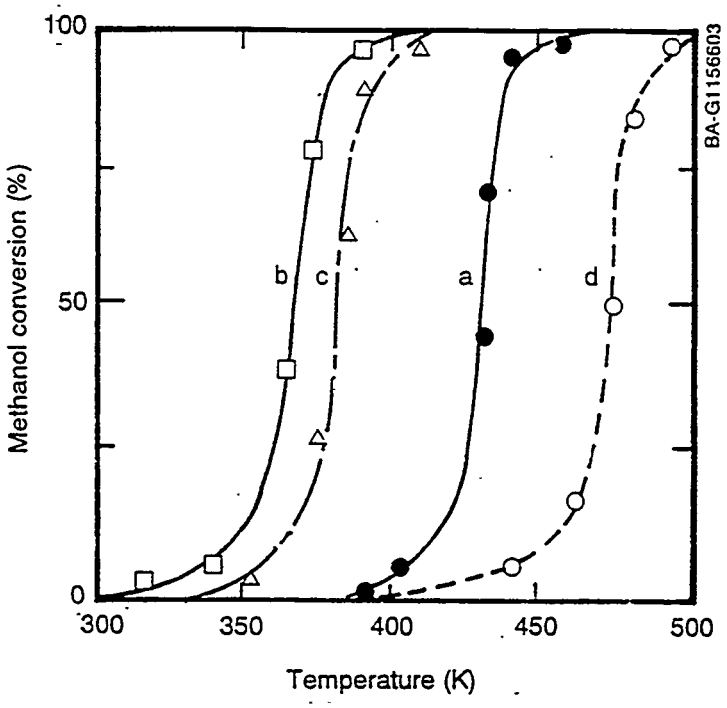


Figure 6. Variation of conversion with temperature for methanol

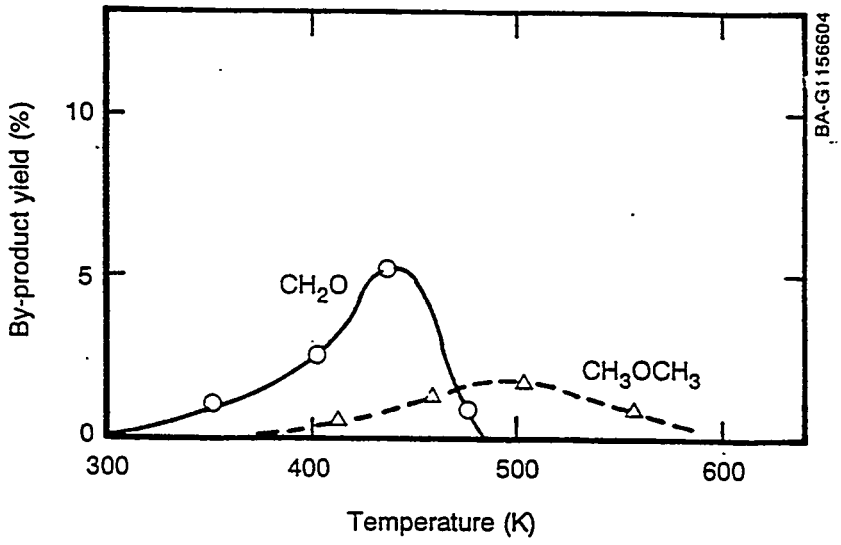


Figure 7. Yields of CH_2O and CH_3OCH_3 as a function of temperature for methanol oxidation over the Pd/Al_2O_3 catalyst

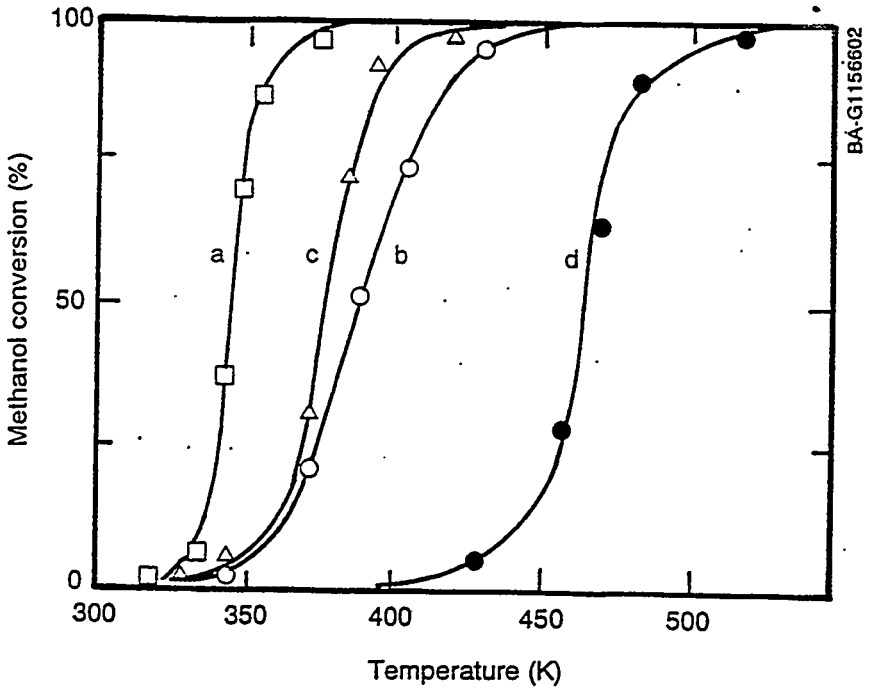


Figure 8. A comparison of conversion VS temperature data obtained over (a) 0.02% wt% Pd/Al_2O_3 (b) 0.02% wt% Pd-8%Ag/Al_2O_3 (c) 8% wt% Ag/Al_2O_3 (d) 10% wt% CuO/Al_2O_3 for feeds containing 0.2% CO

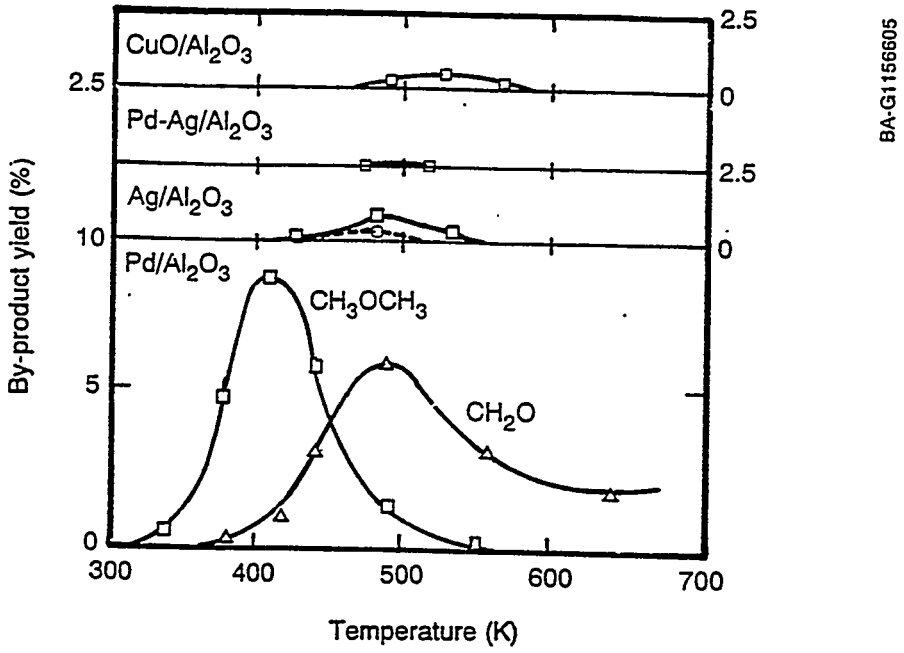
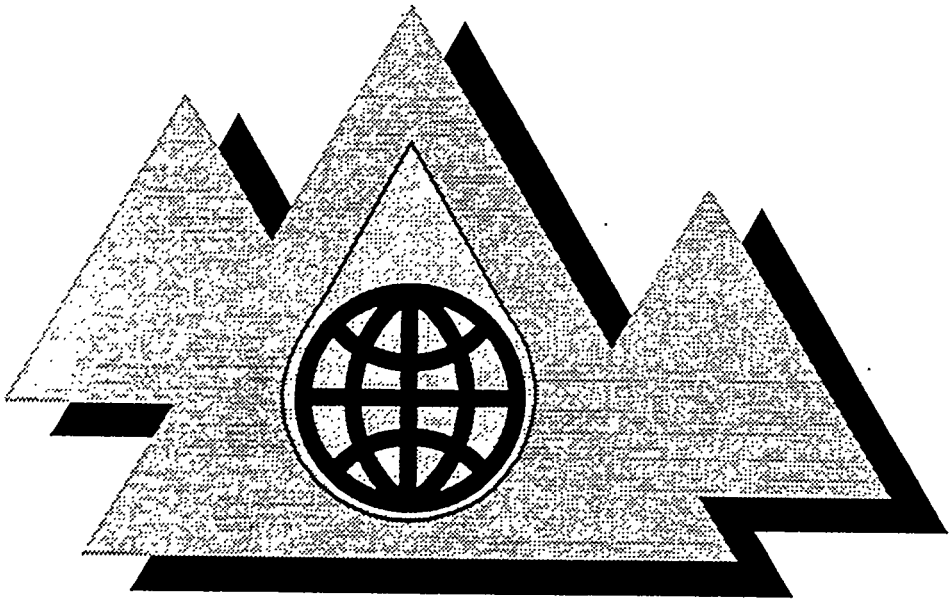


Figure 9. Variation of by-products yield with temperature over (a) Pd/Al_2O_3 (b) Ag/Al_2O_3 (c) Pd-Ag/Al_2O_3 (d) CuO/Al_2O_3 in the presence of carbon monoxide



Chemical and Biochemical Process Routes

THE INFLUENCE OF PRESSURE AND SOME GAS ADDITIVES ON THE HIGH PRESSURE OXIDATION OF METHANE TO METHANOL

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Abstract

The practical realization of a process that permits direct natural gas to methanol requires investigation of optimal operating conditions. The primary operating conditions of concern are pressure and permissible nitrogen content if air is used instead of oxygen.

Low conversion of natural gas to methanol with high pressure oxidation makes it advantageous to recycle the reacting gases. The presence of carbon monoxide and hydrogen in recycling gases can cause some problems due to their high reactivity. The influence of these gases as well as that of operating pressure changes in the range of 20-230 atm and dilution with nitrogen (up to 70%) on the process, was investigated experimentally .

THE INFLUENCE OF PRESSURE AND SOME GAS ADDITIVES ON THE HIGH PRESSURE OXIDATION OF METHANE TO METHANOL

Introduction

The direct conversion of natural gas (NG) to methanol is, undoubtedly, one of the most promising technological processes for synthetic hydrocarbon fuels production. In recent years, interest in this process has grown due to extreme need for a new effective process of methanol production with low energy consumption and capital cost (1,2). In Russia, there is a State project in progress for construction of small plants (10,000 tons a year) producing methanol for local needs of gas industry by direct gas phase oxidation of NG (1). The second catalytic stage of the process makes it possible to convert products from the first stage into high quality motor fuel. Therefore, investigation of the optimum operating conditions for the process is desirable.

It is well known that high pressures favor methanol formation resulting from methane oxidation, but the cost of gas compression is one of the most prominent factors in the cost of production(3). Therefore, it is important to know the actual pressure dependence to determine the optimum operating pressure.

Low conversion of NG to methanol makes it desirable to recycle the reacting gases. Among the principal gas phase products from the process are carbon monoxide and hydrogen. Kinetic simulation of the process showed that these gases can accumulate to a pronounced extent in recycling gases, and their presence may adversely influence the process due to their high reactivity.

In some cases it is less expensive to use air instead of oxygen as a feedstock; therefore, it is important ot investigate the influence of nitrogen dilution on the process. Nitrogen also accumulates in the recycle mixture if industrial grade oxygen is used.

Experimental Design

In this work, pressure change in the range of 30-230 atm, the dilution by nitrogen (up to 70%) and the effect of carbon monoxide (up to 30%) and hydrogen (up to 5%) content in the mixture were investigated to determine the influence on the main product yields.

The experiments were conducted with constant flow pilot facility using prepared NG-air mixtures containing approximately 2.8% of oxygen. Apart from methane, the NG contained minor amounts of ethane (~2.5%) and higher hydrocarbons (~1%). Gas flow rates, Q, ranged from 50 to 350 (usually 100) liters/hour (NTP). Reaction temperatures were from 250 to 450°C. After cooling, liquid products were separated and collected. At twelve hour intervals, the chromatographic analysis were conducted on samples of the collected liquid products, the gas mixture at the reactor inlet, and the gas mixture downstream of the separator. It is worthwhile to note that in all cases the residence time in the reactor mixtures were sufficiently long to maximize oxygen consumption (~95-97%). In a special set of experiments it was shown that increasing or decreasing residence time in the reactor

by a factor of three or more did not change the products yields appreciably, except for a slight change in production of formaldehyde. A more thorough description of these experiments will be given elsewhere.

Experimental Results

The analysis of liquid and gas phase products revealed a large number of components. Most of these have been found in previous investigations. Along with primary liquid products - water, methanol and formaldehyde - some minor products, such as ethanol (0.5-1.5%), acetone (~1%) and organic acids (0.4-0.9% of liquid product) were found. We also observed formation of trace amounts of C_3-C_4 alcohols.

In gas phase, in addition to carbon oxides, we registered the formation of 0.5-0.6% of hydrogen.

Results from these experiments are presented at figures 1 and 2. Each data point shown, represents an average of a number of consequent experiments, each twelve hours in length.

The data shown in figure 1, indicate the influence of increasing pressure leads to an increase total yield of liquid oxidation products, which reaches a maximum at P=100-200 atm. Figure 2 shows the pressure dependence on the composition of these liquid products. The methanol and ethanol concentrations reach maximum at approximately 150 atm, but that of formaldehyde continuously declines with increasing pressure. The dependence of acetone concentration with pressure is similar to that of alcohols and production of organic acids (mainly formic acid) is approximately constant over this pressure range.

The most prominent changes in yield and composition of liquid phase take place at pressures below 100 atm.

The composition of gas phase changes with pressure are due primarily to a rise of carbon dioxide concentrations with increasing pressure. Carbon monoxide concentration shows little dependence on pressure. The rise of carbon dioxide concentration with pressure is probably, in part, connected with formic acid formation, followed by its decay to carbon dioxide. The mechanism of this process was suggested by Vedeenev(4).

The estimated selectivities for products relative to consumed methane (approximately 40% for methanol and 7% for formaldehyde) are very similar to those obtained by Onsayer(5) and Burch(6) and follow the kinetic model of the process (7).

The formation of gas phase components, such as carbon monoxide and hydrogen, may cause some problems if the recycling scheme is to be used. To investigate the influence of these constituents, a number of gas mixtures with varying H_2 and CO concentrations were prepared and tested in the process facility. Other primary process parameters were kept constant (T=400°C, P=100 atm, Q=100 1/h, (O_2)=2.8%).

Figure 3 shows the effect of hydrogen concentration yield. It is clear that up to concentration of 5% H_2, there is practically no impact on total liquid product yields or on the concentrations of primary liquid components.

Figure 4 shows the effect of carbon monoxide concentrations on product yields. As with hydrogen, carbon monoxide at low concentrations (CO)≤5% has little influence on product yields. There is a sharp decrease in product yields with carbon monoxide concentrations in the range of 5-15%. Apparently, at such

concentrations carbon monoxide begins to compete with methane for oxygen.

Dilution of the gas mixture with nitrogen leads to a decrease in the liquid product yield. These experiments were run with a constant oxygen concentration, which suggests that the decrease in the product yield may be due to a decrease in the CH_4/O_2 ratio. This result shows close correspondence with a well established product decline with decreasing CH_4/O_2 ratios. A similar effect could be caused by CO_2 dilution, another principal gas phase product associated with this process, which concentrates as a result of recycling.

Discussion

Our experimental results show that with high pressure oxidation of methane, initial concentrations of carbon monoxide and hydrogen are introduced to the mixture as a result of their formation in the process. The results also show that at low concentrations (<5% of either constituent), the presence of these gases does not adversel affect product yields. This result suggests that the presence of these gases would not detract from the use of a "recycle process scenario" and would not require separation of gas phase reaction products. This analysis holds so long as the concentration of either constituent does not exceed 5% of the recycle mixture.

It can also be concluded from these experiments that there is no advantage to employing process pressures higher than 100 atm.

It is noteworthy that the experimental data from this study show incomplete consumption of oxygen; oxygen consumption never exceeded 95-97%. We could not prevent residual oxygen (3-5% from initial amount) in the gases although, special attention was paid to this issue. From the theoretical point of view, it is very difficult to explain this phenomenon, but analysis of literature shows that incomplete oxygen consumption took place in other works, as well(8-10).

The experimental results were compared with a kinetic simulation of the process developed by Veedenev(7). The model was supplemented with a block of CO reactions and some rate constants were corrected. The calculations and model results showed good correlation with the experimental data.

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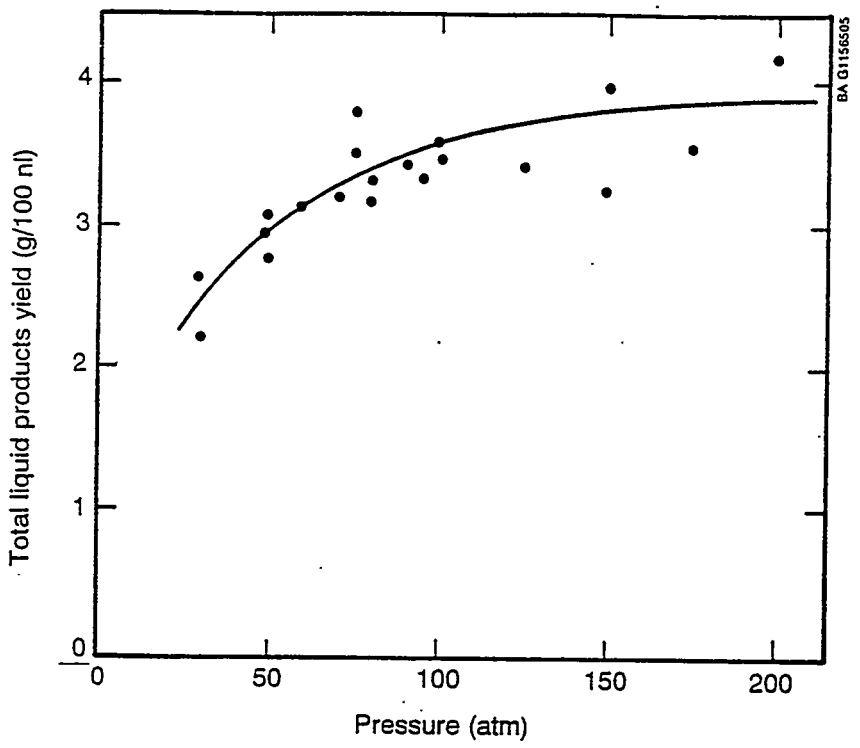

Figure 1. Pressure dependence of total liquid products yield at high pressure methane oxidation. T = 400°C.

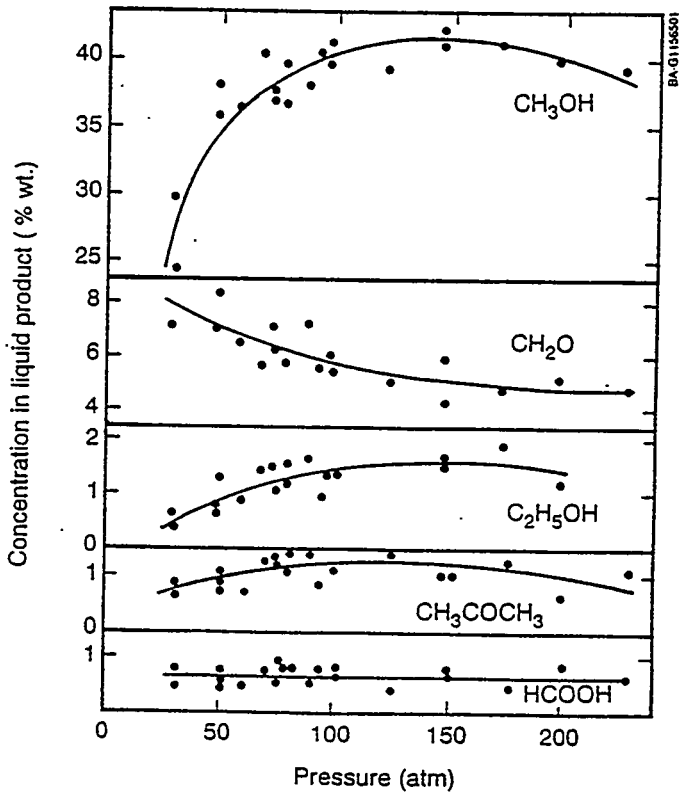

Figure 2. Pressure dependence of main products concentrations in liquid product of high pressure methane oxidation. T = 400°C.

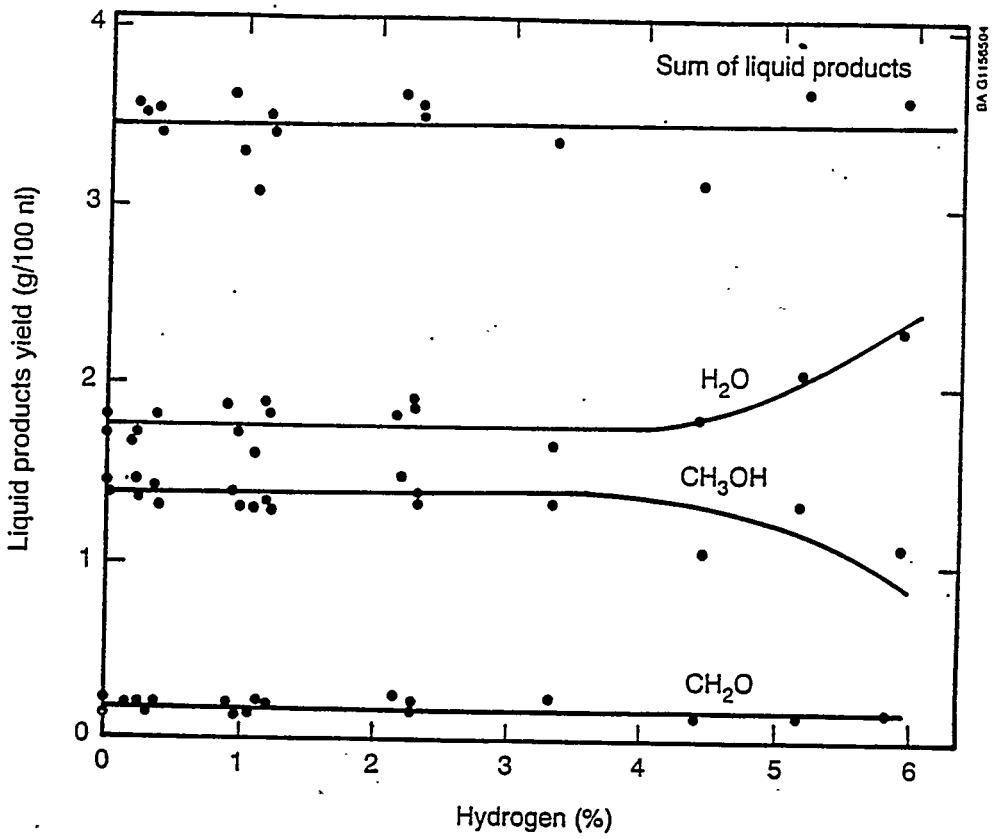

Figure 3. The hydrogen concentration effect on liquid products yields. T = 400°C. P = 100 atm.

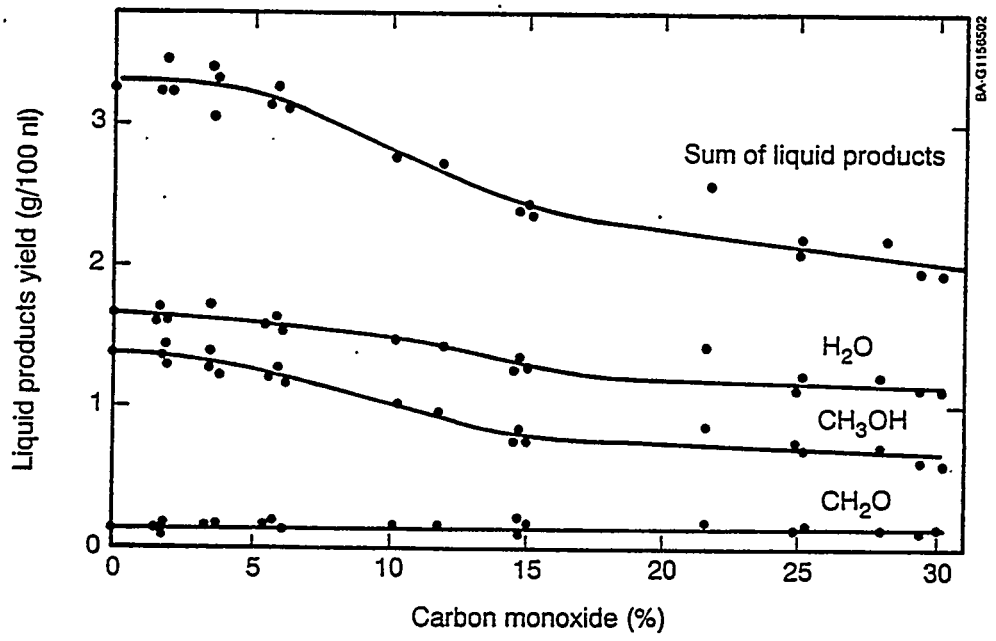

Figure 4. The carbon monoxide concentration effect on liquid products yields. T = 400°C. P = 100 atm.

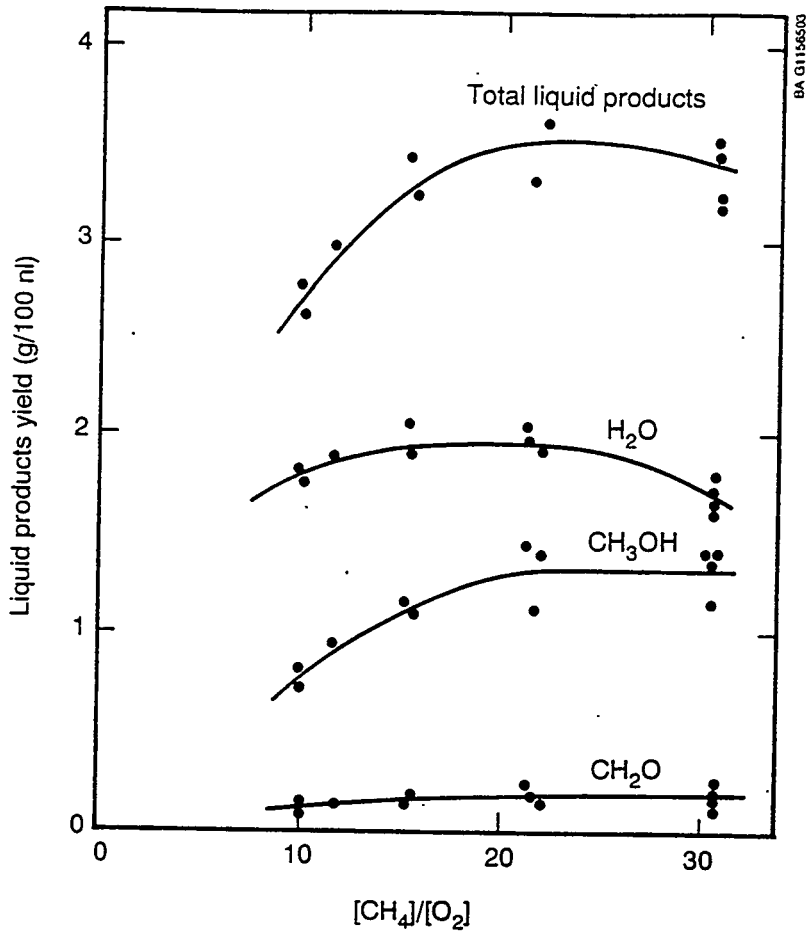

Figure 5. The methane-oxygen ratio effect on liquid products yields. T = 400°C. P = 100 atm.

DEMONSTRATION OF METHANOL PRODUCTION USING THE HYDROCARB PROCESS WITH BIOMASS FEEDSTOCK

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ABSTRACT

A bench scale methanol production plant, using biomass and natural gas as feedstocks, is being built in Southern California with the goal of verifying the feasibility of the Hydrocarb process. The Hydrocarb process, developed by Brookhaven National Laboratory, involves three steps: the hydrogasification of biomass; the pyrolysis of methane into hydrogen and solid carbon; and the catalytic reaction of hydrogen and carbon monoxide into methanol. Excess hydrogen from the methanol production step is recirculated and provides the reducing environment in the hydrogasification process. A preliminary design has been completed, engineering activities are underway, and the project is ready to move to the construction phase.

INTRODUCTION

Producing methanol from biomass offers significant environmental, energy, and economic advantages. Methanol is a clean fuel for transportation applications, and its use could significantly contribute to reduced emissions of criteria pollutants and CO_2. Methanol can be used as a low-emission fuel in currently available vehicles. Furthermore, methanol is also an excellent energy carrier for fuel-cell-powered vehicles. When derived from biomass, methanol displaces fossil fuels and reduces CO_2 emissions.

The Hydrocarb process was originally developed to convert coal to clean carbon. The process can also use biomass and natural gas as feedstocks. Examples of biomass feedstocks are wood, waste products, sewage sludge, and municipal solid waste. In addition to waste biomass, the process can utilize any carbonaceous matter including discarded tires and plastics. Net greenhouse emissions associated with biomass feedstock are essentially zero. While the natural gas feedstock contributes to CO_2 emissions, overall CO_2 emissions from the process using combined natural gas and biomass feedstocks would be lower than those from separately operating methanol plants with natural gas and biomass feedstocks. Using only biomass as a feedstock for a gasification system results in a process gas that is rich in CO and deficient in hydrogen for maximum methanol yield. With such a process, additional hydrogen is produced through the water gas shift and some CO is converted to CO_2. This approach yields less methanol per unit of biomass than the Hydrocarb process yields.

The Hydrocarb process was originally conceived at Brookhaven National Laboratory and further developed by the Hydrocarb Corporation. The process, summarized in Figure 1, is based on the hydrogasification or pyrolysis of biomass in the presence of hydrogen in the hydrogen pyrolysis reactor (HPR). This is followed by the reaction of the resulting methane into hydrogen, carbon monoxide, and solid carbon in the methane pyrolysis reactor (MPR). The catalyzed reaction of hydrogen and carbon monoxide produces methanol in the methanol synthesis reactor (MSR). The excess hydrogen is recirculated to provide the reducing environment required for the hydrogasifier. Natural gas and wood will be used as the feedstock for the proposed project.

EPA has evaluated the economics of methanol production, and found that methanol can be produced competitively with gasoline using the Hydrocarb process (Borgwardt 1993). The Hydrocarb process produces methanol at a lower cost than other biomass-to-methanol processes as well as advanced biomass-to-ethanol processes. By utilizing waste streams, the Hydrocarb process could help avoid the increasing costs for solid waste disposal as landfill options become limited. In California, some sewage treatment plants pay around $25/ton to dispose of sewage sludge. In New York, solid waste disposal costs approach $50/ton. Hydrogasifying and converting such biomass

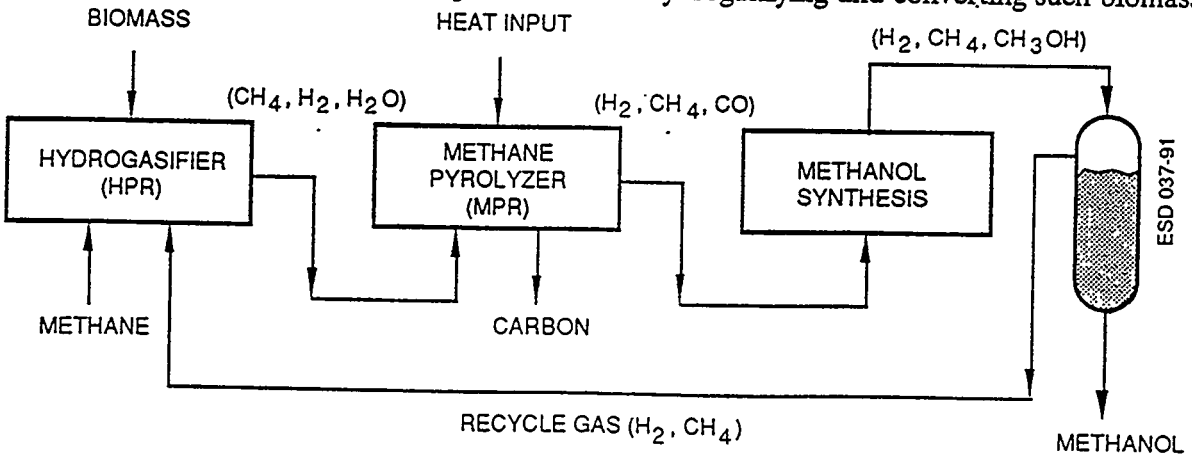

Figure 1. Hydrocarb process block diagram

to methanol offers an opportunity to convert waste into energy while emitting a minimum of criteria pollutants without generating toxic pollutants. This process eliminates a solid waste stream while generating minimal ash and air pollutants. Furthermore, the Hydrocarb process produces methanol and solid carbon a potentially marketable byproduct.

All of the components of the Hydrocarb process have been demonstrated to some extent. Table 1 lists examples of projects that utilize the three process steps in the Hydrocarb process. A pilot plant for the hydrogasification of brown coal was constructed and operated by Rheinbraun near Cologne, Germany (Brüngel 1988). This unit converted 230 tonnes per day of coal into methane. Universal Oil Products (UOP) developed a methane pyrolysis reactor that was used to convert methane into hydrogen (Pohlenz 1966). This atmospheric unit used hot solids to provide the energy for converting methane into carbon and hydrogen. Their unit processed 11 tonnes of methane per day. Methanol production has been a commercial process for decades (Supp 1990). Commercial plants primarily use natural gas as a feedstock, but some plants have been built that use coal, and a biomass plant is planned in Hawaii (Takahashi 1990).

Advanced methanol production processes have been analyzed by others (Larson 1992). Some of the more efficient processes use recirculating solids heat transfer to provide energy for a steam/oxygen gasifier. In the report by Larson, process efficiencies ranged from 53 to 70.5 percent.

PROJECT DESCRIPTION

The overall goal of the project is to demonstrate the viability of methanol production from the Hydrocarb process. The hydrogasification of biomass and recycled process gas of the Hydrocarb process offer advantages from efficiency, cost, and greenhouse gas emissions standpoints. Showing that the process works with biomass feedstock will establish these benefits. The effort is focussed on the simplest feedstocks, white wood and natural gas. Operating the proposed methanol plant will also generate scale-up data for a larger facility. The overall project has been divided into four phases. Phase I, the conceptual design and bench scale plant specification has been completed. The specific objectives for each of the other project phases are shown in Table 2. These objectives are the success criteria for the initial operation of the plant, but plant operation will continue to enable a wide range of parameters to be evaluated.

Table 1. Experience with Hydrocarb Process Systems

Site	Location	Feedstock	System	Capacity (t/d)	Reactor Pressure (bar)
Rheinbraun	Cologne, Germany	Brown coal, H_2	Hydrogen pyrolysis reactor	230	123
AMAX	Golden, Colorado	Gasifier char, H_2	Hydrogen pyrolysis reactor	0.6	27
AMAX	Golden, Colorado	Methane	Methane pyrolysis reactor	0.5	7
UOP	Des Plaines, Illinois	Methane	Methane pyrolysis reactor	11	1
Eastman Chemical Co.	Kingsport, Tennessee	Coal	Methanol production plant	820	41[a]
Hawaii Natural Energy Institute	Maui, Hawaii	Bagasse, biomass	Methanol production plant, planned	100	24[a]

[a]Gasifier pressure. Texaco gasifier at ECC and IGT gasifier at HNEI.

Table 2. Project Objectives

Project Phase	Objectives
II Hydro-gasification	• Carbon conversion greater than 80 percent • 3 hours continuous HPR operation • Gas composition approaches equilibrium
III Methane pyrolysis	• Methane conversion greater than 90 percent • 3 hours continuous MPR operation with HPR feed gas • Process gas contains no catalyst poisons
IV Integrated methanol production	• Produce over 100 gallons methanol per day • 8 hours continuous integrated plant operation • CO conversion to methanol greater than 70 percent

The plant is a bench scale unit designed for the following process conditions:

Solids feed:	26 kg/h, 0.6 t/d
Natural gas feed:	10 kg/h
HPR temperature:	800°C
MPR temperature:	1100°C
MSR temperature:	260°C
System Pressure:	50 bar
Methanol product:	45 kg/h, 360 gal/d

These parameters represent a specific process configuration, intended to produce maximum methanol product. The methanol conversion efficiency is about 67 percent. Other configurations are also possible with variations in parameters such as system pressure, natural gas-to-solids feed ratio, methanol production rate, and reactor temperatures.

Figure 2 shows the process flow diagram for the bench scale system. The diagram is divided into three major systems, HPR, MPR, and MSR, that correspond to the three main reactors in the process.

In the HPR system, natural gas and wood are fed into the pyrolysis reactor in the HPR system. In the bench scale unit, steam will also be fed into the reactor so that wood can be fed with a constant moisture content and the effect of solids moisture content can be simulated parametrically. The reactor is a 150 mm (ID) fluidized bed. A cyclone and high temperature filter remove particles from the gas stream.

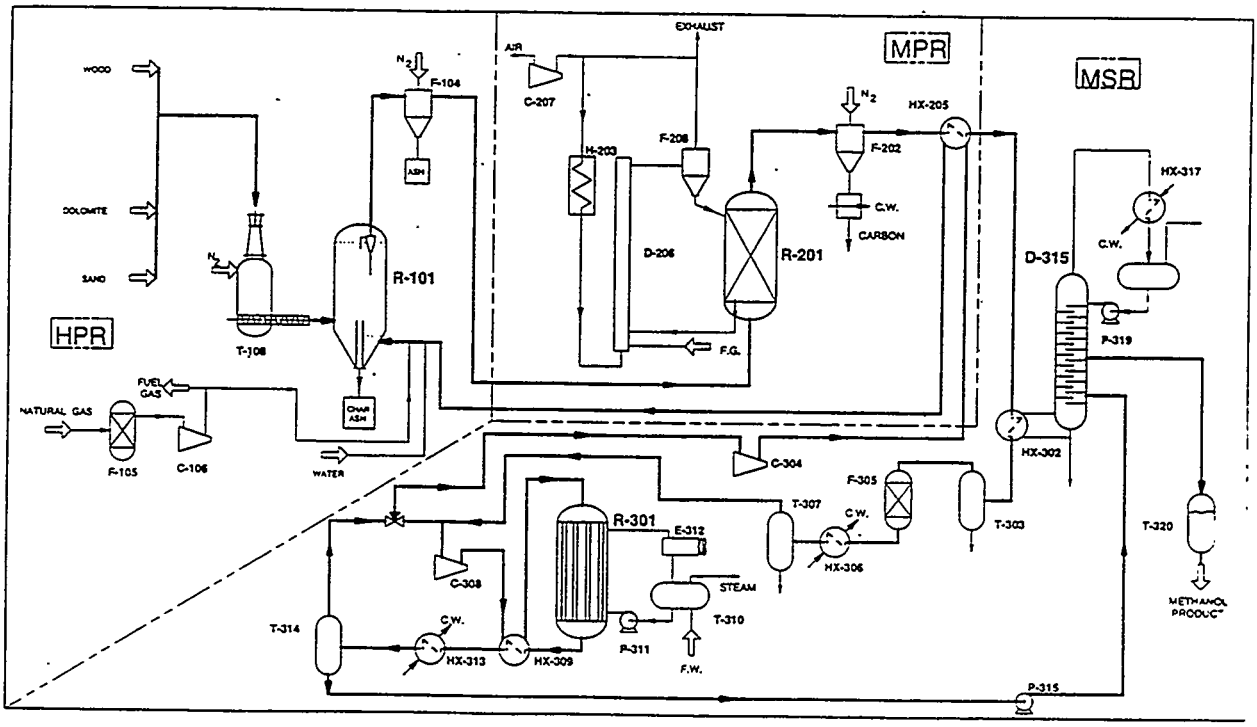

Figure 2. Process flow diagram for bench scale system

Alkali metals that occur naturally in biomass, particularly potassium and sodium, can lead to gasifier operating problems. Alkali adsorbing agents such as dolomite and emathlite will be used to control the formation and subsequent deposition of vapor phase potassium. These materials will be fed into the reactor with the biomass.

A screw feeder will transport solids into the hydropyrolysis reactor. A lock hopper and metering bin system will be pressurized with nitrogen to bring the solids up to pressure.

The HPR system will be constructed and operated first. Rather than using recycled gas from the methanol reactor, bottled hydrogen will be heated and fed into the HPR. After this system is successfully operated, the MPR and MSR systems will be added to the bench scale plant.

A preliminary concept for the MPR system is shown in the figure. Hot solids, such as alumina pellets, provide the energy for dissociating methane in the pyrolysis reactor. The alumina could be separated from the process gas, heated in a fired column, and recirculated back to the MPR. Carbon will be removed from the MPR process gas. The hydrogen and CO produced in the reactor will be filtered and heat-exchanged with recycle gas entering the HPR.

The cooled process gas then passes through a sulfur removal bed, is further cooled, and is circulated to the methanol reactor. This system is currently configured as a multiple pass methanol reactor. The reactor feed gas has a high hydrogen concentration and is expected to result in high CO conversions. The stoichiometry number, SN:

$$SN = (H_2 - CO_2)/(CO + CO_2)$$

is about 7. A stoichiometry number of 2 is normally optimal where hydrogen is not recycled back to the process. Water that is produced with the crude methanol could be removed with a distillation column; however, this polishing step is not necessary to meet the objectives of the bench scale demonstration.

The features of the Hydrocarb process offer potentially higher methanol yields than other processes. The hydropyrolysis step is energy neutral while steam reforming natural gas is endothermic. Recycling hydrogen saves mass and energy for the conversion of biomass to methanol. The two stage hydropyrolysis and methane pyrolysis is thought to be more efficient than conventional gasification where the shift reaction is used to produce hydrogen.

CONCLUSION

This bench scale unit is intended to demonstrate the viability of the Hydrocarb process using a biomass feedstock. A successful demonstration would show high conversion of biomass and natural gas to methanol. Energy losses from a bench scale unit will be greater than those from a larger unit. These losses be compensated for to some extent with steam and electrical heating. The project will demonstrate the mass balance for the Hydrocarb process with hydrogen recirculation. The project will also help stimulate interest in methanol production from thermochemical processes.

ACKNOWLEDGEMENTS

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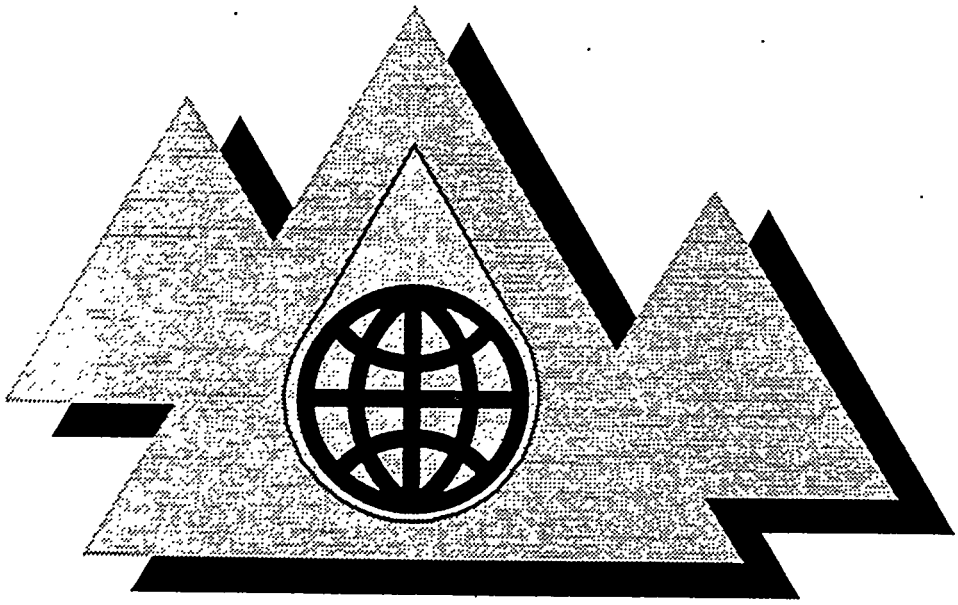

Biomass Production and Feedstock Availability

BIOMASS FEEDSTOCKS IN THE MIDWEST

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Abstract

In early March, 1993, the Union of Concerned Scientists released a report on a two-year study assessing the economic benefits and technical potential of renewable electricity in the Midwest. As part of that study, we evaluated potential biomass feedstocks which might come from existing sources, such as agricultural residues, logging and mill residues, and municipal solid wastes. We estimate the potential biomass resource from these sources to be over 100 million dry tons annually. Future biomass feedstocks could come from energy crops grown on idle agricultural land, which we estimate could produce in excess of 200 million dry tons annually, under certain scenarios. The economic attractiveness of many of these feedstocks will depend on the conversion technology considered. This paper describes our assessment of biomass resources and summarizes some of our results.

BIOMASS FEEDSTOCKS IN THE MIDWEST

Introduction

In early March, 1993, the Union of Concerned Scientists released the report *Powering the Midwest: Renewable Electricity for the Economy and the Environment*, a two year study assessing the economic benefits and technical potential of renewable electricity in the Midwest. The Midwest region is defined as the 12 states of the North Central census region: Illinois, Indiana, Iowa, Kansas, Michigan, Missouri, Minnesota, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin. The report considers three major classes of renewable electricity sources: utility-scale wind power, biomass-electric generation and distributed generation, namely small-scale wind and photovoltaic systems. We recognize that other energy sources and technologies could play a significant role in the Midwest, but we chose to assess a few in depth rather than touch on many.

This paper summarizes our methods and findings for the following selected biomass feedstock resources: forest wood and residues, crop residues, municipal solid wastes, and energy crops. While we considered the potential of these feedstocks to generate utility-scale electricity, many of these resources might be used alternatively for producing alcohol fuels. The full report, available from the Union of Concerned Scientists, contains much more technical and economic analysis, discussion of environmental considerations, and a number of policy recommendations that are not discussed here.

Forest Wood and Residues

Our principal source of information on logging residues was a series of reports published by the North Central Forest Experiment Station of the U.S. Forest Service (1). Mandated by the Forest and Rangeland Renewable Resources Planning Act of 1974, these reports provide periodic inventories of the nation's forest lands for the purpose of determining the extent, condition, and volume of timber, as well as its growth and depletions. The reports from the North Central Forest Experiment Station provide statistics on logging and mill residues at the county level for Illinois, Michigan, Minnesota, Missouri and Wisconsin. Similar statistics are provided for Indiana and Iowa by Forest Survey Units, each of which may include several dozen counties. No statistics were available for Kansas, Nebraska, North Dakota, and South Dakota, which have little or no commercial forest. Although the reporting year varies from state to state (usually mid- to late-1980s), use of these statistics provides a consistent methodology for state-by-state comparisons.

Logging residues, defined as the unused portions of tress cut or killed by logging, were assumed potentially available for biomass energy use. In addition, we assumed that only 50 percent of the logging residues generated in the forest could or would be delivered to energy markets. Logging residues are reported in USDA reports by tree species in thousand cubic feet, which we converted into an oven dry ton weight using representative wood densities (pounds per cubic foot) for each species. Mill residues were assumed to be potentially available if they were not already being put to some use (classified as "not used"). Mill residues are reported in USDA reports by softwood and hardwood wood residues and bark in thousand green tons. These values were converted into a dry ton weight using an average green weight to oven dry weight ratio for hardwoods and softwoods. Wood from logging and mill residues were assumed to contain 17 million Btu per dry ton.

For the state of Ohio, most available reports on forest statistics were based on the last forest survey, conducted in 1979. A more recent report on timber products output in 1989 for

Ohio was recently published by Widmann and Long (2), but this report did not include estimates of logging or mill residues.

We assumed that logging practices in Ohio were similar to those in Illinois and Indiana. To estimate logging residues for the state of Ohio by Forest Survey Unit, we used the reported industrial timber harvest (in thousand cubic feet) for Ohio with an average logging residue to industrial roundwood production ratio, as reported for Illinois and Indiana, to estimate Ohio logging residues. These were converted into dry weights using average dry wood densities for hardwoods and softwoods. It was assumed that mill residues in Ohio, as reported for the state by Widmann and Long, were distributed relative to the distribution of sawlog receipts in the state for 1989. Widmann and Long report sawlog receipts by Forest Survey Unit. Survey unit values were compared to state total receipts. These ratios were applied to the reported unused portion of mill residues. This estimate does not include residues generated at pulpmills.

Results are presented in Table 1. We estimate that roughly 3.4 million dry tons of woody feedstock were potentially available from logging residues across the region, with nearly 65 percent (2.17 million tons) concentrated in Michigan, Minnesota, and Wisconsin. Unused mill residues represent another 500 thousand dry tons, primarily in Minnesota and Missouri (309 thousand tons). Due to lack of information, it was not possible to estimate logging or mill residues in the northern Great Plains states. Due to their geography, and lack of large tracts of forested land, we assumed that no biomass would be available from any logging activities in these states beyond very local use. Regionally, these biomass feedstocks have a heating value on the order of 66 billion Btu.

Additional woody feedstocks could come from expanded harvesting of forest resources. In the 1980's, about 19 million dry tons of industrial roundwood were harvested each year from forests in the Midwest. At the same time, the total forest inventory increased as stands

Table 1: Deliverable Forest Wood and Residues Million dry tons (for various years)

State	Expanded*	Logging**	Mill**	Total
Illinois	0.43	0.17	0.03	0.63
Indiana	0.19	0.32	0.06	0.57
Iowa	0.13	0.06	0.02	0.21
Kansas	N/A	N/A	N/A	N/A
Michigan	1.0	0.56	0.08	1.65
Minnesota	0.63	0.66	0.11	1.40
Missouri	0.29	0.35	0.20	0.85
Nebraska	N/A	N/A	N/A	N/A
N. Dakota	N/A	N/A	N/A	N/A
Ohio	0.26	0.29	0.01	0.56
S. Dakota	N/A	N/A	N/A	N/A
Wisconsin	0.95	0.95	0.03	1.93
Midwest	3.90	3.36	0.52	7.78

*Assumes 20 percent increase in roundwood harvests over current levels. **Assumes 50 percent of unused logging residues and all unused mill residues available for energy conversion. Source: USDA Forest Service. N/A = not available.

were allowed to return to forest. If wood production across the region were increased by 20 percent over the current harvesting rate, about 3.9 million dry tons of fuel-wood would be available per year. In many forest areas, the increase in wood removals would still be far less than the net annual growth of the forest.

Estimating the cost of woody biomass is difficult, and will tend to be somewhat site specific. If the market for fuelwood expands, then whole-tree hardwood chips might be expected to cost anywhere from $26 per dry ton to $38 per dry ton ($1.50 to $2.20 per million Btu). This price range is in rough agreement with experience in New England, where wood chips are sold to power plants for around $35 per dry ton.

Crop Residues

Our estimates of crop residues were developed by Windy Peak Associates of Golden, Colorado, from county acreage of crop land and crop yields provided by state agricultural statistical services offices for 1990 (1989 for Iowa) (3). For each crop type, the reported yield per acre was multiplied by a residue factor, or number of pounds of dry residue produced for every pound of grain harvested, to give an estimate of the total residue produced in the field. We then applied the following assumptions to arrive at a total potentially deliverable residue:

- only grain crops that produce stover and straw were considered appropriate for commercial residue harvesting.
- residues from soybeans, potatoes, and other vegetable crops were not considered appropriate for commercial energy use because of harvesting equipment limitations and fertility concerns.
- a farmer participation rate of 50 percent.
- a minimum of one ton of residue per acre would be left in the field for erosion control.
- a farmer would not collect residues unless there was one or more tons of residue available above the one ton erosion level.

The result was an estimate of the total deliverable residue for each crop type in each county and state in the region (Table 2). For the Midwest as a whole, the study found that nearly 400 million dry tons of various cereal crop residues were produced in 1990. Of this, over 300 million dry tons, or three quarters, would or should be left in the field, leaving 93 million dry tons potentially usable for energy production. (This estimate assumes that 50 percent of the crop residue that is technically and physically available will not be harvested for energy use.) If converted entirely to energy, these residues would generate approximately 1.5 quadrillion Btu (1.5 quads). Crop residues were assumed to contain 16 million Btu per dry ton. The top three residue-producing states--Iowa, Illinois, and Minnesota--provide over half this potential, with another quarter coming from Indiana, Nebraska, and Ohio.

The crop residue resource is clearly very large, but it comes at a relatively high price compared to, say, that of wood. The Windy Peak study estimated the price that would have to be paid for residues delivered to an energy facility to cover the costs of harvesting, storage, and transportation as well as a profit for the farmer. (No loss of material during storage was assumed.) The costs were developed from published information on enterprise budgets and custom rates for mowing, conditioning, swathing, baling, and other farming activities in various states and for various crop types. They also included a cost of truck hauling assuming an average hauling distance of 35 miles. The study found that none of the crop residues could be

Table 2: Deliverable Crop Residues Million dry tons (for year 1990)

State	Wheat	Corn	Small Grains	Total
Illinois	0.37	13.41	0.06	13.84
Indiana	0.29	9.12	0.01	9.42
Iowa	0.02	17.53	0.09	17.64
Kansas	1.27	1.69	0.82	3.77
Michigan	0.29	2.30	0.04	2.64
Minnesota	0.90	9.62	0.48	11.0
Missouri	0.16	1.68	0.21	2.06
Nebraska	0.15	6.66	1.07	7.88
N. Dakota	0.59	0.29	0.49	1.38
Ohio	0.62	4.48	0.04	5.14
S. Dakota	0.18	1.92	0.20	2.30
Wisconsin	0.08	1.66	0.17	1.91
Midwest	**4.92**	**70.36**	**3.68**	**78.98**

Numbers may not add to totals due to rounding. Corn includes stover and corncobs; small grains includes barley, rye, oats, and sorghum residues.

delivered for under $40 per dry ton ($2.50/MBtu) without price subsidies of some kind. At a price of $50 per dry ton ($3.10/MBtu), most of the residues in Iowa (17 million tons) and Wisconsin (1.9 million tons) might be brought to market, whereas at $65 per dry ton ($4.10/MBtu) up to 79 million tons could be delivered.

The driving favor in the cost is the residue yield per acre. Wherever the yield is just a few tons per acre above the one-ton conservation minimum, the fixed costs of collection push the price per ton very high. For this reason, the least expensive residues are generally found in the states with the highest agricultural yields, in particular, Iowa.

Municipal Solid Wastes

Our estimates of municipal solid waste (MSW) potential were based on state populations, average composition of MSW, and assumed a recycling rate of 50 percent for waste paper, cardboard, wood, plastics, rubber, and other combustible components. Most plastics and some other combustible components of the waste stream are not renewable in origin. Nevertheless, for simplicity, we included them in estimates of the total waste resource. Not included was the inert fraction of MSW, such as metal, rock, glass, and concrete, nor was wood from construction and demolition materials considered. The estimates also assumed that all yard wastes (leaves and clippings) will be composted, as some communities now require.

To calculate the waste potential, we multiplied county populations (1990 census) in each state by an estimated average per capita waste production of 3.5 pounds per person, adjusted for size of urban areas. We then multiplied this figure by the estimated fraction of each type of waste that is not assumed recycled.

The results for our original estimate of combustible materials are shown in Table 3. If only paper, cardboard, wood, and food wastes are considered (excluding plastics, rubber, leather, and textiles), the total is reduced by approximately 20 percent, as shown in Table 3.

Heating value is based on the average heating value of the individual components, but is roughly 16.75 million Btu per dry ton for all

combustible materials. The MSW potential is comparable in size to the potential from forest wood and residues, although it is distributed much more evenly throughout the region.

Table 3: Municipal Solid Wastes
Million dry tons (for year 1990)

State	Combustible* Waste Available	Bio-convertible** Waste Available
Illinois	1.88	1.49
Indiana	0.90	0.71
Iowa	0.43	0.34
Kansas	0.39	0.31
Michigan	1.53	1.21
Minnesota	0.71	0.56
Missouri	0.82	0.65
Nebraska	0.24	0.19
N. Dakota	0.09	0.08
Ohio	1.79	1.42
S. Dakota	0.10	0.08
Wisconsin	0.80	0.63
Midwest	**9.68**	**7.68**

* Combustible waste assumes 50 percent recycling of waste paper, cardboard, wood, plastics, rubber, leather, and textiles, 100 percent composting of yard wastes, and no recycling of food wastes. **Bio-convertible waste would be the paper, cardboard, wood, and food portion of the combustible waste.

Energy Crops

Although forest wood and residues, crop residues, and municipal solid wastes are all important potential resources for biomass feedstocks in the Midwest, energy crops have the greatest potential in the long run. In energy farming, selected species would be grown for their high yield and suitability for conversion to energy. Many species are being investigated. We considered two general groups: fast growing trees (namely hybrid poplar) harvested every few years, and perennial herbaceous crops (namely switchgrass), harvested annually.

Most of the land theoretically available for energy crop production is already being used to grow food for people and animals, however, and much of the rest is of uncertain quality and productivity. To estimate the practical resource and its likely cost requires examining in more detail the physical makeup of existing cropland and its current uses. To avoid the issue of competition with food crops--which could increase costs for both--we assumed that energy crops would be grown only on cropland that is likely to be otherwise idle. This included land enrolled in the Conservation Reserve Program (CRP).

Our projections of the amount of idle cropland that would be available were developed by the Center for Agriculture and Rural Development (CARD) at Iowa State University for the USDA Soil Conservation Service's 2nd RCA Appraisal. Projections of producing and idle cropland were broken down by state and by land group. (A land group is composed of one or more soil classes and subclasses of similar type, e.g., wet soils) Under the CARD baseline projection for the year 2000, which formed the basis of our energy crop production estimates, some 225 million acres of cropland could be available to farmers in the Corn Belt, Great Lakes, and Northern Great Plains, of which 146 million acres would be needed for production of food crops, while 79 million acres could be idle. (It should be noted that the idle land estimates may be too high because of optimistic assumptions of future crop yields, but they are the best available.) The one modification we made to the CARD estimates was to shift highly erodible land in the Corn Belt out of food production.

The potential production of energy crops depends not only on the amount of idle land available but also on energy crop yields, which can vary widely depending on soil type and other conditions. For our study we adapted estimates of probable yields developed by

researchers at Oak Ridge National Laboratory (4). For hybrid poplar, yields across the region ranged from 8 dry tons per acre per year on the best soils to four dry tons per acre per year on the poorest soils. Switchgrass yields ranged from a high of seven dry tons per acre per year, down to zero. Because hybrid poplar are expected to need a lot of water to achieve the highest yields, this species was restricted to prime and wet soils in areas which naturally support forest ecosystems; switchgrass was assumed able to grow on all other soil types able to support tall-grass species. A 15 percent loss in harvesting, storage, and transportation was assumed.

In all, we estimate that up to 250 million dry tons of switchgrass and 20 million dry tons of hybrid poplar might be grown across the Midwest without competing with food crops. This biomass would have a combined energy value of over 4 quads. We assumed an energy value of 16 million Btu per dry ton of switchgrass and 17 million Btu per dry ton of hybrid poplar. Most states, with the possible exception of Ohio, have good prospects for growing switchgrass, although Kansas, Minnesota, Nebraska, and South Dakota account for over half the total potential. Hybrid poplar production, on the other hand, would be most heavily concentrated in the Great Lakes states.

The price that would be paid for energy crops depends on several factors, including planting, maintenance, and harvesting costs, crop yields, losses, land rent, transportation, storage, and expected profit. Keeping in mind especially the importance of land rent, we estimated the energy crop production potential for each county and state over a range of costs. Overall, some 54 million dry tons of switchgrass might be made available at a cost of under $40 per dry ton ($2.50/MBtu). At $50 per dry ton, the production potential rises to 171 million dry tons, which is equivalent to 2.7 quads. Hybrid poplar would be somewhat more expensive. At a cost of under $50 per dry ton about 7.3 million tons might be made available, whereas 15.7 million dry tons could be produced at a cost under $70 per dry ton (Table 4). In these quantities, energy crops could have a major impact on energy supplies in the Midwest.

Table 4: Energy Crop Cost and Supply Million dry tons (for year 2000)

State	Switchgrass*			Hybrid Poplar**		
	<$40/ton	<$50/ton	<$70/ton	<$50/ton	<$70/ton	<$90/ton
Illinois	0.0	2.90	16.59	0.0	3.25	3.29
Indiana	1.18	7.01	9.47	3.34	3.62	3.96
Iowa	0.0	4.22	23.92	0.0	0.23	0.23
Kansas	19.06	44.71	44.71	0.0	0.0	0.0
Michigan	0.04	2.93	6.27	0.23	0.36	2.20
Minnesota	3.01	24.12	24.12	0.39	1.67	2.17
Missouri	1.40	16.70	18.36	0.75	1.10	1.10
Nebraska	3.06	30.50	33.90	0.00	0.00	0.00
N. Dakota	0.00	0.00	18.20	0.00	0.00	0.00
Ohio	0.02	0.81	1.65	2.10	2.29	3.07
S. Dakota	25.43	30.08	32.57	0.00	0.00	0.00
Wisconsin	0.41	7.19	9.65	0.51	3.25	3.51
Midwest	**53.61**	**171.17**	**239.42**	**7.31**	**15.77**	**19.51**

* Switchgrass growth restricted to areas naturally able to support tall-grass or forest ecosystems.
** Hybrid poplar growth restricted to areas naturally able to support forest ecosystems.

Discussion

The above analysis discusses major biomass feedstocks which might be available for conversion into energy in the Midwest region. Additional feedstocks will be found in other resources, such as animal manures, wood from construction and demolition activities, or energy crops attractive for conversion into liquid fuels. Taken together, a significant amount of energy is potentially available from these renewable resources.

Not discussed in detail are barriers or other considerations which may limit the availability of these resources to be brought to energy markets. Soil conservation, water quality, and other environmental considerations will need to be carefully evaluated before some of these biomass resources are used. It may be that their value for reducing soil erosion, maintaining soil fertility, or providing habitat for wildlife, to name a few, far out-weigh their value as an energy feedstock. In addition, the market infrastructure needed to bring these potential feedstocks to conversion facilities is poorly developed, or non-existent, in many areas. The final cost of energy from these feedstocks will depend not only on the quality of the feedstocks and the efficiency of the conversion technology, but also on how markets develop to make the feedstocks available.

Acknowledgements

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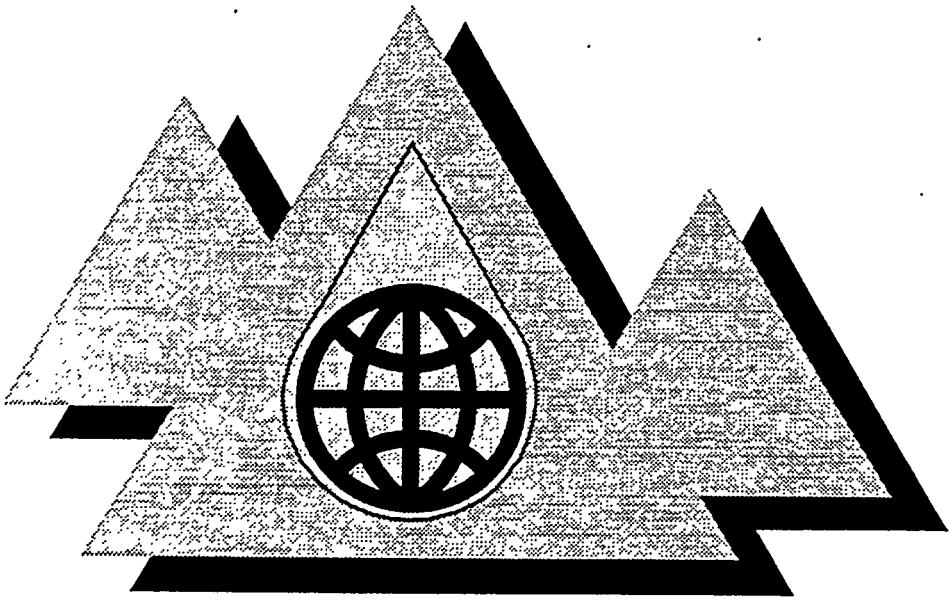

Fuel Cycle Analyses

VEGETABLE ALCOHOL FUEL PRODUCTION AND UTILIZATION IN HUNGARY

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Alcohol Factory, Győr, Hungary

Abstract

The yield of bio-ethanol production from vegetable crops (like corn, sugar beets, potatoes, and recently, sweet sorghum) could be 1.0-1.5 tons of oil equivalent per hectare (tOE/ha) under good conditions in Hungary. Considering our arable land use for energy crops, the total bio-ethanol production could be 0.5-1.0 million tOE. In order to utilize this capacity, we have made laboratory and field tests with a mixture of 10% ethyl-alcohol, 15% water, 1.2% emulsifier, and diesel fuel. The results of a MTZ-80 tractor (with a type D-240 engine) tests show that specific fuel consumption decreases 0%-4% at heavy loads and increases 0%-6% at light loads. During the field test (up to 1200 hours), there were no serious problems with the engine. We are currently preparing a project to develop an environmentally friendly production facility to satisfy multiple goals. The main goals of the new project are:

- Choosing the new crop varieties (e.g., sweet sorghum)
- Developing an environmentally friendly alcohol production technology
- Producing alcohol for human and industrial consumption
- Producing bio-ethanol
- Utilizing the by-products (e.g., molasses) for crop production and animal husbandry
- Using surplus arable land and decreasing the number of unemployed farmers in the rural region.

Introduction

Unfortunately, environmental problems across the globe and political and economic difficulties on the national scene have arisen simultaneously. To address these problems and concerns, we should develop a model to guide national agricultural policy, which considers the following:

- The application of environmentally friendly operations and technologies
- The marketing effect of European Union integration
- The acclimation opportunities during drought periods
- The effects of changing land ownership and farming practices.

A clear focus on the stated goals is the most useful way to study the agricultural production and utilization possibilities of renewable energy resources. Agricultural production plays a special role because the resulting biomass can be generated year after year and is potentially the most important renewable energy resource technology. Furthermore, the closed-CO_2 cycle of biomass production and utilization could help maintain or improve the environmental characteristics of the atmosphere. Beyond the environmental and energy benefits, conversion of agricultural materials to energy supplies could help reduce surplus agricultural stockpiles in highly industrialized countries. From the environmental and landscape farming view point, withdrawing 10 million hectares from cultivation in Europe is not acceptable. In this case, non-food farming could provide a new agro-political opportunity for national land use and help to sustain rural employment.

Alcohol Fuel Research in Hungary

The first research on using alcohol for fuel took place in the 1930s. As a result of this research, a new fuel named MOTALKO was developed. It consists of 20% alcohol and 80% gasoline.

Subsequent research with alcohol took place in the mid-1980s using sweet sorghum as a feedstock. From this new crop, a special fuel mixture was developed. Water was added to improve the stability of the gas-oil-alcohol mixture (Table 1).

The goal of the research was two-fold: successful application of ethyl-alcohol and successful application of the gas-oil-alcohol mixture. Engine bench tests have been conducted with the fuel mixture on a diesel engine (type D-240 from a Russian Belarus tractor). This diesel engine is a four-cylinder, four-stroke, water-cooled, swirl-chamber design.

Engine test results show the performance (power production), fuel consumption, and specific energy consumption for both pure gas-oil and the gas-oil-alcohol fuel mixture. As can be seen from the figures, the maximum power from the engine operating on the mixture is 20% less than that of the engine operating on gas-oil (the difference derives from the lower energy content resulting from the water/alcohol concentration). The efficiency of the engine operating at loads of 50% or more (of the nominal engine power rating), is in the range of 0% to 4% lower when operating on the mixture relative to the operations conducted on gas-oil. Whereas, at power production levels below 50%, the engine efficiency measurements show decreased specific energy consumption rates in the range of 0% to 6% with the fuel mixture.

Following the engine dynamometer tests, field tests were made with the engine in a MTZ-80 tractor, operating on the fuel mixture. With the tractor performing in the farming applications for 1,200 hours, no serious operating problems were experienced. There were problems with the water in the mixture coating the paper fuel filter element, and thereby interfering with proper fuel flow. Unfortunately, this research was not completed because of the uncertainty of raw material supply for alcohol production and the favorable price changes of gas-oil supplies.

Agricultural and Industrial Capabilities for Alcohol Production

The global and regional changes in recent years provide new opportunities for the production and application of fuels from renewable biomass. We have investigated the crops that have good potential as biomass feedstocks for fuel-alcohol production in Hungary (Table 2). Production areas and yields of the most promising crops are given in Table 3.

From this data we can determine the amount of fuel-alcohol production that is possible with our current ecological condition (Table 4). The amount of arable land suitable for the production of fuel-crops is approximately 300-400 hectares. This would equate to an annual production potential of 0.5 to 1.0 million tOE for Hungary.

The utilization of our ecological potential is less than optimum because two of the three biggest alcohol factories (Győr and Budapest) produce alcohol from molasses rather than corn (Szabadegyhaza); see Table 5. The bulk of alcohol production remains in the home market for production of beverages, medicine, and chemicals.

As can be seen from the data, utilization of alcohol as fuel is not yet a common practice in Hungary. This is partly because of technological problems but mostly because of the economics, which contribute to the very high price of alcohol. In the last year, we conducted a study to evaluate the production and application opportunities of different kinds of fuels. Some of the most interesting points gleaned from this relate to economics and commodity prices (Table 6). Economic calculations show that alternative fuels cannot compete with current production costs and tax rates. Favorable conditions for alternative fuels could only be achieved in Hungary with government intervention and/or support, such as increasing tax rates for fossil fuels to account for environmental implications associated with fossil fuel use.

Pilot Project for the Production and Utilization of Fuel Alcohol

There are several opportunities to derive fuel from agricultural renewable energy sources. One of the most interesting fuels is alcohol because it can be derived from many crops, has many uses, and generates by-products that can be fed back into the process.

It seems that the fuel alcohol has good potential for the near future. In order to produce quality R&D results, reflecting the most modern technology, we are developing a pilot alcohol production facility. The goals of this project are to develop a closed-cycle system that incorporates the crop production system as a raw material provider and outputs by-products to an animal husbandry enterprise. The main goals of the pilot project are as follows:

- The adaptation and development of new fuel crops
- The development of a resource efficient, low-energy consumption and environmentally friendly alcohol production technology
- The production of material for fuel alcohol manufacture to conduct engine research
- The development of by-product utilization processes.

Sugar beets, wheat, corn, potatoes, and sweet sorghum are potential energy crops for feeding the pilot plant. Considering soil and weather conditions, and Hungarian farming practices, wheat and corn appear to have the greatest potential for success. These crops are also important for food production. They can be cultivated on marginal land that is not in prime competition for other purposes, such as the production of food, feed, or fiber crops.

If the pilot plant project is successful, it could be used to justify a network of "built-in-the-country" factories. Such a network could:

- Improve environmental and landscape management by
  - decreasing CO_2 emissions to the atmosphere
  - keeping agricultural lands in cultivation
  - protecting soil and water quality
- Improve national land use by providing
  - alternatives to food overproduction
  - provide better utilization of marginal lands
- Improve rural labor management by
  - introducing new production profiles
  - extending agricultural products processing
  - establishing new work places
- Improve the nation's energy supply by
  - promoting the use of renewable energy resources
  - creating self-sufficient energy supplies for the rural community
  - decreasing fossil energy consumption.

Acknowledgments

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Table 1. Specification of the Fuel Mixture	
Parameters	**Value, units**
Diesel	74.40%
Alcohol	9.50%
Water	14.90%
Emulgeator	1.20%
Specific gravity (at 20°C)	0.863 g.cm-
Viscosity (at 20°C)	9.03 mm .s-l

Table 2. The Mass of Alcohol from 1 kg Raw Material			
Raw Material	**Starch %**	**Sugar %**	**Alcohol hℓ degree**
Sugar beet	0	16–17	0.09
Sugar beet molasses	0	42–50	0.30–0.31
Molasses	0	35–40	0.26–0.28
Sweet sorghum	0	15–16	0.09
Potato	10–20	0.5–1.5	0.10–0.115
Corn	65	2.0–3.0	0.33–0.35
Rye	65	4	0.36
Wheat	65	1.4	0.35–0.36
Oat	53	0	0.28
Rice	70	0	0.40–0.45
Barley	58	0	0.36
Jerusalem artichoke (inulin)	16	0	0.06–0.09
Horse chestnut	50	0	0.25
Sunflower (cellulose)	25–28	0	0.09–0.10
Corn cob (cellulose)	18–22	0	0
Straw (cellulose)	34	0	0
Wooden chips:			
pine (cellulose)	56	0	0.2
leafy (cellulose)	47	0	0.16–0.17

Table 3. Production Area, Mass, and Yield of the Different Crops						
	1986			1990		
Crop	Area 1000 ha	Yield t/ha	Mass t	Area 1000 ha	Yield t/ha	Mass t
Corn	1118	6.29	7261	1082	3.99	4317
Wheat	1318	4.36	5793	1220	5.05	6161
Barley	252	3.34	857	299	4.57	1386
Rye	89	1.91	1.72	93	2.5	232
Oat	43	2.93	126	49	3.31	163
Sugar beet	104	36.18	3760	131	36.09	4741
Potato	44	18.63	1264	44	16.92	746

Table 4. Specific Mass of Cropable Fuel Alcohol		
Crop	Fuel kg/ha	Energy equivalent MJ/ha
Sweet sorghum	2525.0	68084
Corn	1668.7	44995
Wheat	1394.5	37601
Oat	731.1	19724
Rye	710.1	19147
Jerusalem artichoke	3337.1	89992
Sugar beet	2562.7	69100

Table 5. Production and Market % of Home Market of the Three Biggest Alcohol Factory (ABS.HL/%)				
Factory	**1989**	**1990**	**1991**	**1992**
Gyor Distillery	352932	371915	343331	351301
	48%	53%	47%	50%
BUSZESZ	186962	130696	202179	153053
	25%	19%	27%	22%
Hungrana	194639	202172	191332	197364
	27%	28%	26%	28%
Total	735533	704783	736842	701718

Source: Hajdu, 1993

Table 6. The Cost and Price of the Fuels					
Fuel	**Units**	**Production Cost net**	**Production Cost gross**	**Taxes**	**Price**
Gas	HUF/litre	16,50	20,60	53,40	74,00
Diesel (public)	HUF/litre	16,19	19,10	40,90	60,00
Diesel (enterpr)	HUF/litre	16,19	19,10	28,90	48,00
Diesel (agricult)	HUF/litre	16,19	19,10	17,75	36,85
LPG	HUF/kg	25,40	41,76	38,97	80,73
Rape-oil	HUF/litre				
	min	21,72	23,72	0,00	23,72
	max	64,75	66,75	0,00	66,75
RME	HUF/litre				
	min	31,76	33,76	0,00	33.76
	max	84,87	86,87	0,00	86,87
Natural Gas	HUF/m	12,10	22,21	18,29	40,50
Ethanol	HUF/litre	56	58	14,5	72,5
Methanol	HUF/litre	22,00	24,00	6,00	30,00

Source: Gockler, 1993

Figure 1a.

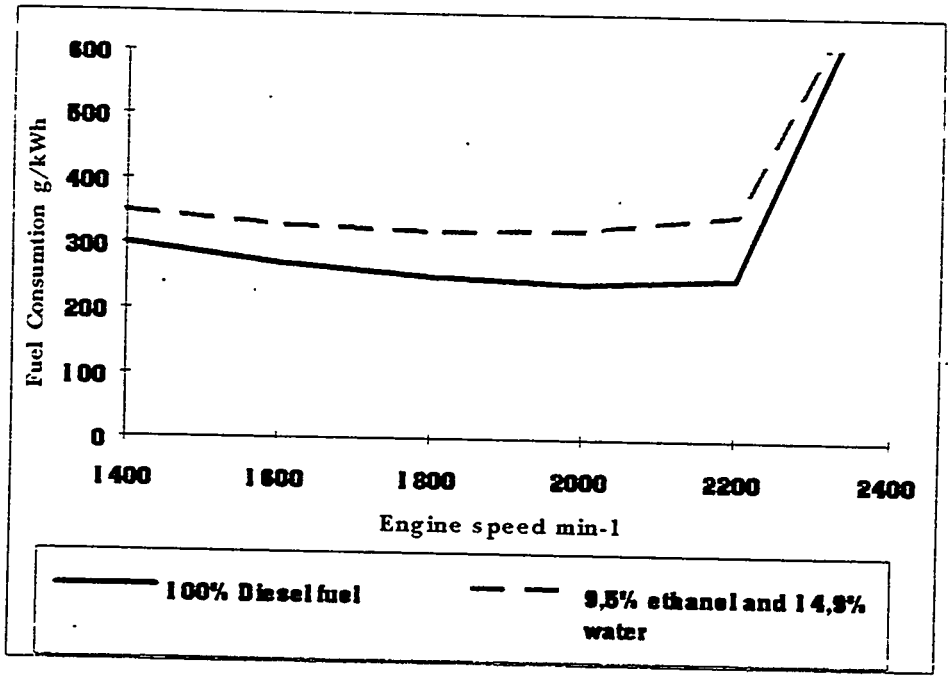


Figure 1b.

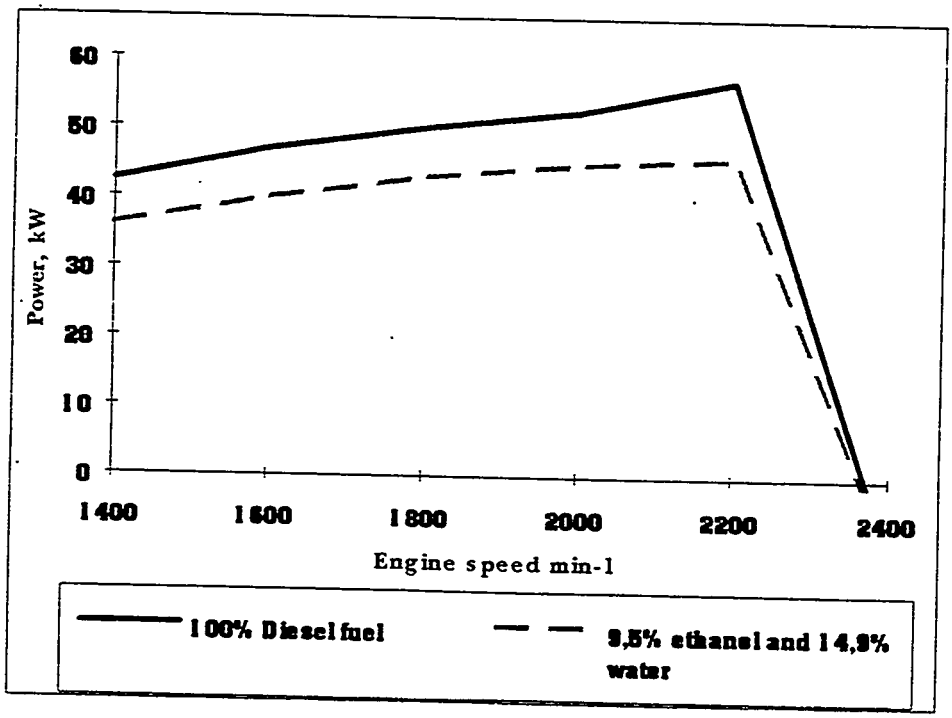


Figure 2.

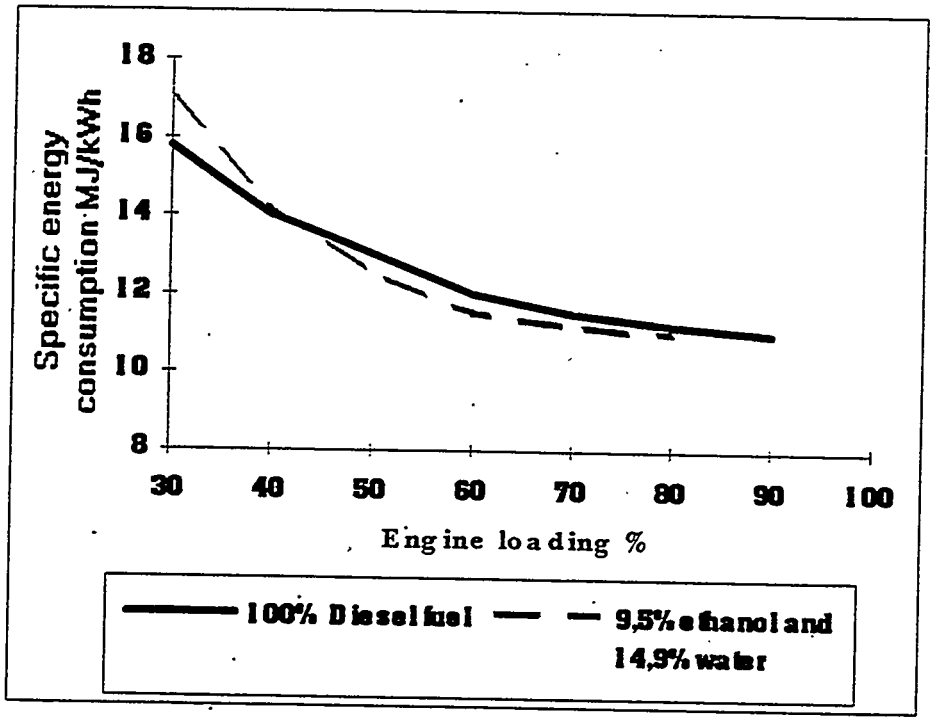
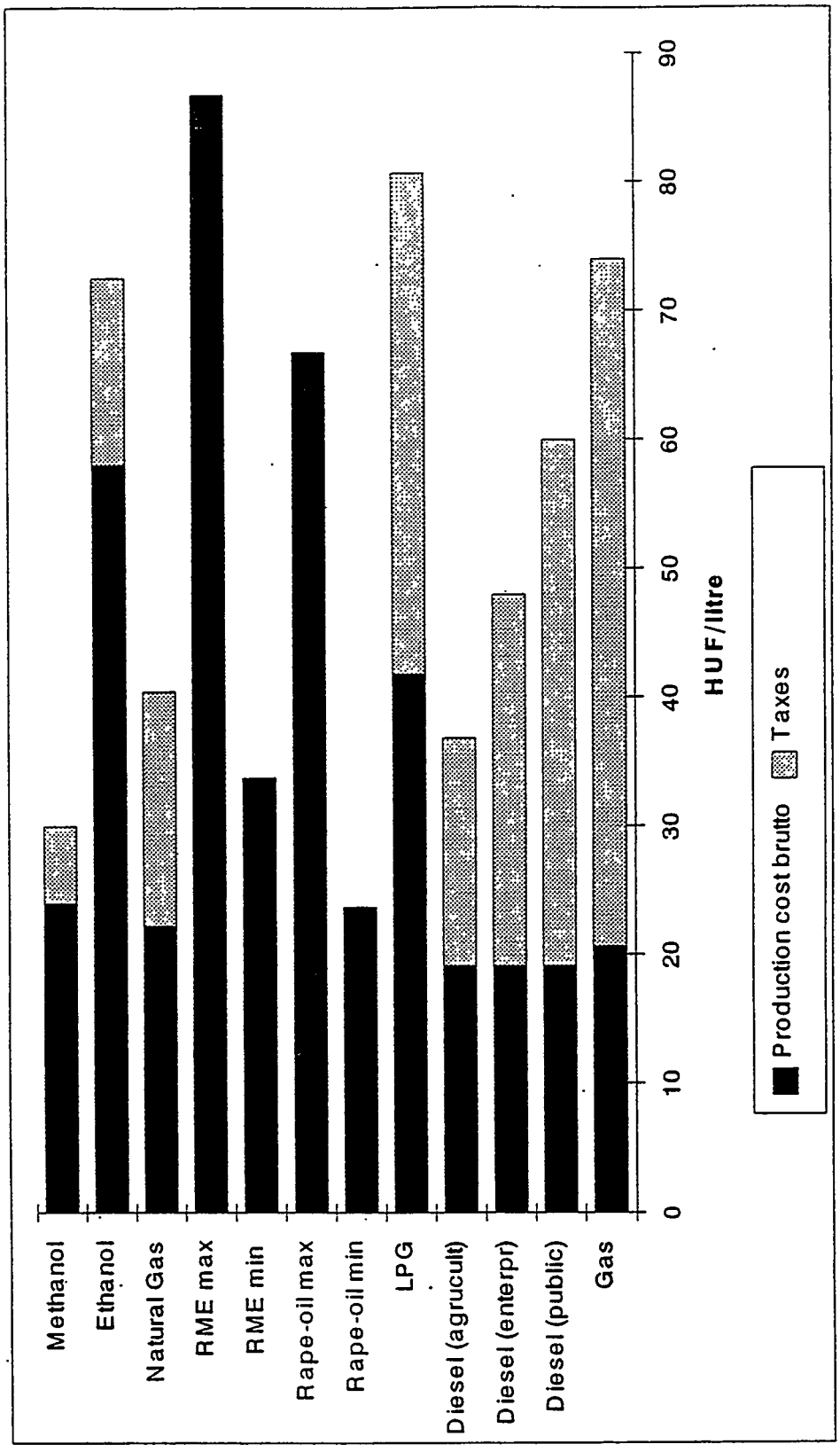

Specific energy consumption MJ/kWh
18
16
14
12
10
8
30
40
50
60
70
80
90
100
Engine loading %
100% Diesel fuel
9,5% ethanol and 14,9% water

Figure 3.


Methanol
Ethanol
Natural Gas
RME max
RME min
Rape-oil max
Rape-oil min
LPG
Diesel (agrucult)
Diesel (enterpr)
Diesel (public)
Gas
0
10
20
30
40
50
60
70
80
90
HUF/litre
Production cost brutto
Taxes

TOTAL FUEL CYCLE EMISSIONS ANALYSIS OF BIOMASS-ETHANOL TRANSPORTATION FUEL

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Abstract

The National Energy Strategy (NES) and the Clean Air Act Amendments (CAAA) of 1990 support the development of alternative transportation fuels including oxygenates for reformulated gasoline. The U.S. Department of Energy (DOE) chose ethanol produced from lignocellulosic biomass as a high-priority option for research and development. Biomass includes lignocellulosic crops such as trees, grasses, and organic wastes. Ethanol from grain is not discussed in this paper. At the request of DOE, a fuel cycle analysis was completed to quantify the inputs and outputs of a hypothetical biomass-ethanol industry in the year 2010, and to compare the results to a similar analysis of reformulated gasoline. This paper is an excerpted summary of selected results from the final study *Fuel Cycle Evaluations of Biomass-Ethanol and Reformulated Gasoline Fuels, Volumes I and II.*

TOTAL FUEL CYCLE EMISSIONS ANALYSIS OF BIOMASS-ETHANOL TRANSPORTATION FUEL

Introduction

In 1991, the U.S. Department of Energy (DOE) unveiled its National Energy Strategy (NES), a framework of policy initiatives to increase energy efficiency and reduce U.S. dependence on imports and fossil fuels. The strategy endorsed a particular methodology, the full fuel cycle analysis, to quantify the costs and benefits of energy policy choices.

Many of DOE's policy choices involve alternative fuels, nonfossil fuels made from renewable energy resources such as biomass (wood, grass, and cellulosic wastes), wind, and solar radiation. Some wind and solar technologies are in the early stages of commercialization. Other technologies require more research and development to become commercial. Promising research results for the biomass-ethanol technology lead DOE to assume that a biomass-ethanol technology could be commercial by 2005 (or earlier with increased research and development budgets). Ethanol fuels could make a significant contribution to the transportation industry by 2010.

At the request of DOE, fuel cycle analyses were completed for a hypothetical biomass-ethanol industry in the year 2010 and for reformulated gasoline in the year 2010.

The objectives of this analysis were severalfold:

- Detail the biomass-ethanol technologies, including biomass production, ethanol production, and fuel end use.
- Describe a likely biomass-ethanol industry.
- Examine, and when possible, quantify the inputs, outputs, and environmental emissions attributable to the manufacture, storage, transportation, and use of ethanol fuel.
- Compare ethanol fuel cycle results to a similar study of reformulated gasoline.

This paper is an excerpted summary of selected results from the final study *Fuel Cycle Evaluations of Biomass-Ethanol and Reformulated Gasoline Fuels, Volumes I and II.* This paper will focus primarily on air emissions because the central issue of the public policy debate on alternative fuels is air quality.

Methodology

A total fuel cycle analysis is a research project with several steps. Step one quantifies the amount of inputs and outputs associated with the production, use, and disposal of a product. Step two estimates the impacts that inputs or outputs create. The third step involves assigning a value to the impacts and prorating the value on a unit measure to the original inputs or outputs. The end result is a cost-benefit measure that can be used to rank policy options.

This study focuses on step one of the total fuel cycle approach for two different fuels. The fuels are neat ethanol denatured with 5% gasoline (E95) and reformulated gasoline (RFG). We quantified inputs and outputs for the two fuel cycles, based on engineering designs, research trends, past industrial experience, and expert opinion. Because of the nature of precommercial technologies, the quantities of inputs, outputs, impacts, and their values are only projections. We hope that by quantifying the available information on inputs and outputs, future researchers will be able to estimate impacts under various scenarios. Due to the variability of sites, and the sensitivity of impacts to site characteristics, we believe that impact analysis is better done on a case-by-case basis.

Each fuel cycle was divided into five stages: feedstock production, feedstock transportation, fuel production, fuel transportation, and end use (Figure 1). The activities associated with each stage were identified (Figure 2) and characterized. Based on the technical characterizations, data was generated regarding the levels of inputs required and outputs and emissions generated by carrying out each

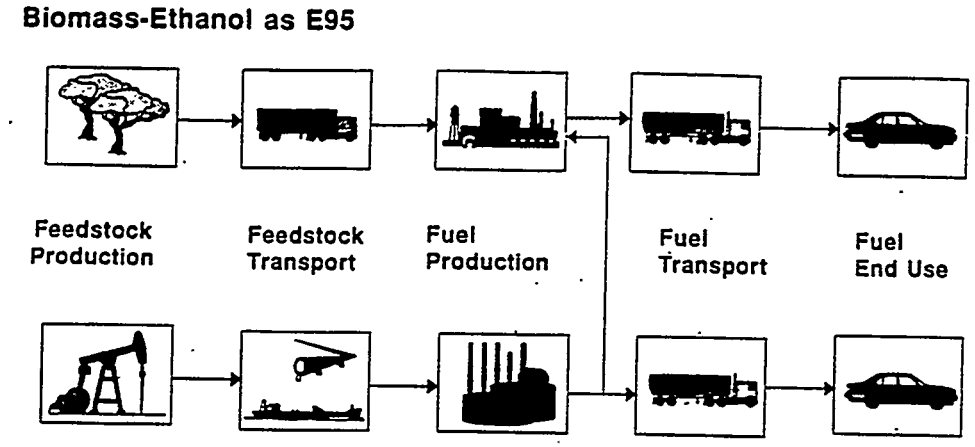


Figure 1. Fuel cycles evaluated

activity. The data collected for each fuel cycle were organized and maintained as an inventory for subsequent analysis. Exhibit 1 shows a sample of the types of data collected for each activity.

The E95 produced is used in dedicated ethanol vehicles. Both E95 and reformulated gasoline would be consumed by light-duty passenger vehicles that reflect engineering advances that could be possible by 2010.

Construction, exploration, and decommissioning activities were not included. The data inventories were prorated between coproducts (Figures 3 and 4). The data shown in this paper have already been allocated, and the emission estimates shown represent the contribution to the environment from fuel production and use. We assumed that a fledgling biomass-ethanol industry could exist by 2010. The ethanol would be produced from a mix of lignocellulosic crops: tree crops, referred to as short-rotation woody crops; annual crops, such as forage sorghum; and perennial grass crops, such as switchgrass. Five U.S. sites were modeled for biomass-ethanol production that represent reasonable locations and provide a range of differences that may be important from the standpoint of inputs and outputs (Figure 5).

Inputs	Outputs	Emissions
Feedstocks	Fuels	Air
• Crude oil	• Gasoline	• CO_2
• Biomass	• Ethanol	• CO
Fuels	Coproducts	• NO_x
• Diesel	• Refined	• VOC
• MTBE	products	• SO_2
• Natural gas	• Electricity	• Particulates
Chemicals		• Toxics
• Fertilizer		Wastewater
• Pesticides		Solid waste
• Catalysts		
Water		
Labor		
Electricity		

Exhibit 1. Fuel Cycle Data Inventory

Similarly, we assumed that the reformulated gasoline would be produced from a mix of domestic and imported crude oils by 2010. We also assumed that the refining industry would adopt various environmental controls that are under consideration today. The mix of petroleum products manufactured by the refining industry is taken from projections in the NES. The composition of reformulated gasoline is assumed to meet standards published in the CAAA (Exhibit 2).

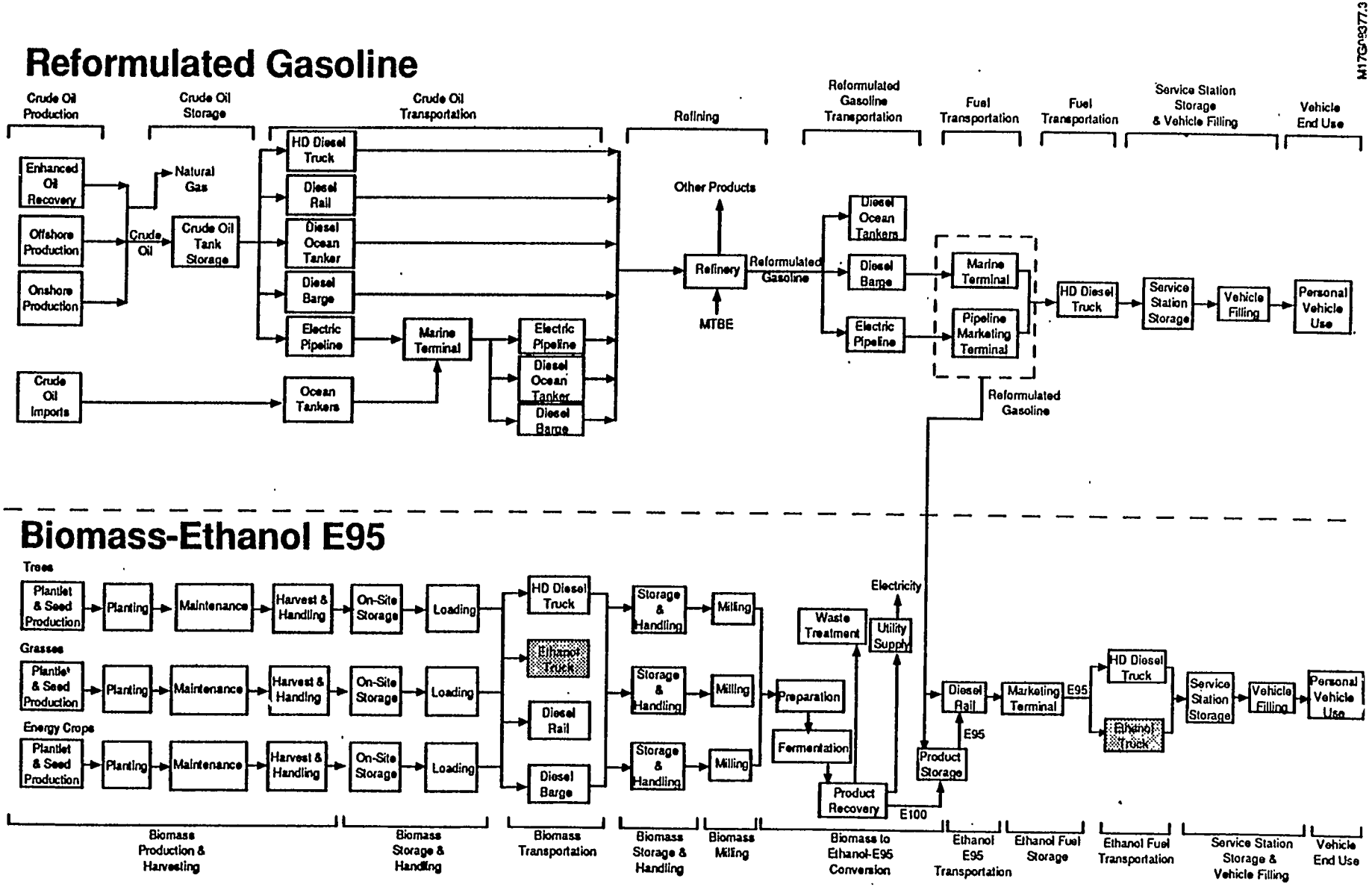


Figure 2. Activities included in the fuel cycle analyses

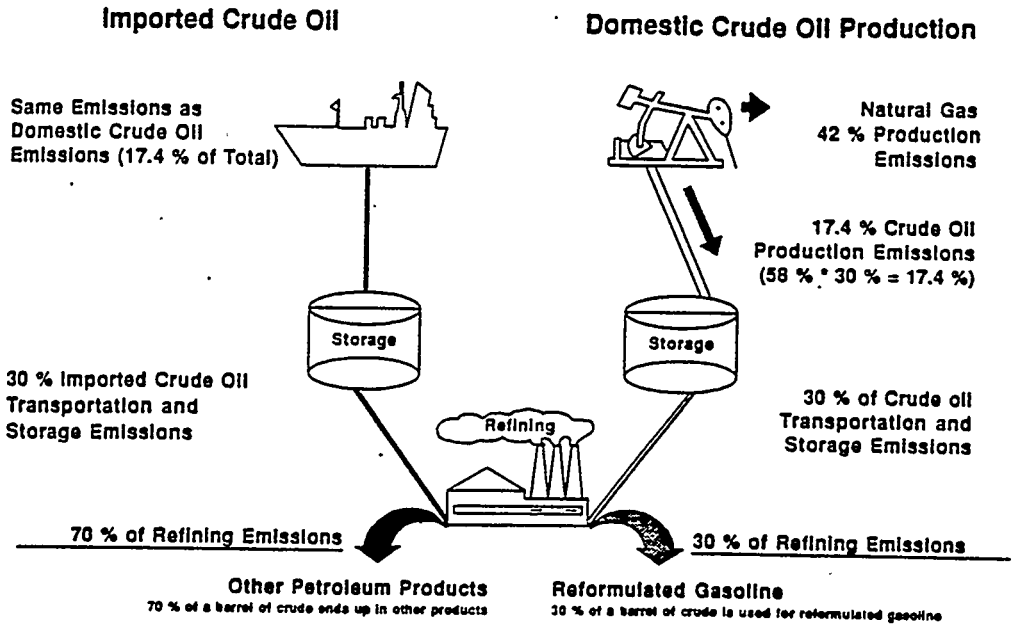


Figure 3. Allocation assumptions for crude oil reformulated gasoline fuel cycle

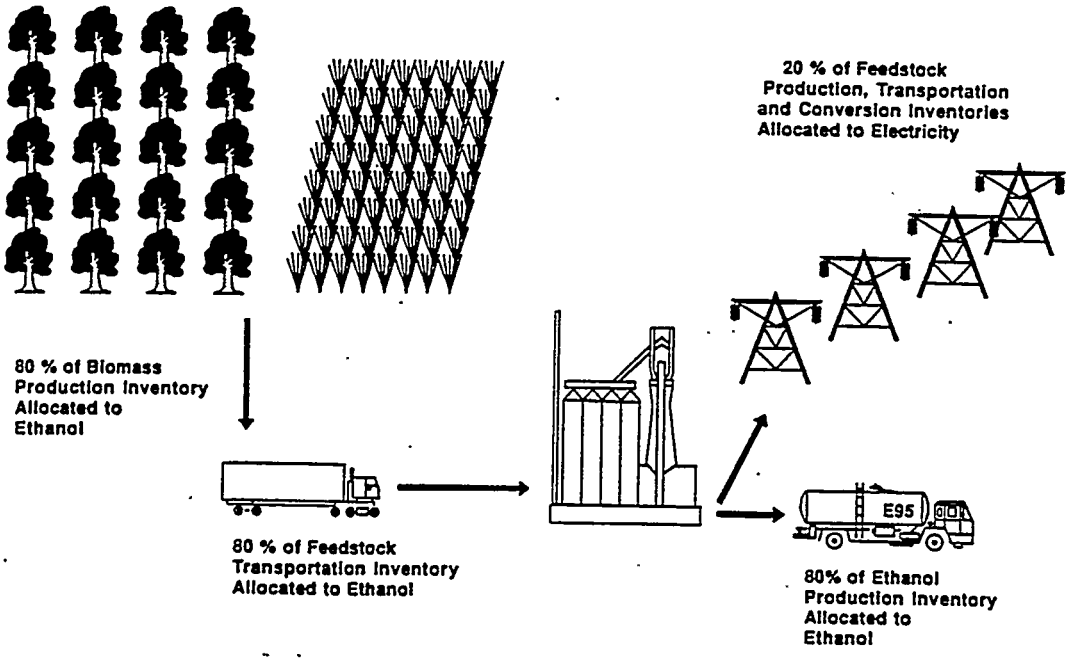


Figure 4. Allocation assumptions for the biomass-ethanol fuel cycle

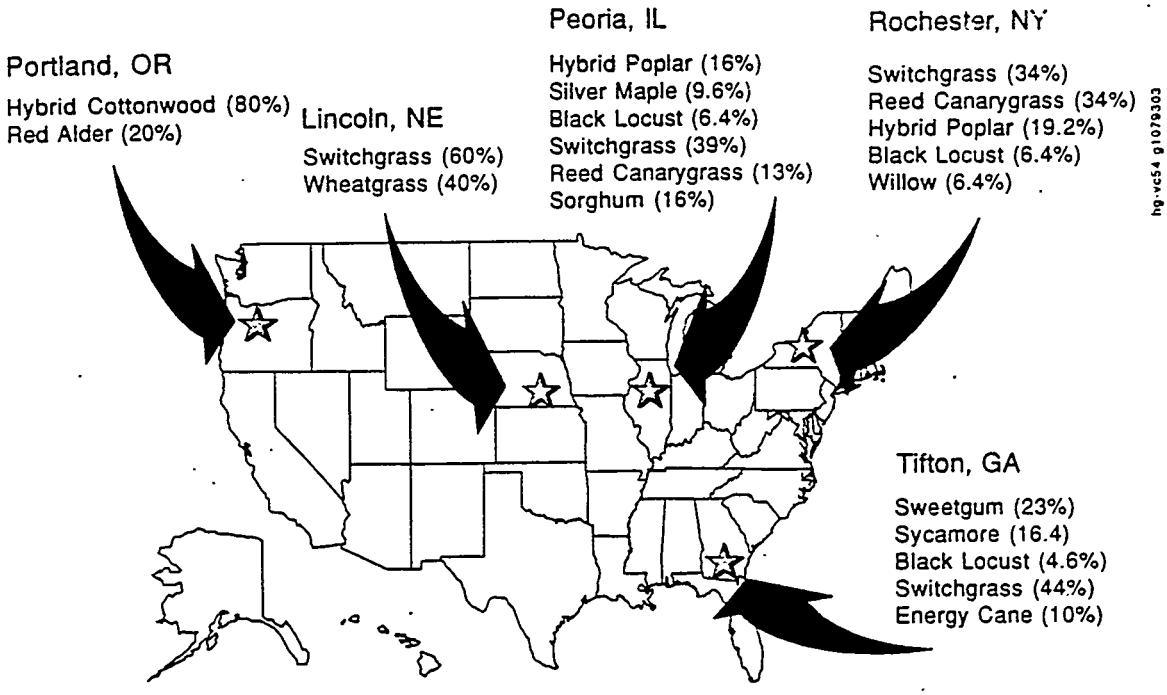


Figure 5. Biomass-ethanol fuel cycle feedstock locations and types

Based on engine efficiency projections for 2010, we assumed that the dedicated ethanol vehicle and the gasoline vehicle could attain 28.25 miles per gallon (mpg) and 35.6 mpg, respectively. Given the uncertainty of projecting technology advances in automobile performance, we assumed that automobile emissions would not exceed limits proposed by the U.S. Environmental Protection Agency (EPA) Tier II Standards for light-duty spark ignition vehicles. Thus, end use emissions are substantially similar for both vehicles; some differences are due to the composition of fuel.

In the original study, a fleet of light-duty passenger vehicles was assumed to travel 1 billion miles. The amount of fuel required to supply this fleet was determined from the fuel efficiency of the vehicles. The amount of inputs consumed and outputs created to produce and use enough fuel to travel 1 billion miles was summed over all of the activities in the fuel cycle. These sums were normalized to units per mile by dividing by 1 billion. Thus, the two fuel cycles can be compared on an equal basis—emissions per mile traveled.

Aromatic content: 25% by volume
Benzene content: 1% by volume
Olefin content: 15% by volume maximum
Oxygen content: 2% by weight
(15% MTBE assumed as additive)
Summer RVP (Reid vapor pressure): 8.5 PSI

Exhibit 2. Reformulated Gasoline Characteristics

Most fuel cycle estimates are provided as ranges because the performance of an industry can rarely be characterized by a single point estimate. Data or repeated estimates are required to create a probability distribution of values. In this case, we have created a model industry, in which all firms have identical resources and produce identical mixes of products and emissions. Without any introduced variation in engineering designs, product mixes, or feedstock mixes, we do not create any variation in the results Therefore, the results presented are point estimates that describe selected scenarios and are not projections of future industrial performances.

Results

This paper will focus primarily on air emissions because the central issue of the public policy debate on alternative fuels is air quality. Table 1 provides a summary of selected emissions from the ethanol and reformulated gasoline (RFG) fuel cycles by stage of production. The E95 estimates are averages of the emissions per mile for each ethanol production site shown in Figure 5. There are differences in the emission levels for the five cases. These are due to different feedstock compositions for each case. Most air emissions are produced in the end use stage, a combination of running losses and tailpipe emissions. From the distribution of emissions by stage, we conclude that advances in engine and vehicle technology could provide the most benefit in reducing air emissions.

The ethanol fuel cycle produces 6% to 8% more carbon monoxide (CO) than the gasoline fuel cycle, primarily as a result of the type of boiler and fuel used to power the ethanol plant. (Note that 92% of the CO emissions are produced in the end use stage.) The wastes produced from the ethanol conversion process are used to fire the boilers that provide plant heat and power. Enough wastes are produced to provide 15 MW_e electricity in addition to meeting facility requirements. The emissions from the biomass production, transportation, and conversion stages have already been allocated between the primary product, ethanol, and the coproduct, electricity.

There is no significant difference between the ethanol and gasoline fuel cycles with respect to the amount of nitrogen oxides (NO_x) produced. E95 offers nearly a 70% reduction in sulfur dioxide (SO_2) emissions compared to reformulated gasoline. Pure ethanol does not contain any sulfur compounds. The SO_2 emissions from the E95 and use stage are from the gasoline denaturant. Most of the SO_2 emissions from the E95 fuel cycle are produced during the combustion of wastes in the conversion facility's boilers. Protein in biomass contains sulfur, which is the source of SO_2 emissions from the boiler. Diesel fuel used in transportation and farming vehicles produces the remainder of SO_2 emissions in the E95 fuel cycle.

E95 fuels could reduce volatile organic carbon (VOC) emissions by 15% compared to reformulated gasoline, primarily because they are less volatile. The species of VOCs produced are different for the two fuel cycles. At this time, not enough information is available on dedicated

Table 1. Air Emission Summary by Fuel Cycle Stage (mg/mile)

Air Emission	Fuel	Feedstock Production	Feedstock Transport	Fuel Production	Fuel Transport	Fuel End Use	Fuel Cycle Total
CO	E95	43.5	7.3	100.0	2.0	1700	1853
	RFG	6.4	9.0	7.3	3.0	1700	1726
NO_x	E95	44.0	11.0	67.0	7.0	200	329
	RFG	37.0	21.0	66.0	5.0	200	329
SO_2	E95	2.0	0.8	21.0	0.2	3.7	27.7
	RFG	5.0	0.9	40.0	0.3	40	86.2
VOC*	E95	10.0	2.0	18.0	17.0	160	207
	RFG	13.0	12.0	4.0	35.0	180	244

*Nonbiogenic VOCs

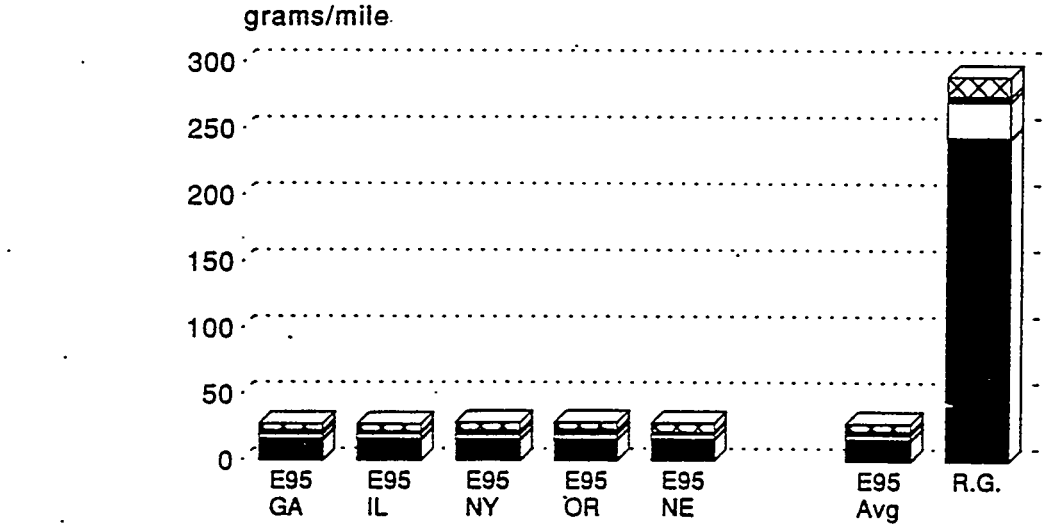
ethanol engines designed to meet CAAA standards to predict the composition of VOCs.

E95 fuels can reduce net CO_2 emissions by 91% compared to reformulated gasoline (Figure 6). The regeneration of feedstock crops offsets the combustion of organic wastes in the boiler and the combustion of E95 in vehicle engines. Only net CO_2 emissions are included in Figure 6. The CO_2 emissions created in the E95 fuel cycle result from the denaturant used and emissions produced by diesel vehicles used in farming and transportation. Substitution of organically derived fuels (vegetable oil esters) for diesel could provide further benefits in the form of CO_2 reductions.

An overall energy balance was conducted for each case based on the levels of feedstock and fuel inputs and fuel outputs. An analysis of fossil energy inputs showed that only 1 Btu of fossil fuel energy is required to produce 4.07 Btu of E95, but 1 Btu of fossil fuel energy produces only 0.79 Btu of reformulated gasoline. Most of the energy consumed in the E95 fuel cycle is in feedstock production, E95 distribution, and transportation. Most of the energy consumed in the reformulated gasoline fuel cycle is in refining and fuel distribution and transportation. When the relative engine energy efficiencies are taken into account (miles/fuel energy input), the E95 fuel cycle has about 5.8 times the fossil energy efficiency of the gasoline fuel cycle. Using more ethanol fuels to replace gasoline can extend our limited supplies of oil over a longer period. Other benefits include energy diversity, lower foreign payments for imported crude oil, and a larger domestic energy production base.

Conclusions

Based solely on quantities of emissions, we cannot claim that ethanol is preferred over gasoline. However, E95 provides a number of benefits, such as a 90% reduction in net CO_2 emissions, nearly a 70% reduction in SO_2 emissions on a per-mile basis, and 5.8 times the fossil energy efficiency of gasoline fuel cycles. Both E95 and reformulated gasoline produce similar amounts of CO, NO_x, and nonbiogenic



	E95 GA	E95 IL	E95 NY	E95 OR	E95 NE		E95 Avg	R.G.
Feedstock Production	5.12	5.65	6.1	5.47	6.7		5.81	14.7
Feedstock Transport	2.56	1.64	2.9	3.6	1.66		2.47	4.08
Fuel Production	3.61	3.61	3.61	3.61	3.61		3.61	26.94
Fuel Transport	1	1.09	0.64	0.82	0.91		0.89	1
Fuel End Use	15.12	15.12	15.12	15.12	15.12		15.12	243

Figure 6. Carbon dioxide emissions

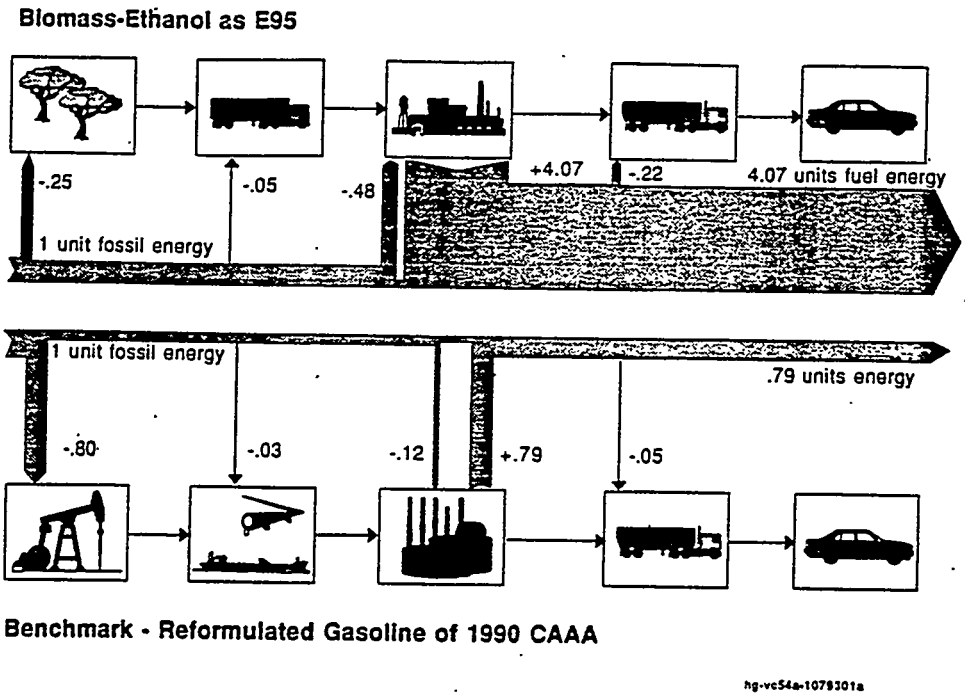


Figure 7. Fossil energy inputs and fuel energy outputs

VOCs. (Differences may not be statistically significant.)

The most immediate use of this study has been to identify where information is missing, such as the composition of VOCs from various sources, and to target research and development toward issues that may lead to the largest benefits. The quantitative results in this report can be used to estimate environmental and social impacts associated with ethanol production. These results, once evaluated and transformed into monetary estimates, can be used to rank alternative transportation fuels. Only if the goal is specific—such as the reduction of CO emissions—can this study be used to establish the priority of either fuel.

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ENERGY AND CRUDE OIL INPUT REQUIREMENTS FOR THE PRODUCTION OF REFORMULATED GASOLINES

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Abstract

The energy and crude oil requirements for the production of reformulated gasolines (RFG) are estimated. Both the energy and crude oil embodied in the final product and the process energy required to manufacture the RFG and its components are included. The effects on energy and crude oil use of using various oxygenates to meet the minimum oxygen content level required by the Clean Air Act Amendments are evaluated. The analysis illustrates that production of RFG requires more total energy than that of conventional gasoline but uses less crude oil. The energy and crude oil use requirements of the different RFGs vary considerably. For the same emissions performance level, RFG with ethanol requires substantially more total energy and crude oil than RFG with MTBE or ETBE. A specific proposal by the EPA designed to allow the use of ethanol in RFG would increase the total energy required to produce RFG by 2% and the total crude oil required by 2.0 to 2.5% over that for the base RFG with MTBE.

ENERGY AND CRUDE OIL INPUT REQUIREMENTS FOR THE PRODUCTION OF REFORMULATED GASOLINES

Introduction

The Clean Air Act Amendments (CAAA) of 1990 require that, beginning in 1995, reformulated gasoline (RFG) replace conventional gasoline in the nine worst ozone nonattainment areas in the United States with a 1980 population of 250,000 or more (Section 211(k)). All other ozone nonattainment areas may also require the use of RFG as an element of their states' State Implementation Plans. The CAAA establishes general requirements to be met by RFG (nitrogen oxide emissions and oxygen, benzene, and heavy metals content), as well as a requirement that RFG meet the more stringent of either a formula or performance standard for volatile organic compounds (VOC) and toxic air pollutants. The performance standards are more stringent for 2000 than 1995. The U.S. Environmental Protection Agency (EPA) is responsible for promulgating the regulations implementing the RFG program.

The CAAA state that in developing the RFG regulations, the EPA should require the greatest reductions achievable in ozone-forming VOC and toxic air pollutant emissions, taking into consideration the cost of achieving the emission reductions, any nonair-quality- and other air-quality-related health and environmental impacts, and *energy requirements* (Sec. 211(k)(1)). This paper analyzes the energy and crude oil input requirements associated with the production of various RFGs that would meet the EPA RFG program requirements. Differences in energy and crude oil use among RFGs meeting the same performance standards exist for a number of reasons. In particular, the oxygenates used to provide the required oxygen content for RFGs vary in volume, energy content, volatility, and energy required to produce them. The oxygenates, in turn, affect the volume and composition of the hydrocarbon portion of the RFG.

The specific stimulus for this analysis is the February 1993 EPA Notice of Proposed Rulemaking (NPRM) on RFG, which would allow RFG blended with ethanol to meet a lesser VOC reduction standard (Phase I and II) or a lesser Reid vapor pressure (RVP) standard (Phase I) than RFGs produced with other oxygenates (FR Vol. 58, No. 37). (Phase I RFG is required from 1995 through 1999, and Phase II RFG is required beginning in 2000.) However, the results of the analysis are more generally applicable than to the proposal above. Alternative forms of using ethanol in RFG other than that proposed are considered in this analysis (e.g., ethanol in ethyl tertiary butyl ether [ETBE]). This paper also provides estimates of energy and crude oil requirements associated with RFG with methyl tertiary butyl ether (MTBE), as well as such requirements associated with the production of conventional and oxygenated gasolines for use in the carbon monoxide (CO) control program.

Methodology

Analysis Framework

Both feedstock and process energies are estimated in this analysis. For each type of RFG, the volume and type of feedstock (hydrocarbon, alcohol, isobutylene) required for the gasoline and oxygenate components are estimated. The process energies are also estimated by amount and type for refining the hydrocarbons and producing the alcohols, the isobutylene, and the ethers. Together, these process energies and feedstocks define the composite energy requirements of RFG with MTBE, ethanol, and ETBE as oxygenates. The crude oil component of the total energy requirements is specifically identified. The various RFGs are evaluated on the basis of delivering equal energy for constant vehicle miles travelled (VMT).

The analysis focuses on the production of year 2000 summer (VOC-controlled) RFGs. The RFGs contain 2.1% oxygen by weight, incorporating a compliance margin to meet the CAAA requirement of 2.0%. The RFGs are produced in a modeled, typical Petroleum Administration Defense District (PADD) II (Chicago area) complex refinery. The Chicago area is one of the nine areas required to use RFG and is a key market for fuel ethanol sales. Although RFG production will vary among PADDs, we believe the direction of the results presented below would be the same in other PADDs.

The refinery-related energy and oil inputs required to produce several gasolines were calculated by Turner, Mason and Co. (TM) for the National Petroleum Council (NPC) Refining Study, which used the TM refinery linear programming (LP) model (Turner, Mason, and Co. 1993). LP model runs were used to estimate the energy and oil required (1) to produce RFG with MTBE only and (2) to produce a mixed RFG pool, with 70% of the RFG using MTBE as the oxygenate and 30% using ethanol. Both of the oxygenates were used at the 2.1% oxygen content level, consistent with the requirements of the February 1993 EPA NPRM. Both the RFG with MTBE only and the mixed RFG pool were held to the same VOC performance levels (41%, per the April 1992 version of the EPA's proposed complex model). The total energy content of the total volume of RFG produced daily (i.e., volume × specific energy content) and other key product characteristics and product volumes (e.g., diesel fuel) were held constant. The refinery model was allowed, within these constraints, to optimize on cost.

Ethanol may be used in RFG in other ways than that proposed by EPA. This analysis examines two such additional uses: all the RFG being produced with ethanol only and with ETBE only. The NPC Refining Study did not include separate runs for either of these RFGs. However, data from the LP model runs just presented and other available LP model runs (which evaluated the energy and oil impacts of changes in the RVP of the hydrocarbon portion of the RFG) were used to approximate the change in the RFG hydrocarbon energy and oil input requirements for these two cases. As with the other RFGs analyzed in this report, these two RFGs comply with EPA's RFG performance standard requirements. The NPC Refining Study also provided an LP model run for conventional gasoline produced in PADD II.

Argonne National Laboratory (ANL) developed a spreadsheet model that incorporates (1) the above computations of energy and oil use in the refinery production of RFG and (2) other estimates of the energy required to produce the various oxygenates outside the refinery. The model also normalizes both sets of estimates to the delivery of equal energy content.

Key Assumptions and Inputs

The key assumptions and inputs for this analysis include the following:

- The PADD II Complex Refinery Model producing 100% RFG is representative of the gasoline refining situation that would exist if the regulations were imposed as proposed.
- The VOC standard for 2000 is such that the refinery must operate at the "knee" in the VOC/cost curve, with a cost-effectiveness value of about $10,000 per summer ton of VOC reduced.
- All marginal changes in isobutylene demand for ether production in merchant ether plants are derived from natural gas liquids.
- Ethanol, methanol, and ether production is as described in the sources referenced below.

RFG Energy and Crude Oil Requirements

Volume of RFG Required to Deliver Equal Energy Content

Four RFGs or RFG product mixes are compared in Table 1: RFG with MTBE, RFG with ETBE, RFG with ethanol, and a mixed RFG pool containing both MTBE and ethanol that would satisfy the recent EPA proposal that (up to) 30% of the RFG sold in northern nonattainment areas contain ethanol. Also represented is conventional gasoline sold or likely to be sold in PADD II in the absence of regulations requiring RFG; it contains 2% MTBE.

For each of the gasolines, Table 1 presents (1) the volume of hydrocarbons, ethers, and ethanol in the gasoline needed to achieve the 2.1% oxygen content ("initial volume") and (2) the energy content of a gallon of the gasoline. These estimates are based on the oxygen content and energy content estimates for the various gasoline components presented in Table 2.

Table 1 also presents, for each gasoline, the volume of gasoline required to deliver the same total energy as is delivered by a gallon of RFG with MTBE at 2.1% oxygen ("revised volume"). The remaining analysis is based on these revised fuel volumes. RFG with MTBE serves as the baseline for this analysis because it is currently considered the most likely oxygenate. The RFGs are actually very similar in terms of the volume of fuel required to deliver the same energy. As expected, because of the addition of oxygen and the subsequent lower energy content of RFG, a greater volume of RFG is required than is the case with conventional gasoline.

Feedstock Requirements

The crude oil content of the gasolines varies as shown in Table 1. The estimates of crude oil content take into account the feedstock used to produce these components, but not the process energy requirements.

The hydrocarbon portion of gasoline is assumed to come from 100% crude oil feedstock. In fact, some natural gas (as hydrogen) and some natural gas liquids (NGLs) are used as feedstocks, and their proportion of the final fuel may vary across gasoline formulations. We have not accounted for this potential shift in feedstock.

The crude oil content of ETBE and MTBE reflects the crude oil feedstock used to produce the isobutylene component of these ethers. Ethanol and methanol have 0% crude oil content. Isobutylene may be produced from crude oil or NGLs. In this analysis, we assume that all isobutylenes produced outside the refinery and used to make ethers outside the refinery are derived from NGLs. These NGLs are assumed to be derived from natural gas-related sources, not crude oil. We also assume that the isobutylenes used within the refinery to produce ethers are made from crude oil.

The proportion of isobutylene used within the refinery to produce ethers is derived from the NPC Refining Study. For that study, TM developed estimates of the materials that would be used in the refinery in the production of various gasolines, both conventional and reformulated. Table 3 contains TM estimates of the raw materials that would be used in the refinery to produce the MTBE needed for RFG and conventional gasoline production. The listing of MTBE as a "raw material" implies that it (and its isobutylene content) is produced outside the refinery. Where methanol is listed as a "raw material," it is assumed that the isobutylene used with this methanol to produce MTBE is produced in the refinery. Thus, it is straightforward to estimate the proportion of the total MTBE produced within the refinery.

We estimate that, for the case where all the RFG contains MTBE, 7.5% of the ethers is produced within the refinery. For the RFG with MTBE that is part of the mixed RFG pool containing 30% RFG with ethanol, the TM estimates suggest that just 2% of the ether and isobutylene is produced within the refinery. These levels of internal ether production may appear low but are consistent with other process changes within the

TABLE 1 Energy and Crude Oil Content of 2.1% RFG

Fuel Type	Components	Initial Volume (gal)	Energy Content of Initial Volume (Btu)	Revised Volume to Deliver Equal Btu as RFG with MTBE Only (gal)	Revised Energy Content of Fuel (Btu)	Oil Content of Equal Btu RFG [Feedstock] (Btu)
RFG with MTBE at 2.1% O_2	HCs	0.883	101,142	0.883	101,142	101,142
	MTBE	0.117	10,912	0.117	10,912	647
	Total	1.000	112,053	1.000	112,053	101,789
RFG with ETBE at 2.1% O_2	HCs	0.867	99,272	0.866	99,175	99,175
	ETBE	0.133	12,891	0.133	12,879	665
	Total	1.000	112,163	0.999	112,053	99,840
RFG with Ethanol at 2.1% O_2	HCs	0.940	107,630	0.939	107,518	107,518
	ETOH	0.060	4,540	0.060	4,535	0
	Total	1.000	112,170	0.999	112,053	107,518
RFG Mix (70% RFG with MTBE at 2.1% O_2; 30% RFG with ETOH at 2.1% O_2)	HCs	0.900	103,088	0.900	103,056	103,056
	MTBE	0.082	7,638	0.082	7,636	121
	ETOH	0.018	1,362	0.018	1,362	0
	Total	1.000	112,088	1.000	112,053	103,177
CG in PADD II	HCs	0.980	112,210	0.963	110,216	110,216
	MTBE	0.020	1,871	0.020	1,837	1,032
	Total	1.000	114,081	0.982	112,053	111,248

refinery related to production of severely reformulated gasoline. Finally, we estimate that 71% of the smaller volume of MTBE produced for use with conventional gasoline in PADD II is produced internally.

No separate runs of the RFG made with ETBE were performed. In this analysis, we assume that the crude oil feedstock for isobutylene used in the production of ETBE is the same as that for MTBE only. Because the alcohol content of ETBE and MTBE differ, the crude oil content of the ethers themselves will differ.

The lowest crude oil content of all the fuels delivering equal energy is calculated to be that of RFG with ETBE, and the next-lowest is that of RFG with MTBE only. The mixed RFG pool uses more crude oil feedstock. The RFG with ethanol uses the most crude oil feedstock. All RFGs, of course, reduce crude oil use compared with that of conventional gasoline.

Process Energy Requirements

Estimates of the energy and crude oil used to produce the components of the various gasolines were derived from several sources. This section presents these estimates.

Energy and Crude Oil Required to Produce Hydrocarbons

As indicated above, TM refinery LP model runs determined the energy and materials that would be used in the production of various fuels. Table 3 presents a summary of the key results. The estimates were used to determine the energy and oil required to produce the hydrocarbons (HCs) used in the fuels.

TABLE 2 Oxygen, Alcohol, and Energy Content of Oxygenates and Hydrocarbons

Item	Oxygen/ Alcohol/Energy Content
Oxygen Content in RFG (%)	
2.1% O_2	13.30 ETBE
	11.67 MTBE
	6.00 Ethanol
2.7% O_2	17.10 ETBE
	15.00 MTBE
	7.71 Ethanol
Alcohol Content of Ethers (%)	
ETBE	42.5
MTBE	33.9
Energy Content (Btu/gal)	
Ethanol	75,670
Methanol	56,560
Isobutylene	94,000
ETBE	96,926
MTBE	93,528
HCs Typical in RFG	114,500
Butane	95,038

For all the runs of RFG and conventional gasoline, it was assumed that all the plant fuel, natural gas, and electricity used in the refinery are used to produce the HCs for motor gasoline, diesel fuels, and jet fuel. These three fuels represent over 75% of the products of the refinery. The diesel and jet fuel product volumes were held constant between the various RFG and conventional fuel runs and all the runs resulted in the production of an equal amount of gasoline energy for vehicular propulsion, so any differences in the energy and oil required per gallon of HCs produced were attributed to the different processing requirements of the various RFGs.

Table 4 presents these estimates for the three LP runs indicated in Table 3. The energy required to produce the HCs used in the mixed RFG pool is greater than for those used in the RFG with MTBE only, because the former HCs need to be more severely processed to achieve the incremental VOC reductions needed to offset the VOC increase from ethanol. Ethanol has a higher blending RVP than MTBE, which, if no other adjustments are made, increases the VOC level of the final fuel. Additional processing of the HC components is required to achieve a lower RVP level and maintain the same overall VOC level.

Table 4 also presents estimates of the energy required to produce the HCs used in RFG with ETBE only and RFG with ethanol only. No separate refinery runs were made for these fuels. 100% production of RFG with ethanol only would require even more severe processing of HCs than that of the HCs in the mixed RFG pool, and additional measures would have to be taken to produce an RFG that maintains the required VOC reduction. Thus, the energy required to produce these HCs is higher than for the HCs used in other RFGs. Because ETBE has a substantially lower blending RVP than MTBE, refiners could use higher-RVP HCs in the RFG. Use of these higher-RVP HCs should, at a minimum, result in lower plant fuel requirements because less processing of the HCs would be required. Several LP runs of RFG with MTBE and the mixed RFG pool were used to derive estimates of these changes in processing requirements.

Energy and Crude Oil Required to Produce MTBE

Table 5 presents estimates of the energy and crude oil required to produce ethers and ethanol. Estimates of the energy and crude oil required to produce MTBE are largely based on a report by Chem Systems (1992). This report provides estimates of the amount of plant energy required

TABLE 3 Refinery Products, Fuels Usage, and MTBE Raw Materials for PADD II Gasoline: 2000

Item	Base Case (No CAAA)	100% RFT (MTBE Only)	100% RFG (30% ETOH)
Products (Bbl/d)			
Gasoline	1.682E+06	1.713E+06	1.717E+06
(% Ether or Ethanol)	2	12	10
Diesel	6.820E+05	6.820E+05	6.820E+05
Jet Fuel	2.050E+05	2.050E+05	2.050E+05
Subtotal	3.569E+06	2.600E+06	2.604E+06
Plant Fuel Burned	2.306E+05	1.855E+05	2.007E+05
Other	3.620E+05	3.775E+05	4.293E+05
Total	3.162E+06	3.163E+06	3.234E+06
Fuels Used for Production (Bbl/d FOE[a])			
Plant Fuel Burned	2.306E+05	1.855E+05	2.007E+05
Natural Gas Purchased	3.290E+04	6.820E+04	7.090E+04
Electricity	4.021E+04	3.763E+04	4.183E+04
(kWh/d)	2.490E+07	2.330E+07	2.590E+07
Total (FOE)	3.037E+05	2.913E+05	3.134E+05
Raw Materials for MTBE			
MTBE	1.000E+04	1.840E+05	1.390E+05
Methanol	8.000E+03	5.000E+03	1.000E+03
Total MTBE Used	3.400E+04	1.990E+05	1.420E+05

[a] FOE: Fuel Oil Equivalent.

Sources: Turner, Mason, and Co., NPC Refining Study, Table F-3, 1/8/93 draft; Table Y-1, 3/30/93 draft; and unpublished information.

for various MTBE production processes. We assume use of the process in which MTBE is produced from field butanes and methanol. Feedstock for the plant energy and feedstock for the butanes and methanol are estimated on the basis of this report and a report on greenhouse gas emissions by DeLuchi (1991).

Several assumptions deserve comment. First, we assume that the Btu ratio of natural gas feedstock to methanol produced is 1.5:1. The Chem Systems report suggests a lower ratio, but the one we are using is consistent with the references cited by DeLuchi. Second, all the ether plant energy use is assigned to the production of the ether; we do not account for the fuel gas by-products that are also produced. Third, we assume that the energy required to produce the field butanes and natural gas used in the system is negligible.

As indicated above, some MTBE will be produced within the oil refinery. The final estimates used in the analysis are weighted to

TABLE 4 Plant Fuel Burned and Other Purchased Fuels to Produce HCs

Fuels	Energy in Plant Fuel Burned, Natural Gas, and Electricity to Produce HCs (Btu/Btu HC Produced)	Energy in Plant Fuel Burned to Produce HCs (Btu/Btu HC Produced)
Base Case	0.155	0.118
RFG with MTBE Only	0.158	0.090
RFG with 70% MTBE and 30% ETOH	0.173	0.100
RFG with ETBE Only	0.156	0.087
RFG with ETOH Only	0.208	0.125

account for the fact that MTBE plant energy would not be used in their production.

Energy and Crude Oil Required to Produce Ethanol

The energy requirements for corn and ethanol production were derived from a paper by Marland and Turhollow (1991). Their paper provides estimates of the energy and crude oil required to produce ethanol without accounting for by-products of the ethanol production process. However, it also provides estimates of the CO_2 emissions associated with ethanol production; these estimates do account for by-products. Turhollow indicated that the proportion of gross CO_2 emissions that their paper assigns to by-products could also be applied to the energy and crude oil use associated with the production of ethanol (Turhollow 1993). We did this, and the results are presented in Table 5.

The Marland and Turhollow estimates are representative of current industry best practice. Ethanol produced to meet incremental RFG demand may be nearer to industry average, and thus more energy-intensive, than indicated here.

TABLE 5 Energy and Crude Oil Required to Produce Ethers and Ethanol (outside the refinery)

	Btu Required per Gallon of Oxygenate	
Oxygenate	Energy	Crude Oil
MTBE	17,941	0
ETBE	32,116	2,281
Ethanol	65,547	6,292

Energy and Crude Oil Required to Produce ETBE

We adapted the MTBE production process to develop estimates of the ETBE production process. This may slightly understate ETBE process energy because additional distillation steps are required in ETBE production to achieve the required water removal. The major adaptation is the substitution of the energy required to produce ethanol for that of methanol.

Energy and Oil Required to Produce RFG

Table 6 gives the final estimates of the energy and crude oil required to produce the various RFGs and conventional gasoline on the basis of delivering equal energy content. RFG with MTBE only requires the least energy of all RFGs, while RFG with ethanol requires the most. RFG with ETBE requires the least crude oil, while RFG with ethanol again requires the most.

Total Energy and Crude Oil Requirements for RFG at 2.1% Oxygen Content

Table 6 also gives the estimates of the total energy required to deliver equal energy for propulsion using year 2000 RFG (at 2.1% oxygen). If RFG with MTBE is the base fuel, the results presented in this table and Table 7 indicate that the least energy-intensive of the RFG options is RFG with MTBE only. RFG with ETBE and the mixed RFG pool require

TABLE 6 Energy and Crude Oil Required to Produce 2.1% RFG and Total RFG Energy and Crude Oil Requirements

Fuel Type	Components	Energy Required to Produce Equal Btu RFG (Btu)	Oil Required to Produce Equal Btu RFG (Btu)	Total Energy Required to Deliver Equal Btu RFG (Btu)	Total Oil Required to Deliver Equal Btu RFG (Btu)
RFG with MTBE at 2.1% O_2	HCs	15,996	9,060	117,138	110,202
	MTBE	2,037	0	12,949	647
	Total	18,033	9,060	130,087	110,849
RFG with ETBE at 2.1% O_2	HCs	15,469	8,667	114,643	107,842
	ETBE	4,203	303	17,081	969
	Total	19,671	8,970	131,725	108,811
RFG with Ethanol at 2.1% O_2	HCs	22,314	13,434	129,832	120,952
	ETOH	3,531	339	8,067	339
	Total	25,845	13,773	137,899	121,291
RFG Mix (70% RFG with MTBE at 2.1% O_2; 30% RFG with ETOH at 2.1% O_2)	HCs	17,841	10,336	120,897	113,392
	MTBE	1,454	0	9,090	121
	ETOH	1,060	102	2,422	102
	Total	20,356	10,438	132,409	113,615
CG in PADD II	HCs	17,066	12,957	127,282	123,173
	MTBE	263	0	2,101	1,032
	Total	17,329	12,957	129,382	124,205

TABLE 7 Relative RFG Energy and Crude Oil Requirements[a]

Fuel Type	Total Energy Use vs. RFG with MTBE	Total Crude Oil Use vs. RFG with MTBE
RFG with MTBE at 2.1% O_2	1.000	1.000
RFG with ETBE at 2.1% O_2	1.013	0.982
RFG with ETOH at 2.1% O_2	1.060	1.094
RFG mix at 2.1% O_2	1.018	1.025
CG in PADD II	0.995	1.120

[a] Based on Table 6.

approximately 1.3-1.8% more energy. RFG with ethanol requires nearly 6% more total energy. The least crude oil used to deliver equal energy for propulsion is for RFG with ETBE: 1.8% less than the base RFG. The mixed RFG pool increases the use of crude oil over the base by 2.5%. RFG with ethanol increases crude oil use by over 9%. All these RFGs require more total energy than conventional gasoline. All use less crude oil than conventional gasoline.

A second mixed RFG pool was evaluated, though it is not shown in the tables. The EPA proposal would allow the ethanol content to be as much as 2.7% oxygen content by weight. Our analysis indicates that this mixed pool would use 2.0% more energy and 2.1% more crude oil than RFG with MTBE only.

Total Energy and Crude Oil Requirements for Gasolines Used in the CO Control Program

We used a similar process to develop estimates of the energy and crude oil requirements for gasolines used in the CO control program. A 2.7% oxygen content level is required in CO nonattainment areas for a portion of the year (typically 4-5 months). Areas requiring the use of RFG year-round will require that the oxygen content level of the RFG be raised during these months (CO control program RFG). Areas not using RFG will simply require CO control program oxygenated gasoline (OG).

The CO control program RFGs are assumed to differ from the RFGs with 2.1% oxygen content only in the proportion of oxygenates and HCs in the final fuel. For a given oxygenate, the OGs will use the same volume as the CO control program RFGs to achieve the 2.7% oxygen content level. We assume that the energy required to produce the HCs used in OG will be the same as that for conventional gasoline.

The results of this analysis indicate that OGs have lower energy requirements than their counterpart CO control program RFGs but use more crude oil. RFG or OG made with ethanol requires greater energy and crude oil use than RFG or OG made with MTBE or ETBE. Ethanol blends currently used (e.g., 10% ethanol) increase total energy use by 3.2% and total crude oil use by 5.8% vs. CO control program RFG with MTBE at 2.7%. As before, all the fuels presented use more total energy but less crude oil than conventional gasoline.

Conclusions

Our analysis indicates that RFG requires more energy but less crude oil to produce than conventional gasoline. Using RFG with MTBE as a base and normalizing the results so that all RFGs deliver equal energy for propulsion, the least energy-intensive of the RFG options is RFG with MTBE only. RFG with ETBE and the mixed RFG pools of MTBE and ethanol (which would fulfill EPA's February 1993 RFG NPRM) require approximately 1.3-2.0% more energy. RFG with ethanol requires nearly 6% more total energy.

The least crude oil used to deliver equal energy for propulsion is for RFG with ETBE: 1.8% less than the base RFG. The RFG product mixes increase the use of crude oil over the base by 2.1-2.5%. RFG with ethanol alone increases crude oil use by over 9%.

Use of oxygenates at a 2.7% level in the winter does not alter the direction of these results. Non-reformulated oxygenated gasolines have lower total energy requirements than their corresponding RFGs but use more crude oil.

The specific impetus for this report was the EPA proposal that would allow RFG blended with ethanol to meet a lesser VOC reduction standard than RFGs with other oxygenates. If implemented, the proposal would cause increased energy use of 1.8 to 2.0%, depending on the oxygen level (2.1 or 2.7%) achieved with the ethanol portion of the mixed RFG pool. Crude oil use would increase by 2.1 to 2.5%.

The results reported here are based on a number of assumptions and are focused on RFGs produced in one area of the country. Changes in assumptions would obviously change the calculated estimates. However, we believe that the general direction of the results is likely to remain the same across regions and with all but drastic changes in production process assumptions.

Acknowledgment

The authors acknowledge the valuable assistance of Kevin Stork, U.S. Department of Energy intern, and significant data inputs from Bob Cunningham of Turner, Mason & Co., working for the National Petroleum Council; Oak Ridge National Laboratory; and Chem Systems, Inc. We would also like to thank Mr. Cunningham; Richard Long, Ashland Petroleum Co.; and Robert Warden, Chevron Research and Technology Co., for their review of this analysis. This work was supported in part by the U.S. Department of Energy, Office of Policy, Planning, and Program Evaluation, under contract W-31-109-Eng-38.

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THE LIFE OF FUELS

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Abstract

Although an interesting concept, a zero emission vehicle (ZEV) does not and cannot exist. There is no use of energy or use of resource that does not have an environmental impact, either before, during, or after its use in a vehicle.

Admittedly, application of different technologies in engines and vehicles may alter the environmental impact that the use of energy creates. Consideration must also be given to the environmental impact resulting from the series of activities that occur prior to the resource becoming a fuel and delivery of the fuel to the end user.

By examining the activities that occur during resource production, extraction, conversion/processing, refining, cultivating, and compressing, one may obtain a new perspective on which resource and which end-use technology offers

- Energy efficiency
- The best use of different fuels from the point of view of
  - The local environment
  - Global warming
  - Resource use (sustainability)
  - Technology.

This paper examines 16 different fuels from "cradle to grave." The base case conditions used in this study are particular to Sweden, although most of these conditions are not too different from those in other

countries. The infrastructure cost and consequences, such as platforms, roads, refineries, and service stations, are not taken into account because the focus of this study is on fuels.

Gasoline, diesel oil, propane, methane, methanol, ethanol, rapeseed methyl ester (RME), hydrogen, and electricity are considered in this study. The total energy efficiency, greenhouse gas emissions, and acid gas emissions for each fuel use scenario are calculated and reported.

When considering their fuel cycle, fossil fuels are the most energy efficient, with little difference between the most efficient (diesel and natural gas) to the least efficient (methanol from natural gas). Fossil fuels have a decided advantage over renewable fuels because of the extensive amount of work that has been done to advance the refining and processing technology over the past 100 years. The production and processing technologies that support renewable fuels are relatively modest by comparison, both in terms of time and research and development (R&D) investments.

To minimize greenhouse gas emissions, non-fossil fuels should be developed and used. Biologically derived alcohol fuels should be favored, with increasing volumes to displace fossil fuels, while the "greenhouse" debate goes on. The most significant acid gas emissions reductions can be obtained by using Otto cycle engines.

Use of simple fuels such as methanol, ethanol, methane, and electricity produce the largest reductions in toxic gas emissions.

Given the wide range of feedstocks available for alcohol fuels production, the alcohols could become a dominant force in the fuel market, leading to greater diversification of the raw material supply.

The Fundamental Conflict of Transportation

The transportation sector suffers from an imbalanced inner battle. Modern society places significant demands on the transport of people and cargo. The privilege of meeting social obligations, such as attending weddings, the theater, and restaurants has been granted to every citizen (who so desires and can afford the cost) by virtually all governments. Exercise of this privilege produces negative environmental impacts.

It is incumbent on society and governments to take action and establish a direction that will minimize environmental impact and offer continuous technological improvement, until our collective goals and objectives are met without sacrificing environmental quality. It is not practical to work or wait for a final solution; in most respects, it is simply too large a step. If society or the scientific community tries to take too large a step, the "best will be the enemy of the good," and we need the good in order to get the best. An approach of taking advantage of incremental technological improvements would be the wisest course of action.

The Price of Transports

In today's transportation environment, low costs allow for the proliferation of far-flung enterprises; Finland buys coal for heating from Australia; Italy buys milk from Denmark and makes yogurt to sell in Sweden; and Holland produces tomatoes, trucks them to Moscow, and ships them all over the world by air because the airport tariffs are lower in Moscow.

The price of transportation is too low from an environmental and a resource conservation point of view.

There is historical significance to low transportation costs; it underpins free market competition on a national and international basis by providing access to the markets. Low-cost transport provides freedom of movement (liberty) for both people and goods, and has come to be interpreted as an individual's right. Consequently, we use ore, oil, gas, and other traditional natural resources faster than nature can reproduce them. Traditional societal economics consider natural resources to be free and infinite, but they are not. The free resource of clean air is no longer in evidence in the metropolitan areas of Los Angeles, Detroit, Moscow, Bangkok, Mexico City, or many other places in the world.

Pessimism? Maybe Not

The best way of solving these imbalance problems is to develop a better understanding of the circumstances and particulars of the problem. As originally conceived, the "life of fuels" was to respond to a large company's opinion of the future of the diesel engine and the endless opportunities for diesel engine applications. The intent of the project was get certain facts out to industry, supporting new perspectives on alternative fuels, alcohol, gases, RME, and electricity. The life of fuels report is one important piece of a platform that will serve as a common basis on which to judge alternatives.

The demand for better air quality and lower emission levels from the transportation sector has accelerated the development of engines and the enhancement of fuel quality. During recent years, alternative fuels such as natural gas, ethanol, methanol, electricity, hydrogen, and biogas have been evaluated and show high applicability and improved emission test results. Simultaneously, a new initiative that involves the total elimination of emissions from vehicles is being introduced in California. Selling ZEVs would require a fundamental departure from today's technology and fuels.

The Perspective

No matter how vehicles are fueled or what fuel they are using, there is an extraction and production apparatus that supports the end use. That apparatus is still not taken into consideration. The more emissions from vehicles are reduced,

the greater becomes the importance of identifying the industrial emissions generated during extraction and production stages. Ship transport, refineries, storage, road transport, and infrastructure produce emissions as energy is used.

Objective

The study featured here was conducted by Ecotraffic and funded by the Federation of Swedish Farmers, the Swedish Environmental Protection Agency, the Swedish National Board for Industrial and Technical Development, OK Petroleum, the Swedish Ethanol Development Foundation, the Swedish State Power Board, and the Swedish Transport Research Board. The intent of the study is to objectively state and show the amount of energy consumed and the emissions consequences of extracting, processing, and distributing fuels. In the same fashion that energy balances are shown for certain chosen fuels, the emissions of greenhouse gases, acidifying gases, and toxic gases associated with these activities are also projected. Estimations are provided assuming the application of best-known "state-of-the-art" technology for both fuels processing and use in the vehicle. Consideration has also been given to technologies that have been demonstrated but are not currently in prevalent large-scale use by industry (although expected to play a more dominant role in future years).

Conditions

The baseline engine used in the study for light duty vehicles (LDVs) was an Otto cycle; medium duty vehicles (MDVs) and heavy duty vehicles (HDVs) were simulated based on diesel engine performance and characteristics. Roads, vehicle platforms, and refineries are all assumed to be in place and operational. Calculations are based on conditions and circumstances that pertain to Sweden. In terms of transportation technology and emissions characteristics of engines and fuels, however, Sweden is not too different from the rest of the world.

Realization

The fuels studied include "urban diesel," reformulated gasoline, propane, methane steam reformed from natural gas, biogas from two different raw material sources, methanol from natural gas, methanol from two different sources of biological raw materials, ethanol from three different biological resources/processes, rapeseed oil from biomass, and hydrogen from hydropower-supplied electricity. Hydroelectric power is the primary source of electricity in Sweden, followed by electricity produced from natural-gas-fired power plants. The starting point for all study cases was 100 energy units in the vehicle fuel tank. All energy balance estimates were then back-calculated to determine the total energy input.

The calculation method is obvious from the illustrations, which show the energy balances for each fuel-resource-use scenario (Figures 3.1, 3.2, 3.4, 3.6, 3.7, 3.8, 3.13, 3.15, 3.18, and 3.19). These figures were taken from the final report. The height of the columns show the approximate total energy input needed to produce 100 energy units in the fuel tanks or battery of a vehicle. The shaded portion of the bar graph indicates the contribution of fossil fuel and the shaded portion of the bar graph represents the contribution from non-fossil fuel sources.

Extraction, transportation, refining, and compression are considered and included in the calculations used to produce the displayed results.

Conclusions from the energy balance portion of the study follow.

- The effectiveness of fossil energy is still clearly superior to any non-fossil fuel considered in this study.
- It is almost impossible to escape a dependency on fossil fuels (with the exception of biogas from Lucerne),

using techniques, approaches, and resources with which energy should be produced from non-fossil resources, within a reasonable or foreseeable time period.

Vehicles—an Important Part

To make the picture more complete, the energy efficiency of the vehicle must be part of the calculation. Therefore, the report contains estimated energy efficiencies for personal cars, delivery vehicles, and buses. In these vehicles, different fuels are featured in the calculation scheme to satisfy either the diesel or Otto cycle engine, whichever is the more prevalent in a given application.

Energy Efficiency

In the case of powering buses, as illustrated in Figure 5.1c, the conditions and circumstances cited in describing the method for estimating the energy balance still hold. Some exceptions to the standard rules were taken with respect to the electricity-from-natural-gas scenario. Because of their high engine efficiency, the energy efficiency of electric buses is higher than that of conventionally fueled buses. From the energy effectiveness point of view, in the short run fossil fuels are still favored, with electricity being a marginal exception. The most effective biofuel was found to be rapeseed oil, followed by biogas and methanol, respectively. Ethanol takes the position of having the worst energy efficiency, in spite of the fact that the basis for consideration included the use of residue products.

Greenhouse Gases

Carbon dioxide (CO_2), nitrogen oxides (NO_x) and unburned hydrocarbons are known as greenhouse gases. Each has a different degree of effectiveness for creating the greenhouse effect, and each has a different life expectancy in the atmosphere. Figure 5.2 shows the relative contribution of greenhouse gases to the atmosphere, in terms of CO_2 equivalent contributions, for 15 different fuel/process/feedstock scenarios. The analysis of greenhouse gas emissions associated with each technology shows biofuels to be favored over fossil fuels, in terms of minimizing the contribution of greenhouse gases to the atmosphere. Note that this is exactly the opposite result that was produced from the energy efficiency analysis (which favored fossil fuels). Even so, it is clear that no fuel is exempt from producing a net increase in the greenhouse gas contribution to the atmosphere. The shaded portion of the bar graph shows the amount of "other greenhouse gases," expressed in terms of CO_2 equivalence.

Some conclusions from comparison follow:

- Producing electricity via natural gas and using the electricity to power vehicles generates the worst results.

- City diesel and gasoline are the fossil fuels that produce the most greenhouse gas emissions. Methanol from natural gas and natural gas, itself, follow in terms of their relative contributions of greenhouse gas emissions from fossil fuels.

Acidifying Gases

When considering technology that minimizes the acid gas emissions to the atmosphere, an account of NO_x and sulfur oxide (SO) emission contributions is taken. In Figure 5.3, the black portion of each bar represents the estimated emissions of SO at final use. The darker gray portion represents the NO_x generated during production, while the lighter gray portion represents the NO_x emitted during final use. The cross-hatched portion of the graph indicates the range of uncertainty of the analysis. The results of this analysis show some interesting trends. Fuels that are used in a diesel cycle engine show the highest levels of acid gas emissions. This result can be attributed to the fact that the diesel engine technology does not readily lend itself to any NO_x emission after-treatment strategies that can be used with other engines that can operate on methanol, ethanol, or other alternative fuels. Otto cycle engines and their corresponding fuels

coupled with a three-way catalyst or lean-burn engine technology are effective in reducing NO_x emissions. Also, this operating environment and these control strategies offer opportunities for the future development.

Energy based on the production of electricity (via combustion) and hydrogen are only minor acid gas emission sources. Manufacturers of heavy engines (Volvo, Scania, and others) claim that it will be possible to reduce the NO_x emissions from present levels of approximately 8 grams per kilowatt-hour (g/kWh) for diesel engines (operating on diesel fuel) to the 2 to 4 g/kWh. This would have the effect of reducing acid gas emissions to levels corresponding to those produced by alternative fuels. By the same token, industries that develop alternative fuels and associated engine technology point out that even further reductions in NO_x emissions are possible. NO_x values of 0.4 g/kWh have been shown by Finnish researchers. This would indicate that the net difference between diesel fuel and alternative fuels, shown in Figure 5.3, would remain, although there would be a reduction in the overall level.

What Conclusions Can be Reached

Approximately 50% of all energy use in the OECD countries is based on fossil fuels or energy types. The changes in structural purchase patterns for crude oil supplies to Europe seem to be related to the delivery of fuels from places other than OPEC countries, and are not based on large-scale displacement of fossil fuels. Development in the East and Third World, and to a certain degree the industrialized countries, is going to require a larger energy contribution because the number of vehicles is expected to double within one generation.

Current development rates point to an increase in dependence on fossil-based energy supplies, rather than a decrease. The introduction and use of bioenergy-based fuel supplies offers an opportunity to lessen the fossil energy contribution and to increase available supplies. Such an approach would also offer a long-term path for decreasing dependence on fossil fuel supplies.

Bioenergy can be used in energy-consuming sectors other than the transportation sector with less intensive upgrading. However, taking an approach that favors the use of bioenergy in non-transportation applications would inherently force an even greater dependence on fossil fuels for the long term; this is not desirable in many ways. The use of bioenergy offers some added flexibility for finding solutions to local energy problems. For instance, countries like Sweden and several other Western countries have a large agricultural surplus and a large production overcapacity for bioproducts. This situation provides an opportunity to use the surplus production for conversion to fuel that could supply the transportation sector and other industrial energy consumers.

The production of biologically derived alternative fuels like the alcohols would be an approach that would generate significant volumes, which would attract governments, users, and distributors.

Fossil energy should be avoided on the grounds that fossil energy use contributes relatively significant greenhouse gas emissions and exacerbates the greenhouse effect.

To reduce emissions of acidifying gases, electricity and engines that operate on the Otto cycles should be favored. To reduce the emissions of toxic gases, simple fuels and electricity are preferred. Methane gas and alcohol are the simplest fuels to handle from an environmental point of view.

Recommendations for Activities

Short-run development activities should unequivocally lead to a product or end result that satisfies a long-term objective. To reach these long-term objectives, four activities are recommended:

(1) An economic analysis of the transition from conventional to alternative fuels is needed.

Infrastructure costs need to be weighed against the value of independence from foreign imports. Societal costs need to be compared with health effects, employment implications, and other socioeconomic factors.

The success of different fuels in both the short and long term depends on societal and industrial incentives to stimulate the introduction of these fuels. The creation of a proper and efficient incentive program is largely within the realm of a political decision, which would be based on the outcome of these analysis and evaluations.

(2) Development of biofuels refining processes to provide more energy-efficient product upgrading is an area where much effort needs to be placed. Current methods for refining biofuels are less efficient than comparable fossil refining processes.

An active program should be initiated for the development of non-fossil refining processes, which reduce energy demand and are more economic.

(3) Development of battery technologies that provide improved storage capacity and durability is recommended. The most significant weakness of an electric vehicle can be attributed to battery technology limitations. An active R&D program to develop batteries and battery systems that could surpass threshold performance (in terms of range, energy density, cost per stored unit of energy, and number of charge/discharge cycles) would be of significant value to the transportation sector, and would produce a significant emissions benefit. Such a technology would also provide an avenue for hybrid vehicles to come into the marketplace; the engines in the hybrid vehicles could use alcohol fuels.

(4) The introduction of alternative fuels at preproduction levels should begin. In this way, an experience base can be built on different operative platforms such as private vehicles, trucks, and buses that feature a range of alternative fuels. Both technical and financial support for such a program should be provided by governments, the transportation industry, and the energy industry.

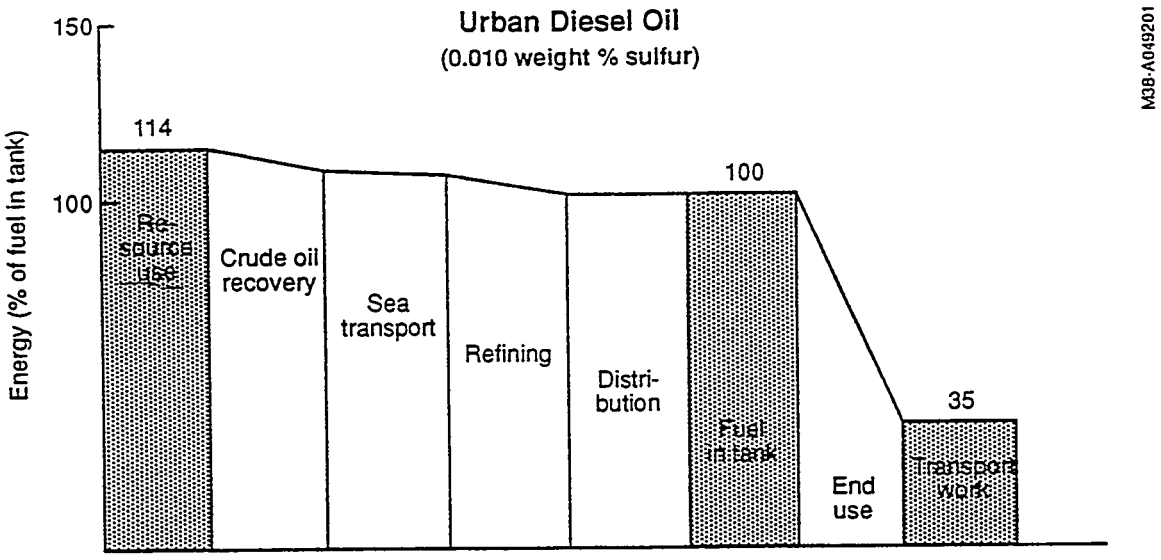


Figure 3.1. Energy turnover in the fuel chain (crude oil recovery to urban diesel oil; use in heavy duty diesel engine operated in bus cycle)

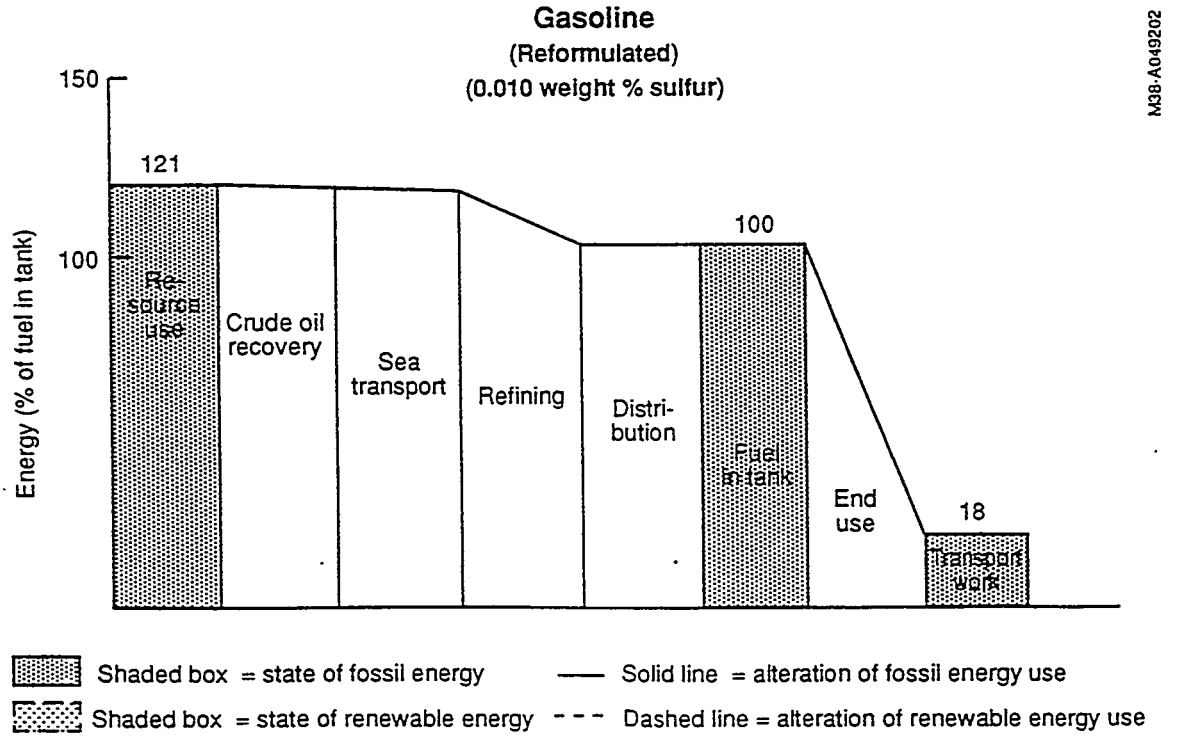


Figure 3.2. Energy turnover in the fuel chain (crude oil recovery to reformulated gasoline; use in a light duty Otto cycle engine operated in FTP cycle)

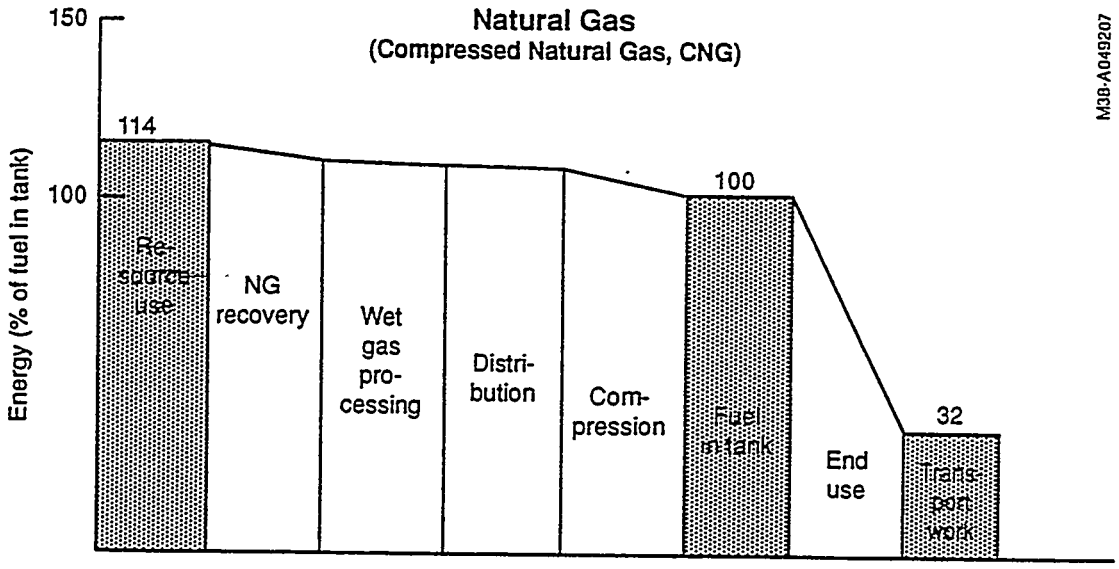


Figure 3.4. Energy turnover in the fuel chain (natural gas recovery to CNG; use in heavy duty Otto engine operated in bus cycle)

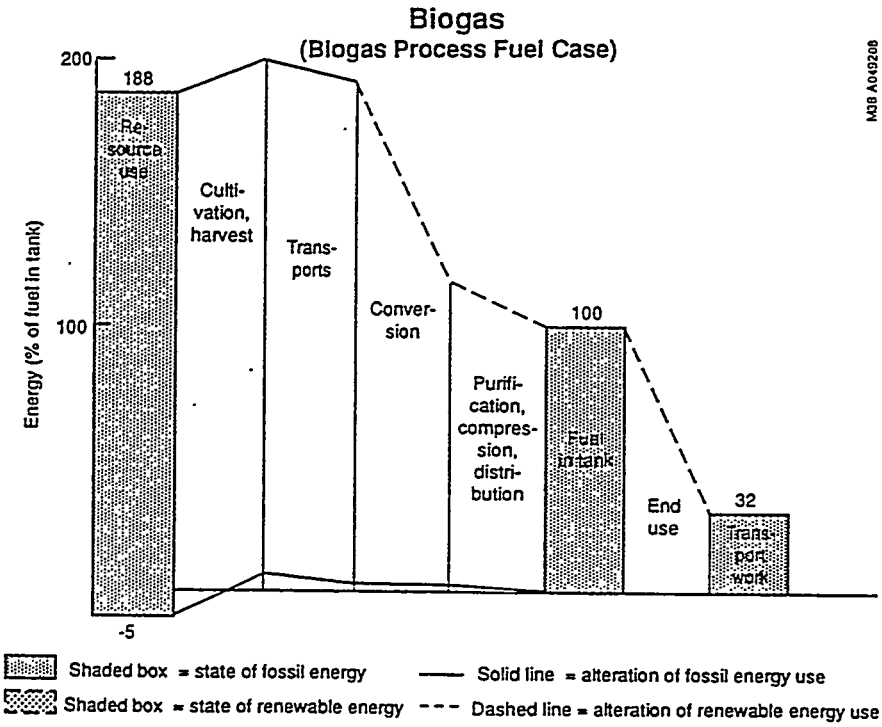


Figure 3.6. Energy turnover in the fuel chain (alfalfa growing to compressed methane; use in heavy duty Otto engine operated in bus cycle)

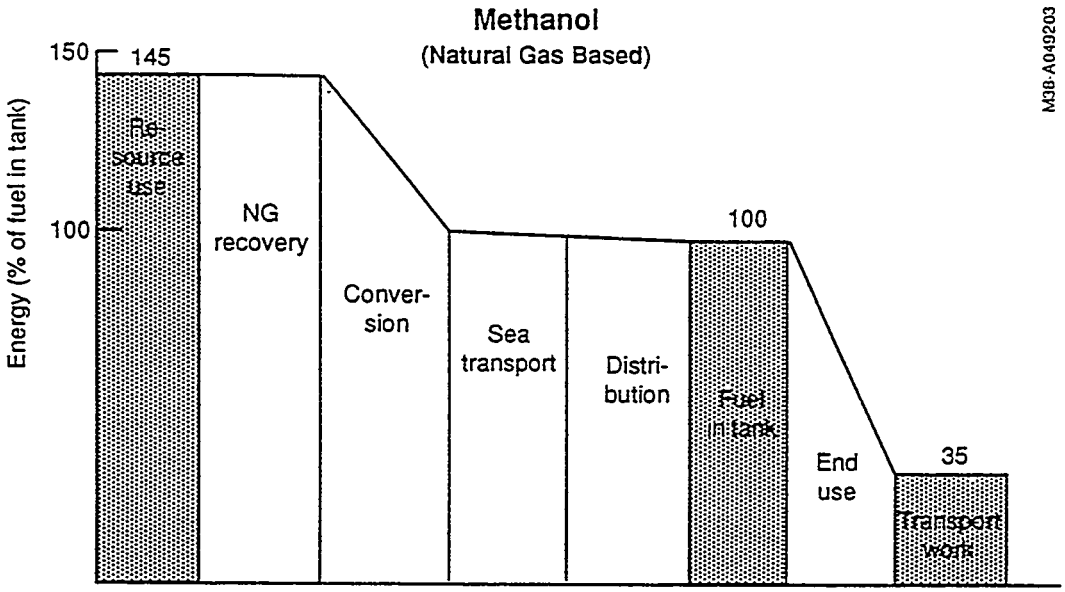


Figure 3.7. Energy turnover in the fuel chain (natural gas recovery to methanol; use in heavy duty engine operated in bus cycle)

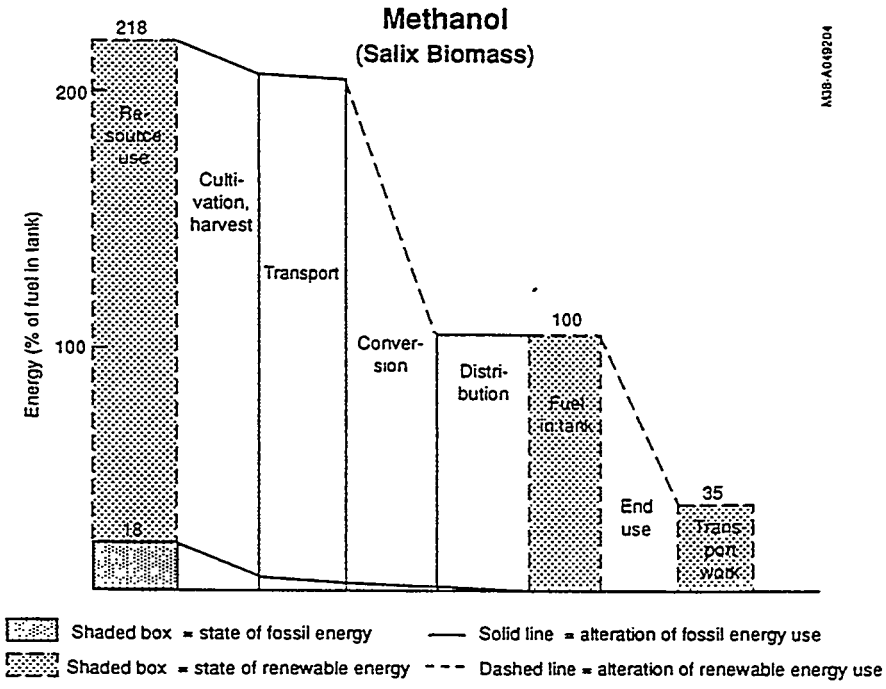


Figure 3.8. Energy turnover in the fuel chain (salix growing to methanol; use in heavy duty diesel engine operated in bus cycle)

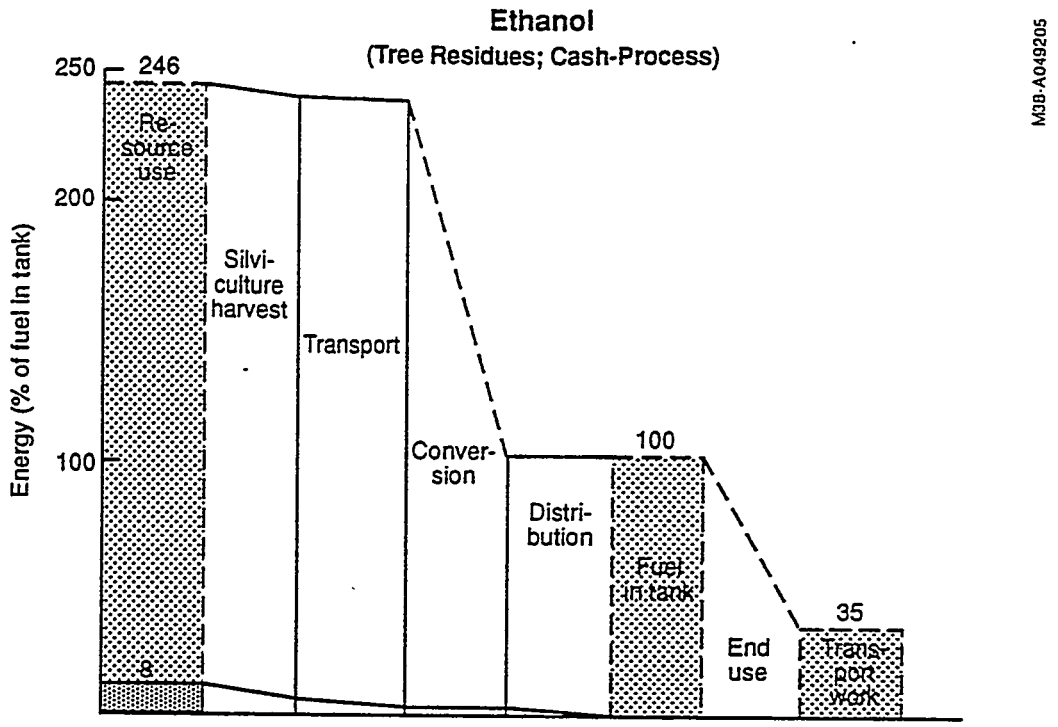


Figure 3.13. Energy turnover in the fuel chain (tree residues to ethanol; use in heavy duty diesel engine operated in bus cycle)

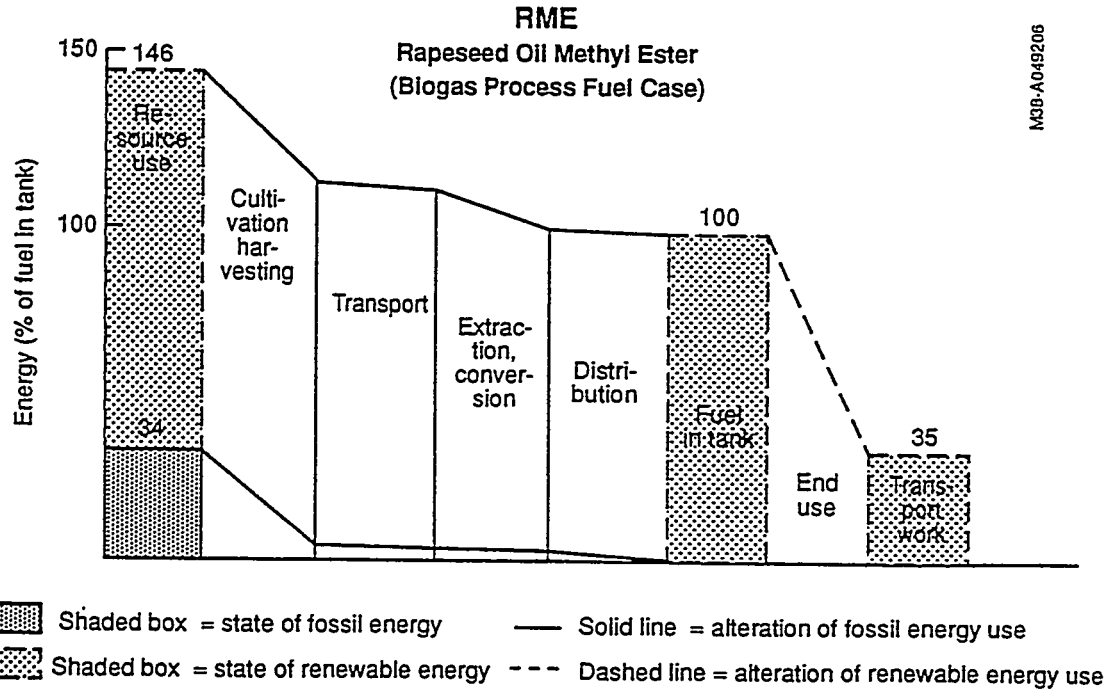


Figure 3.15. Energy turnover in the fuel chain (rapeseed growing to RME; use in heavy duty diesel engine operated in bus cycle)

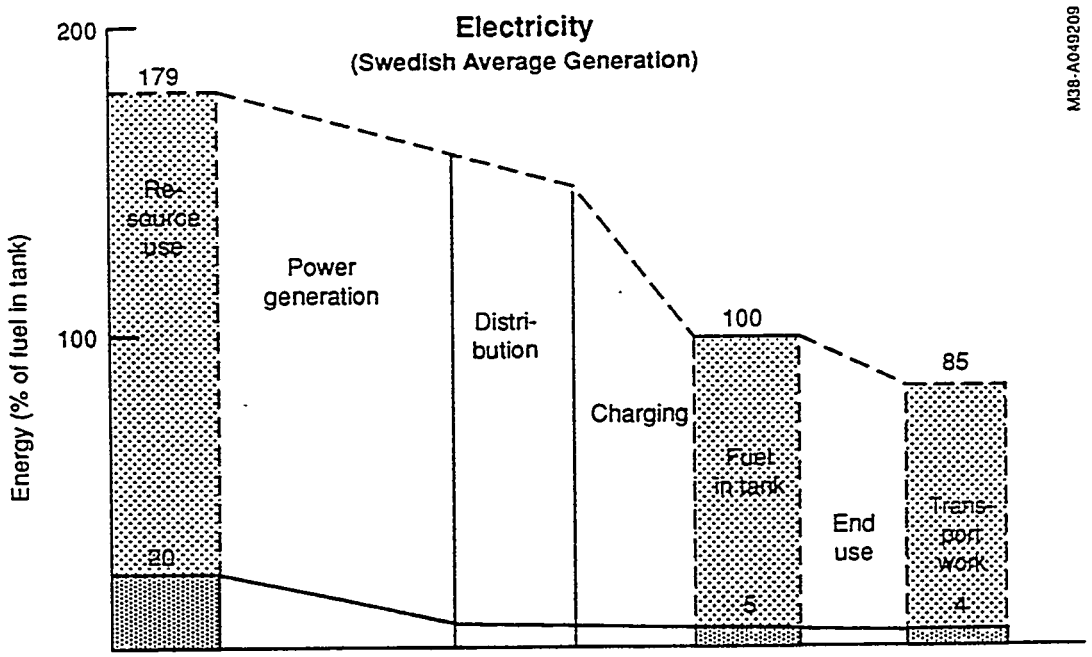


Figure 3.18. Energy turnover in the fuel chain (primary energy to electricity; use in an electric motor)

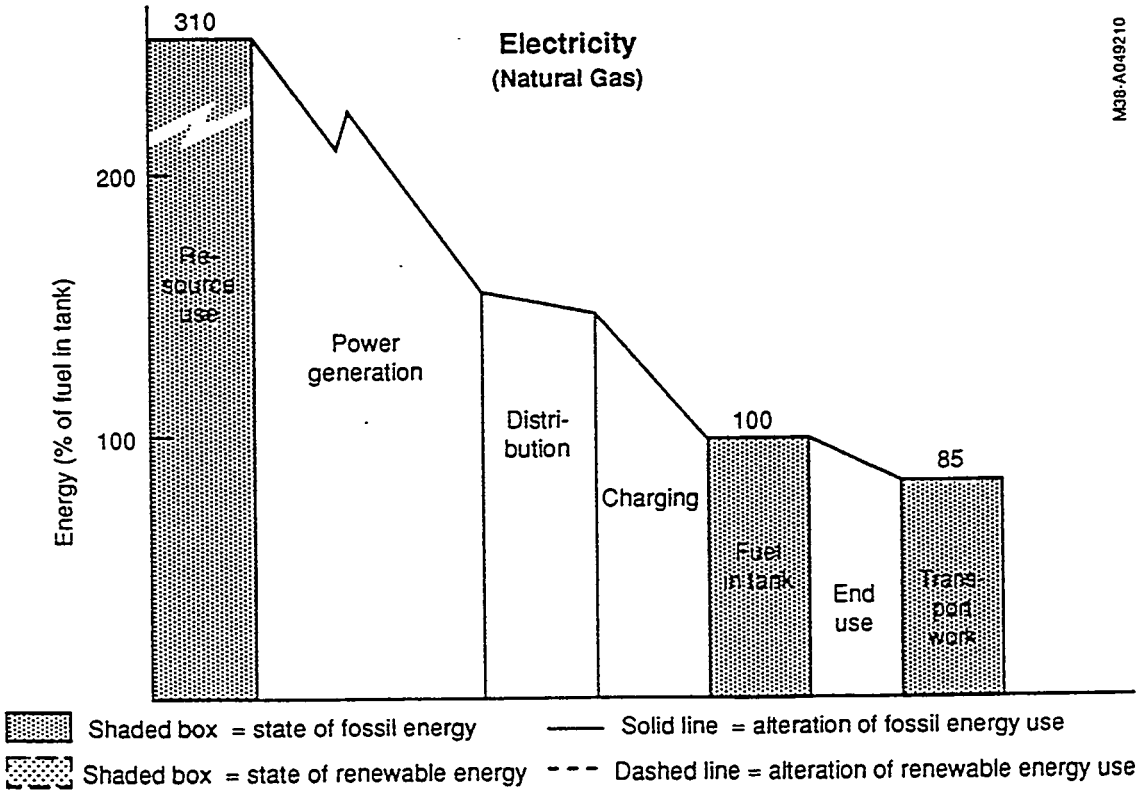


Figure 3.19. Energy turnover in the fuel chain (primary energy to electricity; use in electric motor)

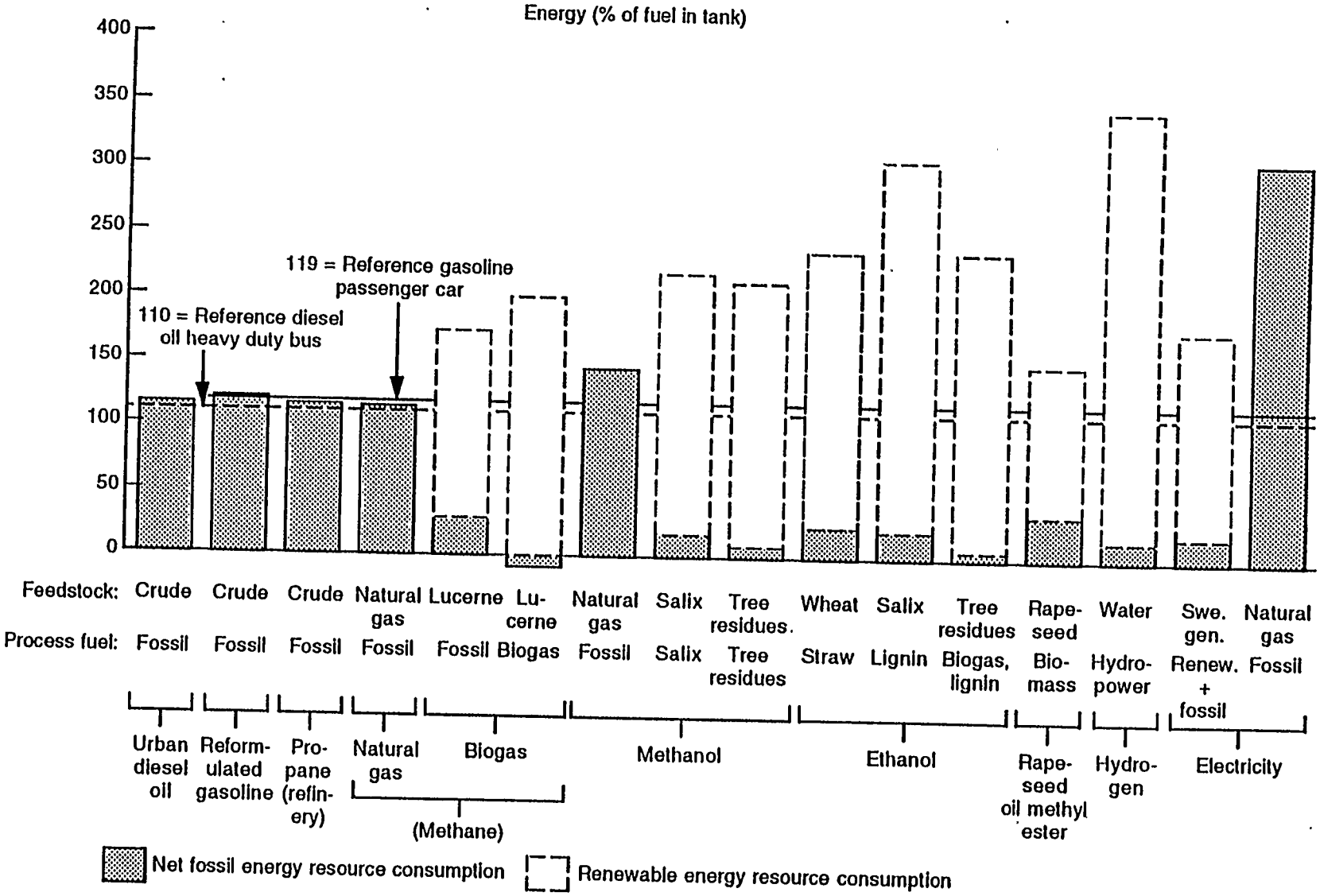


Figure 5.1. Energy resource use for fuel chains (bus diesel engine except for gasoline, hydrogen, and electricity)

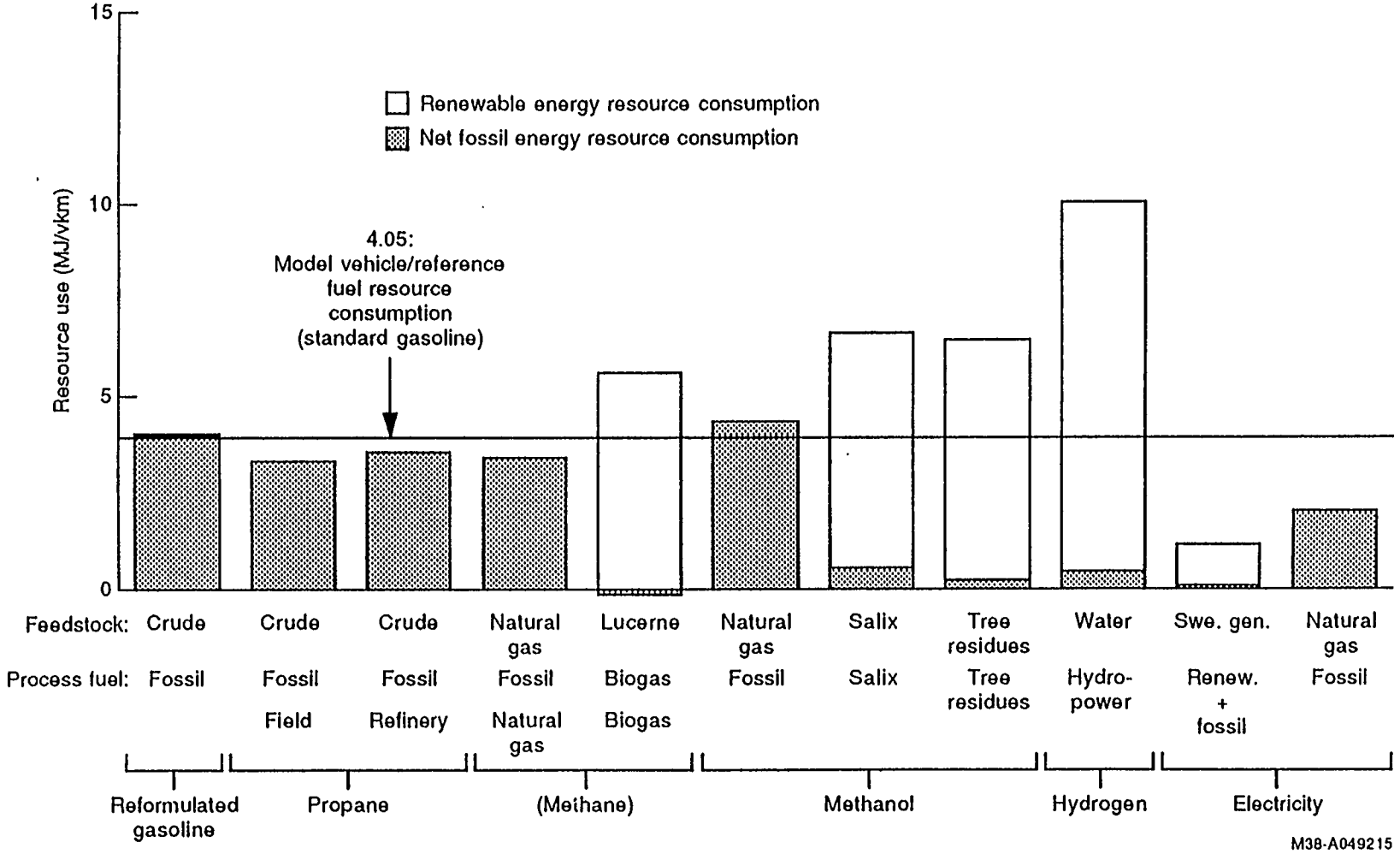


Figure 5.1a. Energy resource consumption in passenger car model vehicle for fuel chains

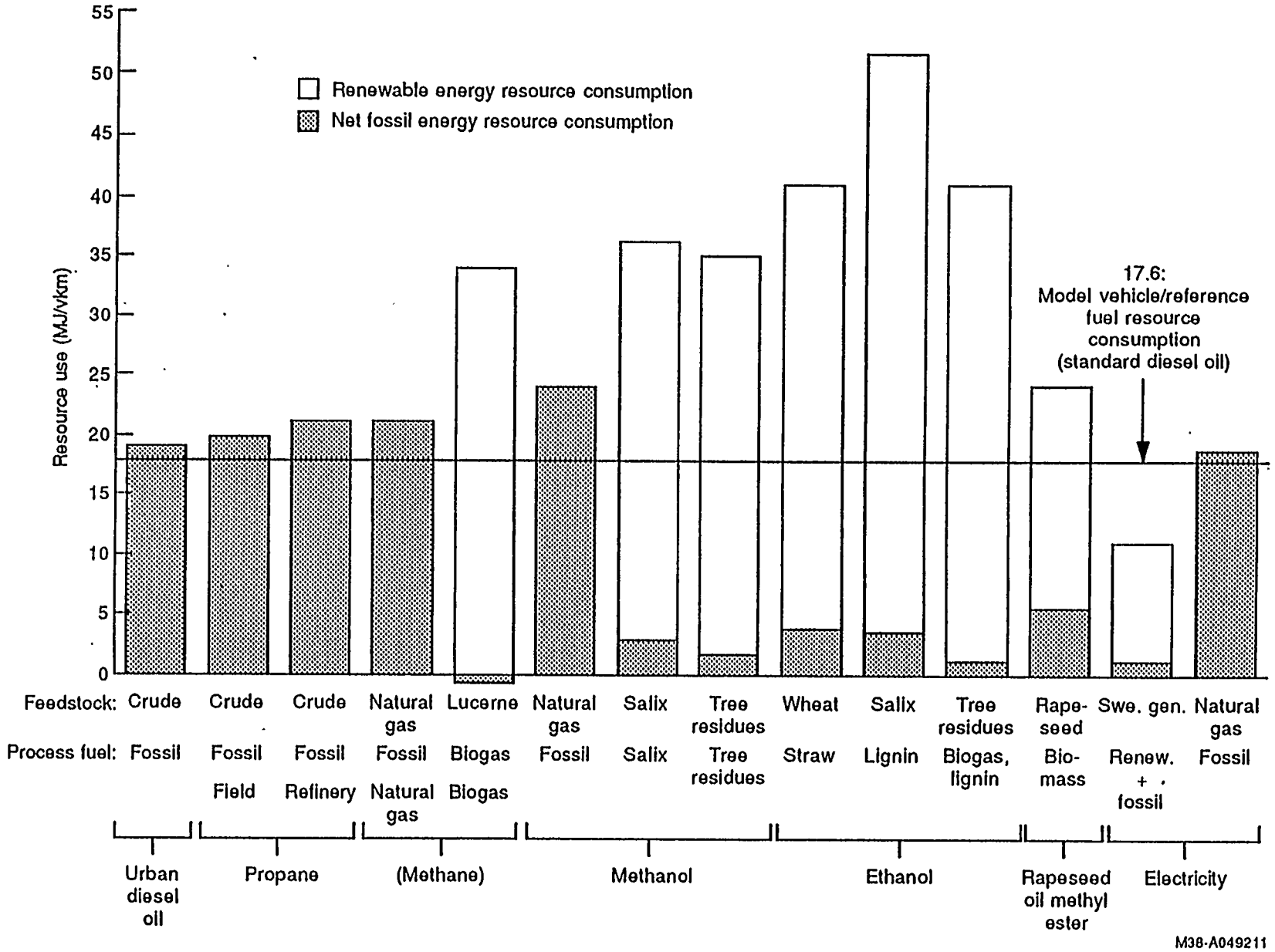


Figure 5.1c. Energy resource consumption in bus model vehicle for fuel chains

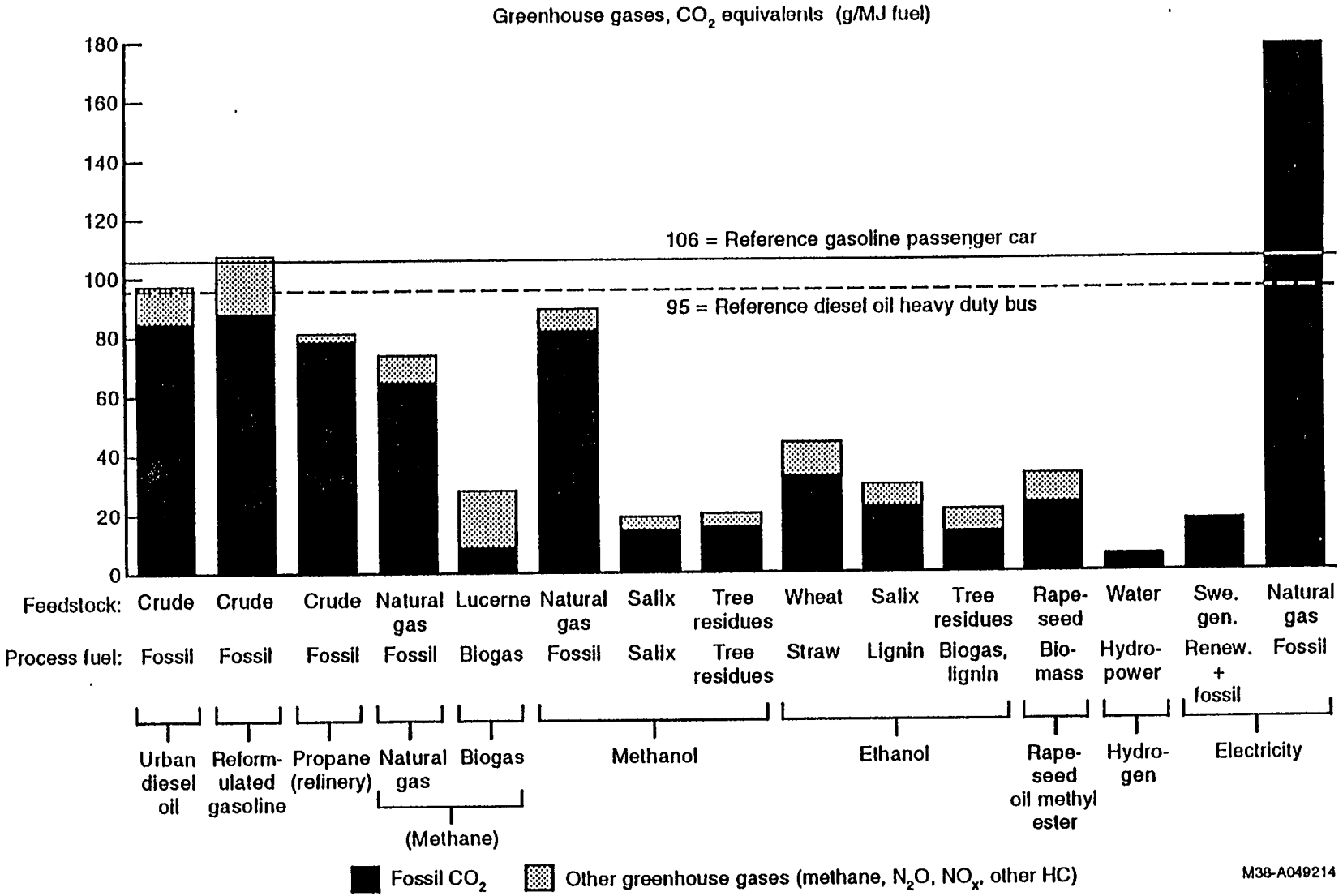


Figure 5.2. Release of greenhouse gases in the fuel chain (biomass-based CO_2 omitted; heavy duty bus engines except for gasoline, hydrogen, and electricity)

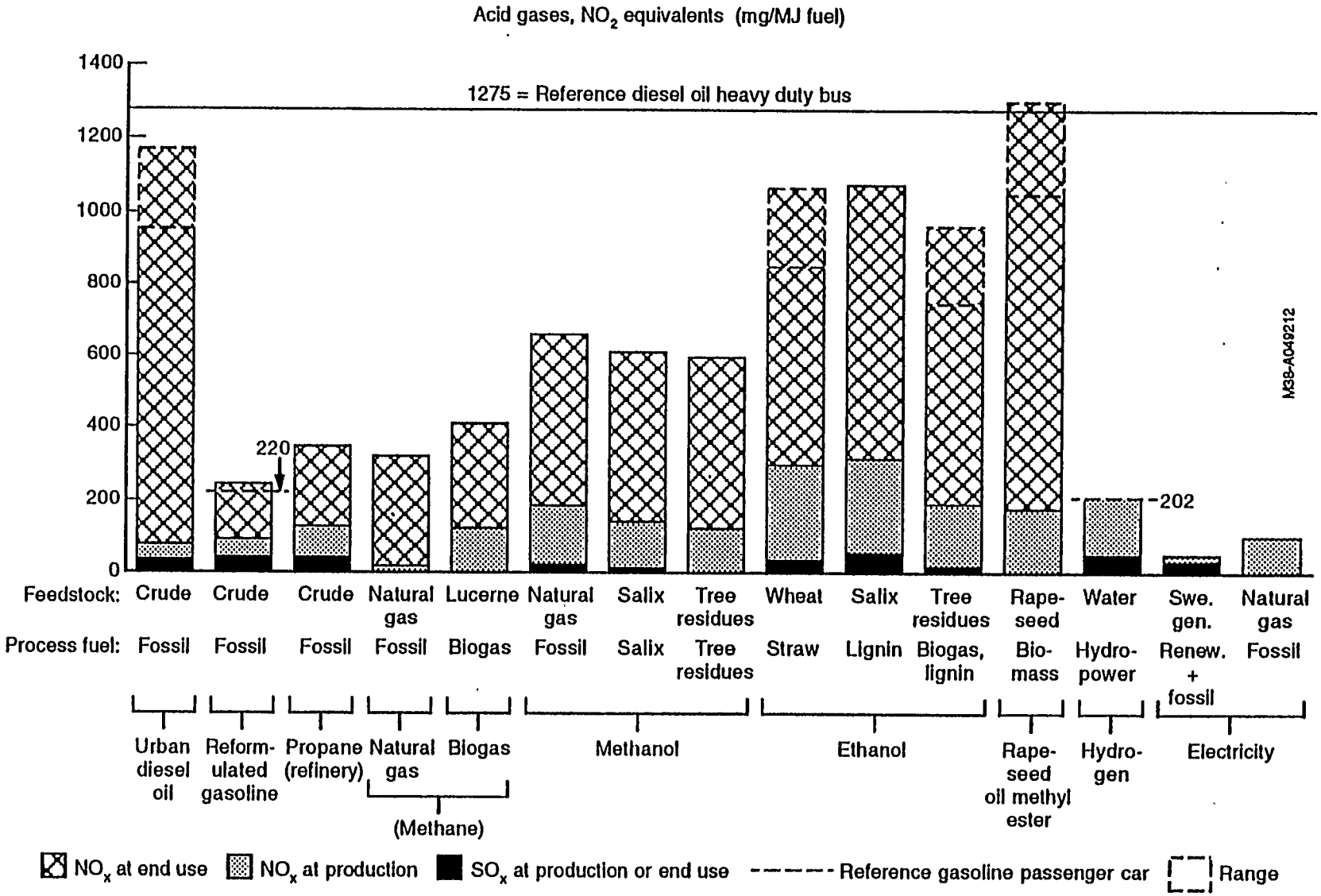
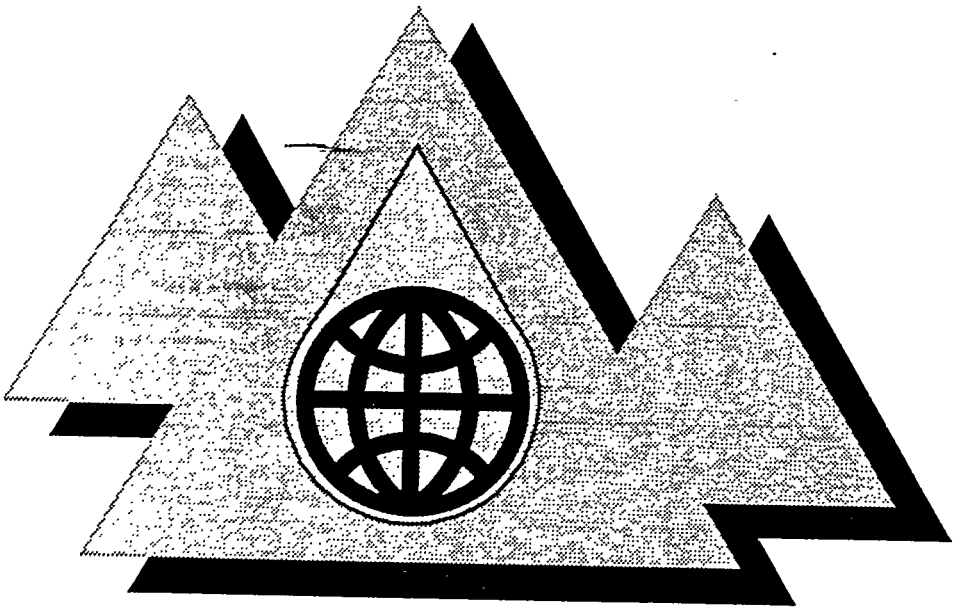


Figure 5.3. Release of acid gases in the fuel chains (heavy duty bus engines except for gasoline, hydrogen, and electricity)



European Implementation Plans

ETBE: ECOFUEL's EXPERIENCE

Introduction

Ecofuel is one of the world leaders in the Oxygenates. It is owned by AgipPetroli and is part of ENI, the Italian Energy Concern recently transformed into a Stock Company to be quoted in the near future in the stock market according to the Government policy of privatization.

Ecofuel was funded seven years ago to deal with the business of Oxygenates, a line of products for which ENI had a large and pioneer experience, having built and operated the first MTBE plant in the world, a unit in Ravenna, in Italy on the Adriatic sea, started in 1973.

The "mission" put forward by ENI to the new Company was to grow up and develop the business.

Today the Company is among the three/four largest producers and marketers of MTBE in the world, having implemented, in addition to the Ravenna production, other capacities through participations in various Joint Ventures:
- a first one in Saudi Arabia (with Sabic, Neste Oy and Apicorp), where the first large-scale MTBE plant ever built in the world is producing since 1989, and where a second line, bringing total capacity up to about 30,000 Bbl/d, is nearly ready to start; - and a second one in Venezuela with Pequiven, where another MTBE plant by 12,500 Bbl/d is in operation and a Methanol plant is under construction.

Ecofuel and Ethanol

Since the beginning of its life, Ecofuel had to deal with Ethanol, a product strongly promoted not only in the USA, but periodically in Europe too, by agricultural lobbies.
The relations between Ecofuel and Ethanol have always been of severe confrontation. Our position was not to argue against ethanol's technical properties, that should convince the market, more than the competitors and that, as expected, have been found unacceptable in Europe where nearly all Oil Companies have rejected ethanol as a direct blending component.

Our position was instead to fight against the heavy subsidies requested by potential ethanol producers to the European Community and to individual Governments. These subsidies in fact would distort in an unacceptable way the market competition, bringing the money of European taxpayers in favour of an inefficient agricultural sector and against the industrial production of Oxygenates, a sector quite profitable also under current market conditions.

However, a certain quantity of ethanol is available in Europe as a by-product from agricultural productions, that is from distillation of surplus wine obtained in years of too large production, or from fermentation and distillation of molasses that are a by-product of sugar from beets. This ethanol therefore is not produced on-purpose for fuel addition, but is there in any case, and its storage is rather costly to the European Community.

Under these circumstances, the European Community is promoting a new agricultural policy, that is to make any effort to reduce the surplus productions by encouraging the set-aside of marginal lands which give large quantities of low-quality crops, including low quality grapes and from them low-quality wine; however, in the medium term, surpluses have to be outlet in a way or another.

For this reason, volumes of this ethanol are periodically sold in the market by the EC Agencies, and their price may be attractive.

With reference to this product, Ecofuel's position obviously is not conflictual: on the contrary, we are providing maximum cooperation to the efforts of the European Community, and have decided to absorb volumes of Ethanol when its price is suitable.

While confirming that Ecofuel clients are against the direct blending of Ethanol to gasoline, due to the well

known problems of fuel stability in presence of water. high vapour pressure and so on, we have found that a good solution for everybody is the utilization of Ethanol instead of Methanol in the traditional Ether production: that is, the production of ETBE.

Ecofuel has started its experience in this line in 1992. with a first limited production of ETBE in its Ravenna plant, and has repeated more extensively this experience this year, by producing ETBE, still in Ravenna, between April and June.

The aims of the industrial test were multiple: the first one was to investigate what modifications were necessary in the plant for a production of ETBE instead of MTBE. for which it was designed, and also to check the capability of the plant, that has always demonstrated a very large technical flexibility, to produce ETBE possibly with no modifications at all.

The second aim was to check the quality of the product and analyze its blending characteristics, and to evaluate the reactions of the market by selling commercial quantities of ETBE to selected clients, for their own evaluations.

In parallel, the test was useful to check the economics of the production, taking into consideration the need of segregating both the feedstocks and the product stocks interrupting the continuity of the production complicating the transportation problems and so on.

The results have been positive in all connections, anc the final decision of Ecofuel is that, whenever surplus ethanol is available on the market at prices competitive with those of Methanol, it is possible to shift production towards ETBE without loosing profits.

Production tests at Ravenna

A simplified process scheme of the Ravenna plant is shown in Fig.1. The plant includes two stage reaction units with their fractionators, one section for Raffinate purification and a distillation column to recover unreacted alcohol.

Ethanol fed to the plant was anhydrous product (99.8% min) from agricultural origin, denaturated with 2% MTBE in order to comply with Italian fiscal regulations.
Iso-Butylene source was a typical Raffinate-1, that is C4 stream from steam-cracker after Butadiene recovery,

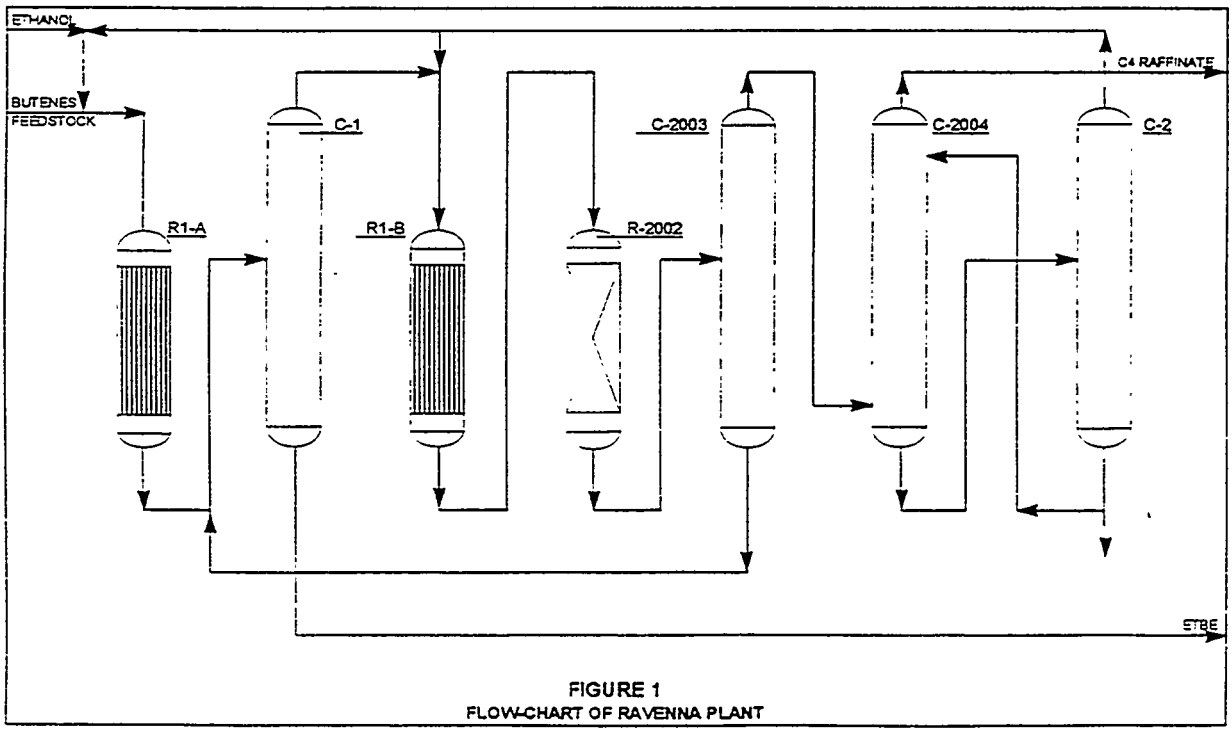


FIGURE 1
FLOW-CHART OF RAVENNA PLANT

having iso-butylene content ranging between 36 and 50% weight.

In production of ETBE, conversion of isoButene reached 99%, that is only marginally lower than the one achieved when producing MTBE.
On this basis, and taking into account the higher molecular weigth of Ethanol vs. Methanol, the productivity of the plant has been higher than the one relevant to MTBE, in certain conditions exceeding it by 15%.

ETBE had a purity over 98%, as shown in Table 1, well in line with the commercial requirements: a modulation of this parameter is possible by simple operating adjustments.

Table 1

RAVENNA TEST RUN: EXAMPLE OF ETBE COMPOSITION

- Component	% weight	% weight
- ETBE	98.10	98.92
- MTBE	0.83	0
- Ethanol	0.49	0.495
- TBA	0.38	0.383
- DIB	0,20	0.201
- C4 HC	<0.05	<0.05
- H2O ppm	28	28

ETBE purification, carried out in the distillation column, was complicated by the formation of azeothropes between ethanol, C4 hydrocarbons and ethers. The presence of Ethanol in ETBE was minimized, by achieving the goal of <0.5% weight.

The by-product, Raffinate-2, had a typical composition as indicated in Table 2, with about 99.4% of C4 olefins. Main impurities are:

- DIB (di-isoButylene), whose formation is favoured by high temperature and low Ethanol/iso-Butylene ratio;

- DEE (di-Ethyl Ether), that is also favoured by high temperature and is increased by excess of Ethanol. Its presence in Raffinate-2 is very crytical to the streams destined to Alkylation units, whose catalyst is sensitive to oxygenated compounds.

Table 2
COMPOSITION OF RAFFINATE-2

Component	% weight
- C4 Hydrocarbons	99.40
- Diolefins	0.46
- C3 and lower	0.06
- C5 and higher	0.02
	ppm
- di-Ethyl Ether (DEE)	200
- ETBE	<20
- Ethanol	< 5
- Sulphur	absent

Production tests in Refinery

Another test was carried out inside a Refinery, at one of the existing Refinery MTBE plants, utilizing C4 streams from FCC as feedstock, with typical contents of isobutene ranging between 12 and 20%.

The main results are the following:

- average conversion of isobutene equal to 81%, about 10% less than the one observed in MTBE production;
- purity of ETBE between 95.5 and 97%, with 2 and 1% ethanol content respectively;
- importance of the optimization of the ethanol/isobutylene ratio;
- negligible selectivity to DIB;

- presence of azeothropes between ethanol and both butylenes and ETBE.

ETBE properties

ETBE properties, slightly different from one run to another, have been satisfactory since the beginning and fully in line with the commercial specifications, that are reported in Table 3.

Table 3

SPECIFICATION QUALITY FOR COMMERCIAL ETBE

- Components		% weight
- ETBE		97.5 min.
- Ethanol + TBA		2.5 max.
		ppm
- Water		500 max
- Antioxidant		50 min
- Color	(APHA)	60 max

Particularly important has been for Ecofuel the evaluation of the blending properties of ETBE, that was necessary not only for scientific reasons, but also to provide our clients with all the possible assistance in the use of a new product, to assess its value and at the end, its price.
The properties have been determined by blending ETBE (both "high purity", from the Ravenna plant, and "low purity" from the Refinery plant), to a number of different basestocks typical of European refineries, with concentrations of 10% and 15% volume, in line with the European Directive for the use of Oxygenates in gasoline: some tests have also been carried out at 5% volume.

The results, that are reported in Figures 2 and 3, indicate a much higher performance for the high purity product, that has been consequently selected by Ecofuel as a commercial standard.

Figure 2
TREND OF BLENDING RESEARCH OCTANE NUMBER

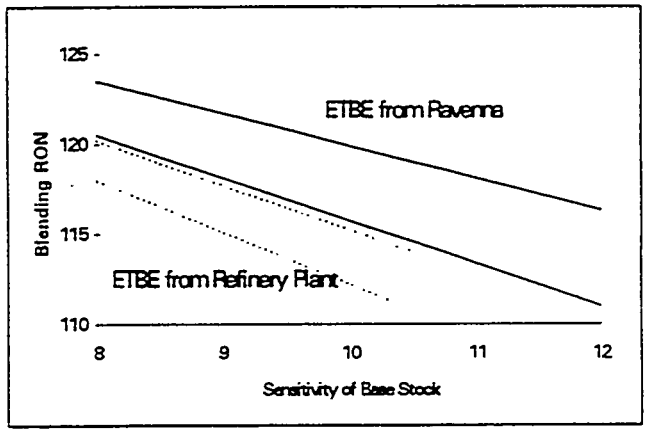
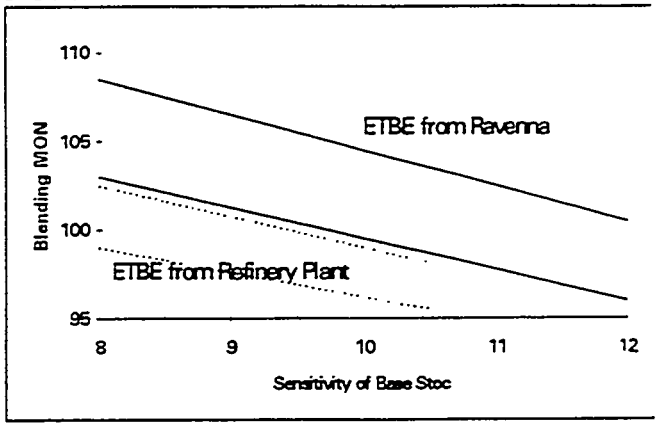


Figure 3
TREND OF BLENDING MOTOR OCTANE NUMBER



As far as the Octane Numbers are concerned, blending RON has been found practically the same of MTBE, while the MON has been found slightly higher

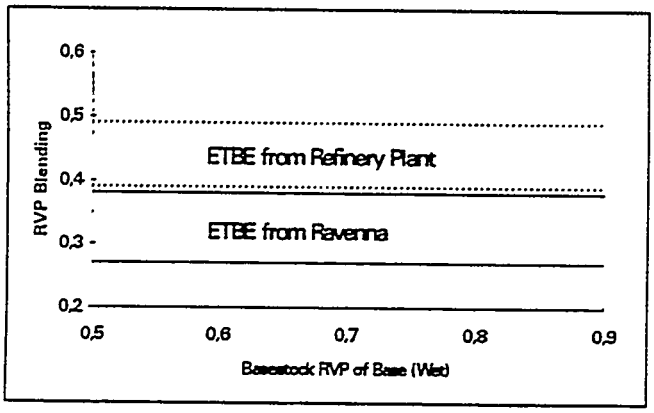
Both numbers are quite sensitive to the basestock characteristics: at sensitivity between 10 and 11, that is the typical for unleaded European gasoline, the following values can be quoted:

RON: 115-120
MON: 98-102.

The blending volatility is probably the most interesting property, particularly in those Countries where RVP limitations are more restrective.

As shown in Figure 4, we have found that the blending RVP of ETBE is practically not affected by the RVP of the basestock, and ranges between 4 and 5.6 psi for high purity product.

Figure 4
TREND OF ETBE BLENDING RVP

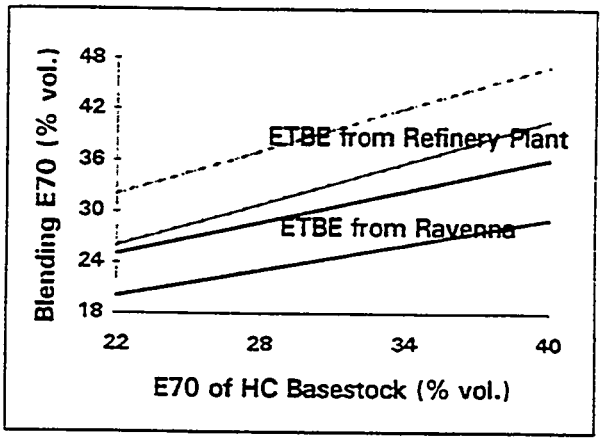


Low purity's RVP is quite higher, the remarkable penalty coming from the ethanol content and from its low boling azeothropes with hydrocarbons.

As far as the E70s (% volume evaporated at 70 C) are concerned, they are plotted in Figure 5; the influence of ETBE, having a boiling point of 73 C, is minimal.
From this point of view, ETBE has an advantage over MTBE whose boiling temperature is 55 C.

The Oxygen content of ETBE is 15.7% weight, lower than MTBE that has 18.2% of oxygen. Consequently, the percentage of ETBE needed to satisfy the Oxygen mandate of 2.7% is 17.2 (against 15 for MTBE).
The corresponding figures for the 2% mandate are 12.7 and 11 respectively.

Figure 5
TREND OF ETBE BLENDING E70 C



Storage Stability

The poor storage stability of ETBE is frequently mentioned in the literature: its tendency to form peroxydes is five times higher than MTBE.
We have checked this behaviour through an extended testing program by adding to ETBE a proper additive, and exposing different samples of ETBE, with and without the additive, to various temperatures and sun light intensities.
After three months, the additivated samples showed no content of peroxydes, while in the others the concentration of peroxydes was up to 32 ppm: the Octane number of the non-additivated samples was reduced by 2 points.

In order to keep the commercial properties, we have decided therefore the utilization of the additive prior to commercialization.

Commercial Experience

The Ravenna test has been continued for two months, and all the production has been normally marketed.

All the Ecofuel clients currently supplied from Ravenna, both in Italy and Switzerland, have accepted ETBE with a price in line with that of MTBE.

All the Refiners have indicated their satisfaction for the results of the blending and their interest to buy more product, mainly during the summer months when gasoline volatility specifications are more severe.
This is particularly important in Switzerland, and more recently also in Italy, where the E70 summer specification has been recently reduced to 30% from the previous 35%, and specially for those refineries that use extensively low boiling components, such as isomerate.

In terms of Octane number, the answer of refiners has confirmed the results of our tests, that is a substantial equivalence between MTBE and ETBE.

Conclusion

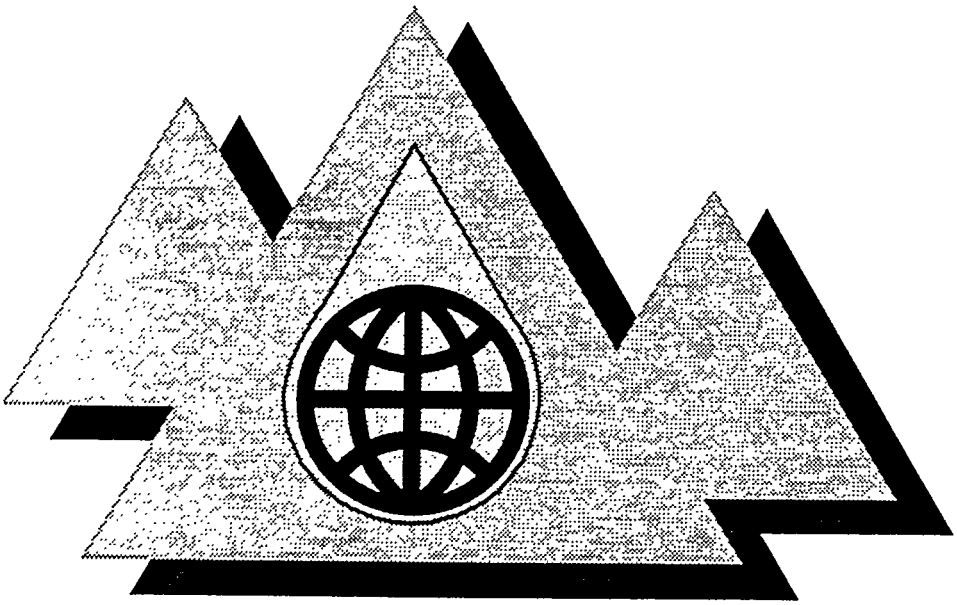
The experience has been totally positive, and we are now ready to extend it in all our facilities worldwide, always on the basis of availability of cheap Ethanol.

We hope now that a wider introduction of ETBE in the European market be possible. In fact, its production may contribute to solve, even only partially, the problem of financing the storage of surplus ethanol; and this may help the European politicians to develop the necessary actions in favour of the environment.

A Clean Air Act does not yet exist in Europe, even if the pollution of certain towns is extremely high, certainly not lower than the one observed in the USA that brought the Administration to promulgate the CAA Amendment in 1990. Our Municipalities have only found the way, in the periods of worst pollution, to expel cars from the towns, that is not the best solution for commuters, workers and tourists.

Consequently, no oxygen content is mandatory in th European gasoline, and the discussions between Oi Companies, car producers and political authoritie about what to do to improve the environment ar keeping totally unfruitful since many years.
Up to now, the diffusion of oxygenates, toda practically MTBE only, is due to their octan contribution, following the diffusion of unleade gasoline, that is growing - more or less quickly - u European Countries.

As producers of Oxygenates we are working hard t promote the sector: we hope to be successful, not onl as sellers but as citizens as well, giving a contribution t the solution of a problem that will be one of the ke problems of the next century.



Regulatory and Policy Issues

The Energy Policy Act of 1992
An Overview with a Perspective To Alcohol Transportation Fuels

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Abstract

The Energy Policy Act of 1992 was signed into law on October 24, 1992, signaling a significant commitment from the U. S. Government to stimulate the private sector to manufacture and provide fuel for Alternative Fuel Capable (AFC) vehicles. The most prolific purchaser and operators of AFC vehicles, in the scenario created by the Act, is the Federal, State and Local governments. This paper will examine the thrust of statute and describe DOE's plans to implement the provisions which relate to alternative transportation fuels.

Introduction

With the passage of Public Law 102-486 (the Energy Policy Act of 1992) the United States of America took a major step forward in addressing the transportation energy requirements of the country. It is well known that in recent years the annual amount of transportation energy consumed in this nation has resumed the dramatic rise that was characteristic of this sector in the late 1960s and early 1970s, prior to the Arab oil embargo. Likewise the annual domestic crude oil production has assumed the decline that was also characteristic of that period. During the ensuing years, a number of dramatic events took place; technical improvements were made to vehicles that resulted in increased fleet average fuel economy, domestic crude oil production was improved with secondary and tertiary oil recovery techniques, a number of synthetic fuel projects from unconventional resources were built (and subsequently discontinued) and a sequence of political events in the Persian Gulf caused crude oil prices to decline and then to stabilize. Although not as dramatic, significant research and development was also taking place within the transportation industry to develop the necessary engine and engine system technology that would allow productive use of alternative fuels for transportation. The end result of this work yielded alcohol-fuel-capable (AFC) vehicles and diesel engines which could operate on high octane alcohol fuels. Important legislation was also passed by the U. S. Congress, to stimulate the use of alternative fuels, such as the Alternative Motor Fuels Act of 1988 (AMFA), and the Clean Air Act Amendments of 1990 (CAAA). The Executive Branch also made independent contributions to the alternative transportation fuels effort with the signing of Executive Order 12759 and subsequently Executive Order 12844. Each of this statutes or orders, provided incentives, quotas and direction for the use of alternative fuels and addressing the infrastructure issues facing large scale use of alternative fuels. The Energy Policy Act of 1992 (EPACT) built upon the features of AMFA and the Executive Orders while acknowledging the provisions of the Clean Air Act Amendments of 1990.

EPACT contains the latest and most comprehensive thinking on all energy issues facing this nation, but this paper will cover only those provisions which deal with alternative transportation fuels. The majority of these provisions are contained in Titles III, IV and V of the statute.

Scope of the Statute

The statute calls for four major program elements to be established with attendant and supporting program elements. These major program elements include:

- The Federal Fleet Program
- The State Fleet Program
- An alternative fuel bus program
- The private and local government program, and
- The U. S. Postal Service Program.

Each of the first four major program initiatives will be discussed in this paper, along with some of the supporting program initiatives. The supporting program initiatives, are:

- An education and training program
- A training certification program
- A data collection program,
- A low interest loan program, and
- A tax benefits program for AF investments.

The major program elements are all fleet programs which in some cases are mandates. Along with the fleet programs comes the requirements for reporting to Congress on the progress of the fleet programs and the use of alternative transportation fuels.

The targeted locations for a number of these fleet vehicle purchases is within metropolitan areas which have a population of 250,000 or more.

There is significant guidance within the statute on issues such as original equipment manufacturer's products versus conversions and use of alternative fuel refueling stations which are available to the public.

An important aspect to the interpretation of EPACT is contained in the definitions of key words, such as 'alternative fuel,' 'covered person,' and 'fleet'. A verbatim recapitulation of some of the key definitions provided by EPACT is provided in Appendix I.

Fleet Programs

The objective of the fleet programs is to create a demand for domestic replacement fuels (Section 502), sufficient to 'replace on an energy equivalent basis -

(A) at least 10 % by the year 2000; and

(B) at least 30 % by the year 2010,

of the projected consumption of motor fuel in the United States'.

For the purposes of illustration, the historical and projected motor fuel consumption, in the United States is shown in Figure 1. The motor fuel consumption is shown on a trillion btu basis for three major transportation sectors: automobiles, trucks and buses, and non-highway applications.

Federal Fleet

This statute offers the Federal Fleet as the first entrant in the effort to stimulate the development of an alternative fuels industry both in the vehicle supply and fuel production and distribution areas. EPACT essentially codified the requirements of Executive Order 12759, which set a schedule for procurement of alternative fuel capable vehicles for the Federal Fleet.

The Federal Fleet is not a homogeneous consumer of transportation vehicle products. The Federal Fleet can be characterized by dividing it into three sectors: vehicles that are purchased by the General Services Administration (GSA) and leased to the various branches of the Federal Government (20 %), vehicles that are purchased under GSA contracts but are owned by the entity within the Federal Government making the purchase (50 %), and vehicles that are purchased under separate (non-GSA) contracts by the individual the U. S. Postal Service branch/agency (30%). The fleet consists of approximately 500,000 vehicles and has a turnover rate of about 10% per year.

The provisions of EPACT require that the Federal Government purchase Alternative Fuel Vehicles at a rate and in the numbers that would produce a fleet approximated by the figures shown in Table #1.

This schedule has since been superseded by Executive Order #12844, which was signed by the President on April 21, 1993. The required number of vehicle purchases and timeframe for those purchases is accelerated, compared to the requirements of EPACT and Executive Order 12759.

The vehicles which satisfy the purchase requirements must be manufactured in the United States or Canada, except to the extent that such a requirement is inconsistent with the General Agreement on Tariffs and Trade.

Although alternative fuel capable vehicles produced by Original Equipment Manufacturers (OEM) are preferred, vehicle conversions are allowed. There seems to be an implication that OEM should be taken to mean the original motor vehicle

manufacturer. This is not consistent with the conventional use of the word 'OEM', which would allow some vehicle conversion companies to be included in the definition of OEM in cases where they manufacture components or complete systems for sale to the public.

The aforementioned implication is reinforced by the discussion of vehicle warranty under Section 302, which discusses vehicle conversions. The provision which allows for conversions (Section 302) requires the conversion company to obtain an agreement from the OEM (vehicle manufacturer) which keeps the vehicle warranty in place after the conversion.

To support and promote the alternative transportation fuels programs within the Federal Government, the Secretary in cooperation with the Administrator of the General Services Administration, is required to educate officials and employees of Federal agencies by providing information on:

- Refueling and maintenance facilities
- Range and performance capabilities of AFVs
- State, local and commercial AFV programs
- Federal AFV purchases and placements
- Operation and maintenance of AFVs
- Incentive programs for Federal agencies and individual Federal employees.

The refueling facilities that supply alternative fuel to the Federal fleet shall to the maximum extent feasible (practicable), be commercial refueling facilities that are available to the public. However, in the event that public refueling facilities are not available or accessible, Federal agencies are authorized to enter into contractual arrangements for the supply of these facilities.

At least 50 % of the alternative fuels used in these vehicles are to be derived from domestic resources, except to the extent such requirement would conflict with the General Agreement on Tariffs and Trade. The Secretary is required to issue regulations to implement this requirement.

State Fleets

Section 409 of EPACT empowers the Secretary to issue regulations which establish guidelines for development, modification and implementation of State plans for purchasing and operating substantial numbers of alternative fuel vehicles by the year 2000. The proposed schedule for the mandated purchase of AFC vehicles by states begins in 1996, and would hypothetically, generate an operating fleet, that would support the numbers reflected in Table 1. (The Secretary has discretionary powers for setting the actual schedule for the state fleet mandates.)

The Secretary is to invite the Governor of each State to submit a State plan which describes how the States efforts will be coordinated with those of the Federal and local governments to support and increasing number of alternative fuel vehicles. By submitting a State Plan and obtaining the approval of the State Plan by the Department of Energy, the State becomes eligible for Federal assistance. The Federal assistance can be in the form of:

- Information and technical assistance
- Financial grants for implementation of plans
- Financial grants for purchase of AFVs.

The State Plan should contain information on and an examination of the following issues:

- Tax exemption for AFVs, fuels, and refueling facilities
- Introduction and use of AFVs
- Special parking privileges for AFVs
- Public education programs to promote the use of AFVs
- Treatment of AF sales
- Methods that State and local governments might employee to enhance the availability of alternative fuels, and allow electric vehicles to recharge at public facilities
- Allow public utilities to rate base, the incremental cost of; new AFVs, vehicle conversions, and installing AF refueling facilities
- Description of other incentives or programs that the State may devise
- Whether implementation of the State plan will require revision of State statutes and/or regulations (including traffic safety prohibitions)
- Services that can or will be provided by municipal, county, and regional transit authorities
- The effects of the State plan on programs authorized by ISTEA.

The Secretary shall consider (among other factors) 1) the energy and environmental impacts of implementing the plan, and 2) the number of AFVs. The State must agree to pay at least 20% of the cost of activities associated with the State Program, in order for their plan to be approved by the Secretary.

The Secretary, in consultation with the GSA Administrator, shall provide assistance to States in procuring AFC vehicles (including coordination with Federal AFC vehicle purchases).

An annual report on the State Program is to be prepared and sent to the President, Congress, and the Governor of each State participating in the program; giving the status of the program and providing recommendations from the Secretary for additional action.

Alternative Fuel Bus Program

EPACT empowers the Secretary of the Department of Transportation, in consultation with the DOE Secretary to enter into cooperative agreements and joint ventures with municipalities, counties, and/or regional transit authorities is urban areas with 100,000 population (or more) to demonstrate the feasibility of commercial applications of alternative fuels in urban buses and other mass transit motor vehicles. Private firms, who are willing to make cash or in-kind contributions to a alternative fuel bus project, are eligible to enter into cooperative agreements and/or joint ventures with the Department of Transportation (DOT). Again, projections for the alternative fuel bus fleet are shown in Table 1.

The minimum amount of cost sharing required for a municipality, county or transit authority to enter into a cooperative agreement for a demonstration project is 20%.

EPACT also empowers the DOT Secretary to provide financial assistance to agencies, municipalities, or political subdivision to cover the incremental cost of school buses which feature dedicated use of an alternative fuel. Allowable costs for support from DOT include:

- The cost of purchase and installation of refueling facilities
- The cost of converting the buses to dedicated AF use.

The DOT may provide this assistance

directly to a person who is the subcontractor (for supply of school bus transportation requirements) to the agency, municipality or political subdivision. Conversions supplied as a result of funding provided under EPACT must comply with the warranty and safety requirements for alternative fuel conversions contained in section 247 of the Clean Air Act.

Funding for implementing this program is not to exceed $30,000,000 for each of the three fiscal years 1993, 1994, and 1995.

Private and Local Government

The Secretary is authorized by EPACT to engage in a rule making exercise which will establish requirements and a schedule for fleet operators (covered persons, as defined in EPACT) to acquire alternative fuel capable light duty vehicles. The proposed schedule for this mandate contained in Section 507, calls for 20% of the LDV purchases made in model years 1999, 2000,and 2001 by covered persons (who are not alternative fuel providers), are to be the alternative fuel capable. The schedule accelerates in model years 2002 and 2003 to 30 and 40%, respectively. The final AFC vehicle purchase level of 70% is to be achieved in model year 2006. Projections for the fleet of operating AFC vehicles for this sector are shown in Table 1.
As shown in Table 1 the private sector and local government sector are the last groups covered by EPACT, scheduled for minimum AFC vehicle purchase requirements.

The Secretary is allowed some discretionary authority in the rulemaking exercise

DOE Response to EPACT

As a result of Executive Order 12759 and the passage of the Alternative Motor Fuels Act (AMFA) of 1988, DOE had some significant projects already underway when EPACT became law in October of 1992. DOE's efforts to date can be described by providing information on three major program areas:

- Alternative Motor Fuels Act
- Executive Orders 12759 and 12844, and
- The Clean Cities Program

AMFA supported demonstration projects in three primary use areas; light duty vehicles, buses, and heavy duty vehicles. DOE, in cooperation with the General Services Administration, had the experience of two major solicitations for alternative fuel capable vehicles. As a result of these procurements approximately 6,500 AFC light duty vehicles, are currently operating within the Federal Fleet. DOE also participates in the Department of Transportation's Clean Air Program which supports the purchase of alternative fuel capable transit buses by transit authorities around the country. To date there are approximately 850 AFC transit buses (using EPACT definintion of AF) operating within transit authorities in the United States. In addition to the joint efforts with DOT, DOE has entered into agreements with a number of school districts around the country to support the purchase and operation of school buses, which operate on alternative fuels. Heavy duty truck projects have also been sponsored; most in cooperation with city, county and state governments, although some private fleets have also been supported. Figure 2 shows a map of the United States with the location of each of the AMFA project sites. (Details on these projects have been reported elsewhere in this conference.)

Executive Orders 12759 and 12844, encouraged an accelerated pace for conversion of the Federal Fleet to alternative transportation fuels. In response to Executive Order 12759, DOE conducted a survey of Federal Agencies to

determine the level of commitment, preferences and planned location of each agency's AFC vehicles. The survey (5) showed the number and type of vehicles that would be requested by the Federal agencies, outstripped the vehicle manufacturer's plans to produce AFC vehicles. The survey also indicated that, in the event the vehicles were not available in the quantity or model types requested, the agency would accept after-market vehicle conversions. These conversions were viewed as an interim measure that would decline over the first few years of the program, in deference to the increased capability of the motor vehicle manufacturers to produce the desired number and type of AFC vehicles.

Detailed information on the number type and location of vehicles identified in the survey is presented in the '5 year plan' (5). The bulk of the requests for AFC vehicles in the passenger car category were alcohol fuel capable vehicles, which could be procured directly from the motor vehicle manufacturers.

In response to the short-fall in AFC manufacturing plans relative to the targets established in the Executive Orders, and the preferences of the other Federal agencies, DOE initiated a vehicle conversion and fuel supply solicitation. This procurement was designed to supply high quality vehicle conversions and fuel supply services for agencies which indicated a desire to operate their vehicles on natural gas or liquified petroleum gas. Awards from the vehicle conversion procurement are just now getting underway.

The third program element devised by DOE to meet the goals of EPACT, is the Clean Cities Program. Again, the details of this program have been provided in a paper which is also part of the Symposium. Information on the design and philosophy of the program are provided in the program plan (6). However, a brief recapitulation of the program and the status of projects that will be supported is within the scope of this paper.

The purpose behind Clean Cities is to organize private, city, county and state interests in a given community in a manner which will allow a collective focus on one or perhaps two alternative fuels. The focus will allow each entity to leverage their purchasing power with the other members within a community to support the purchase, operation and maintenance of alternative fuel capable vehicles. Leadership for the effort in each community is within the city or local government office. The local government officials are most knowledgeable about local resources and private fleets which may be able to contribute to the 'grass roots' level effort to support and concentrate AFC vehicle operations within the community. Also, the local government would be the most logical choice for an information and polling on which alternative fuel would be featured in the community. It is important the local government limit their choices for an alternative fuel to one or perhaps two alternative fuels since, the more numerous the alternative fuels available within a given area, the more dilute the combined investment in any one alternative fuel.

By marshalling the interests and combined purchasing power of the private and governmental entities within a community, the city can capture the combined purchasing power of the community to support the choice for an alternative fuel. With a commitment from the local Clean Cities members, in terms of number of vehicles to be purchased, the group can apply for recognition from DOE and designation as a Clean City. This in turn will allow, that community to obtain a share of the AFC vehicles procured by GSA, to be located and operated within their community (to the extent that there is

a Federal Government presence within the community). This approach and this activity is consistent with the language contained in Section 507. The activity that is currently taking place is several years in advance of the scheduled program.

Currently, DOE has recognized Clean Cities Programs in the following six metropolitan areas:

Washington DC
Atlanta
Philadelphia
Denver
Las Vegas, and
Wilmington.

The alternative fuels chosen for use in these cities include, compressed natural gas, liquified petroleum gas and methanol.

Relevance to Alcohol Fuels

The projects and programs that are currently underway and those that are anticipated to be covered by EPACT represent a significant growth opportunity for alcohol fuels.

In terms of existing engine/vehicle technology, the alcohol fuels have some significant advantages over other alternative fuels. Alcohol fuel capable light duty vehicles are available from the major motor vehicle manufacturers. The dielectric sensor design approach is effective in terms of supplying the engine and emission control components with the required fuel quality information to promote efficient air-fuel ratio control (and thereby efficient emission control and fuel efficiency). These vehicles enjoy full warranty service from the manufacturer. There is no inherent vehicle weight or cargo space disadvantage associated with these vehicles since there is only one fuel tank. The alcohol refueling infrastructure issue is mitigated due to the ability to refuel and operate effectively on gasoline.

The survey of Federal agencies (5) indicated that more than half of the requests for vehicles from this group would be for alcohol fuel capable vehicles. The Clean Cities Program even in its early stages reflects the choice of some cities to use alcohol fuels.

Also, projects being conducted under AMFA demonstrate a fairly mature design technology base for alcohol fuels. Fuel economy for alcohol fuel capable, light duty vehicles is comparable to that gasoline powered vehicles. Exhaust gas emissions are also comparable to slightly lower that those of current technology vehicles operating on gasoline. Heavy duty trucks and transit buses operating on alcohol fuels produce emission test results which meet emission standards for all regulated pollutants, including NOx and particulate (which are of particular difficulty for vehicles powered by conventional fuels).

Based upon the activities supported by EPACT and the current state of development of alcohol fuel utilization technology, it is likely that alcohol fuels will make a significant contribution to the stated fuel replacement goals of EPACT in the years 2000 and 2010.

Relationship to Other Statutes

EPACT relies and builds upon several other existing statutes including the Alternative Motor Fuels Act, and the Clean Air Act Amendments of 1990 (CAAA). It is important to make note of the provision contained in Section 510, which gives precedence to the Clean Air Act Amendments over EPACT. This provision is especially important in terms of how the definition of alternative fuels is to be interpreted. Reformulated gasoline is included in the definition of alternative fuels in the CAAA; in EPACT it is not.

Other statutes which will be effected by

EPACT include the Natural Gas Policy Act and the Intermodal Surface Transportation Efficiency Act of 1991 (ISTEA).

Conclusions

EPACT is a significant step for the United States in terms of addressing the future of transportation fuels in this country. Although the statute has been 'on the books' for more than a year, the regulations which will ultimately define the statute, have yet to be established. The Secretary of the Department of Energy is given significant authority and flexibility in terms of implementing the provisions of the statute. Although, a fundingto implement the statute is authorized, no has been appropriated. So, much of what EPACT will mean for the future of alcohol fuels remains to be seen.

However, the potential does exist for alcohol fuels to contribute to the goals of EPACT. Using the projected number of AFC vehicles that will be operating as a result of EPACT in the year 2000; one could estimate that the fuel supply for these vehicles would require about 0.1 quadrillion Btus per year. If the alternative fuel supply market was fragme in such a way that methanol contributed 25 % and ethanol contributed 15%; this is well within the world production capacity for methanol (7.4 billion gallons per year, estimated) and ethanol (1.3 billion gallons per year, estimated). It is important to recall the fuel supplied to the fleet projected in Table 1, is short of the replacement goal of 2.7 quadrillion Btus (by a factor of 27).

Similarly, the replacement fuel goal for the year 2010, is well beyond the current alcohol production capacity; 10.5 quads required versus 0.58 quads combined worldwide production of methanol and ethanol (estimated).

The future for alcohol fuels, as a result of EPACT, looks positive for growth in terms of AFC vehicle demand and demand for alcohl fuels. It is likely, that alcohol fuels will contribute only a fraction of the replacement fuel goals; perhaps as much as 40% in terms vehicle demand established under AMFA and Executive Order 12759. Even with this portion of the market, the production for AFC vehicles and alcohol fuels would have to undergo rapid expansion. If this favorable market is to become a reality, three things must come to pass, 1) Congress must appropriate the funds to implement EPACT, 2) industry must be ready with proven, commercial AFC vehicles and high quality alcohol fuels and, 3) favorable resolution of how the definition of reformulated gasoline will be handled, in terms of the replacement fuel goals (EPACT versus CAAA).

References

1.) Public Law 102-486, The Energy Policy Act of 1992, October 24, 1992

2) Executive Order 12759, April 1992.

3) Executive Order 12844, April 21, 1993.

4) Public Law 100-494 , The Alternative Motor Fuels Act of 1988, October 1988

5) Alternative Fuel Vehicles for the Federal Fleet: Results of the 5-Year Planning Process, U.S. Department of Energy, August 1992.

6) Clean Cities Implementation Plan, U. S. Department of Energy, March 26, 1993, 19 pp.

Appendix I - Key Definitions

Section 301 of Title III provides a number of key definitions that are important in the interpretation of the statute. Key among these, are as follows:

Alternative Fuel - means methanol, denatured ethanol, and other alcohol; mixtures containing 85 percent or more (or such other percentage , but not less than 70 percent as determined by the Secretary, by rule, to provide for requirements relating to cold start, safety, or vehicle functions) by volume of methanol, denatured ethanol, and other alcohols with gasoline, or other fuels; natural gas; fuels (other than alcohol) derived from biological materials; electricity (including electricity from solar energy); and any ~~other~~ fuel the Secretary determines, by rule, is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits.

Alternative fueled vehicle - means a dedicated vehicle or a dual fueled vehicle.

Covered person - means a person that owns, operates, leases, or otherwise controls -

a) a fleet that contains at least 20 motor vehicles that are centrally fueled or (are) capable of being centrally fueled, and are used primarily within a metropolitan statistical area or a consolidated metropolitan statistical area, as established by the Bureau of Census, with a 1980 population of 250,000 or more; and

b) at least 50 motor vehicles within the United States

Replacement Fuel - means any portion of any motor fuel that is methanol, ethanol, or other alcohols, natural gas, liquified petroleum gas, hydrogen, coal derived liquid fuels, fuels (other than alcohol) derived from biological materials, electricity (including electricity from solar energy), ethers, or any other fuel the Secretary determines, by rule, is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits.

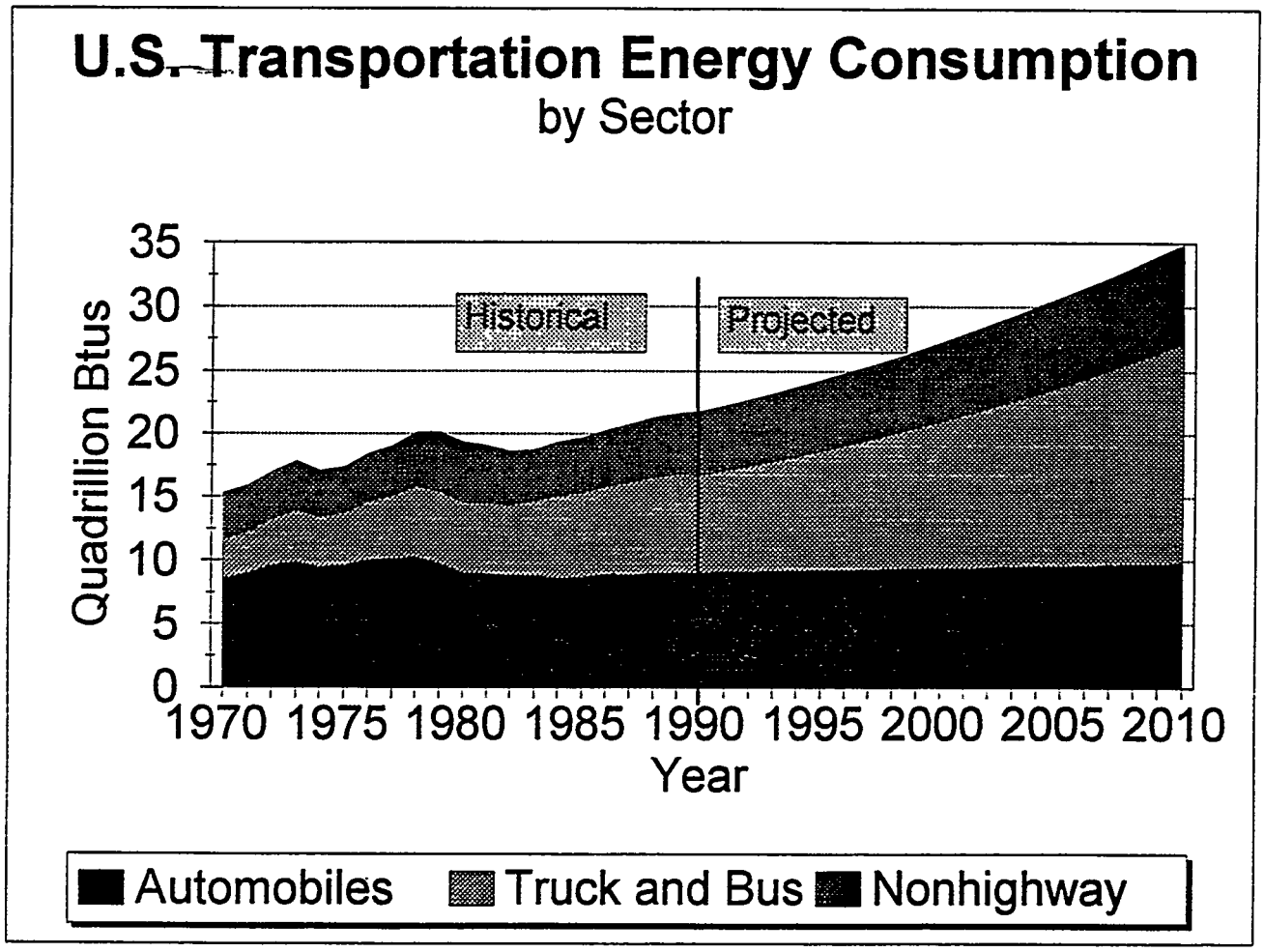

Figure 1. Historical and projected transportation energy consumption patterns, by sector

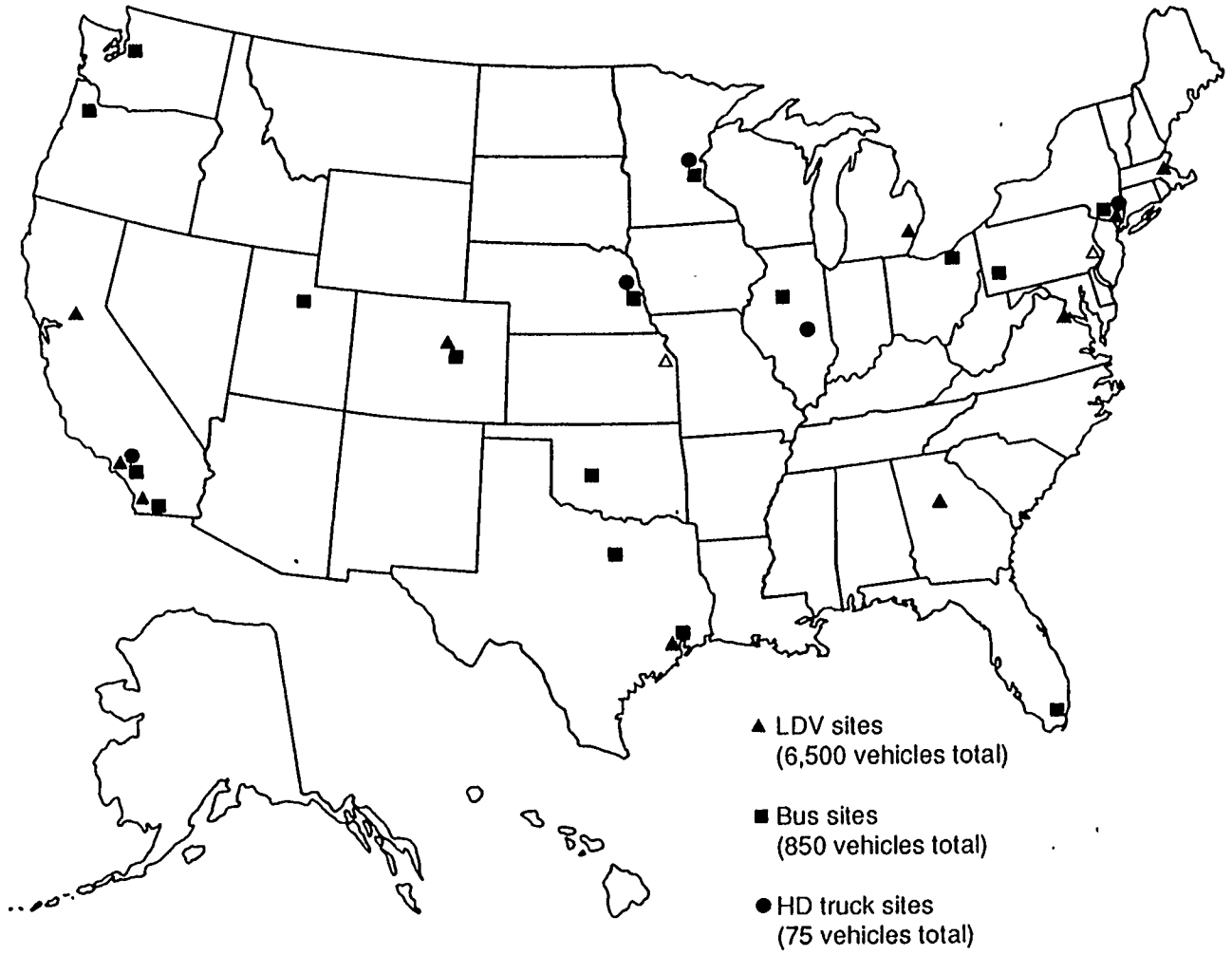

Figure 2. Major Alternative Fuel Operations Sites

Table 1

Projected AFC Vehicle Operations

Vehicles Operating at CY End

Calendar Year	Federal Fleet	State Fleet	AF Provider Fleet	AF Bus	Local and Private	Total
1993	5,000	NR	NR	NR	NR	5,000
1994	12,500	NR	NR	NR	NR	12,500
1995	22,500	NR	NR	NR	NR	22,500
1996	35,000	20,000	7,500	NR	NR	62,500
1997	51,500	65,000	20,000	NR	NR	136,500
1998	71,500	50,000	37,500	NR	NR	159,000
1999	96,500	65,000	47,500	NR	341,000	550,000
2000	111,500	98,500	45,000	NR	682,000	937,000

NR - None Required

AN EVALUATION OF ETHANOL/ETHER BLENDS IN GASOLINE

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Abstract

The following information is in support of a proposed fuel waiver application. the proposed waiver application will seek EPA approval for a mixture of ethanol and various ethers in combinations up to 3.7% oxygen by weight. The preliminary information gathered to date was derived from a variety of sources. Additional technical input and data are being solicited from industry sources in an effort to develop a comprehensive application. Initial data has been developed by the State of Nebraska with technical assistance provided by Mr. Walt Douthit. Technical assistance has also been provided by the Oxygenated Fuels Association. Financial support for this effort has been provided by the State of Nebraska and the United States Department of Agriculture.

AN EVALUATION OF ETHANOL/ETHER BLENDS IN GASOLINE
A COOPERATIVE PROGRAM TO DEVELOP A WAIVER APPLICATION TO THE U.S. EPA

Introduction

Environmental changes in fuel standards will stress refinery economics and fuel logistics to the limit. fuel manufacturers and marketers must develop flexible responses to marketplace challenges, including mandatory, sometimes seasonal use of oxygenates. The Nebraska ethanol development program initiated a cooperative ether development program in 1988. The goal of that program was to increase the use of ethanol-based fuels through development of ethers, potentially opening some fungible gasoline markets. That approach also included the belief that ethanol blends could be more widely used in combination with ethanol-derived ethers.

Several refiners expressed an interest in cooperating with this program to increase flexibility or markets. The Sun Company, along with Arco Chemical and others, agreed to collaborate in this cooperative effort. The goal is to develop a U.S. EPA waiver application which proposes the use of ethanol/ether combinations up to 3.7% wt. oxygen. Preliminary results of this cooperative effort are shown in this report. Work continues to obtain the data necessary to complete the application as outlined here.

Data Development

In an effort to obtain data about ethanol/ether blend characteristics, the Nebraska Ethanol Authority and Development Board (NEADB) initiated a series of tests.

AutoResearch Laboratory Incorporated (ALI), Chicago, Illinois, was contracted by the NEADB to determine the gasoline blending and handling properties of oxygenates and designated ethanol/ether blends. Data developed includes the primary properties of blending vapor pressure, distillation, V/L ratio, water tolerance, and blending octane quality. Commingling data was also generated to assess fuel synergism and to identify any adverse blending effects.

Findings

This work is the initial phase toward obtaining and EPA waiver to allow blends of ethanol and higher molecular wight ethers to 3.7% oxygen by wight equivalent in gasoline. further, these data are a significant contribution to the technology bank for alcohols and ethers. The major findings are as follows:

- The blending value (BV) Reid Vapor pressures (RVP) for TAME and ETBE are significantly lower than the neat RVP values. The BVRP for TAEE is at or above its neat vapor pressure measurement. The differences are believed to be the result of the purity of the product since increased dosages in the fuel depict values close to neat measurements.

- The BVRVP's of the measured oxygenates in the base fuel are an excellent means of predicting final RVP values of the blends. A linear equation for blend vapor pressure can be based on the sum of the partial pressures (or Reid VP) of the constituents; i.e., the concentrations of the materials in the blend and the BV's are multiplied and summed.

- Blending values for ethanol are non-linear since the increased RVP remains about the same for the concentration range of

interest - less than 2% to wl over 10%. This is common knowledge for alcohol blending, but these data show how ethanol blend values can be used with ether blend values to give an accurate vapor pressure prediction.

- Data show that the lower vapor pressure ethers can be mixed with ethanol to overcome/offset the relatively high BVRVP of ethanol. The vapor pressure blending effects of ethers are equivalent to use of blending with low vapor pressure hydrocarbon components, as illustrated in this report using UDEX Raffinate. the data suggest no synergistic effects among the ethanol/ether mixes.

- The temperature [T(V/L = 20)] for a vapor-liquid ratio of 20 is increased and thus improved with ethers mixed with ethanol, relative to blending only ethanol in the gasoline. As expected, the distillation data show that ethers help to moderate the adverse distillation characteristics of ethanol-only blends.

- One area of concern regarding vapor pressure is commingling of the ethanol/ether blends with non-oxygenated gasoline. A significant RVP increase is noted with low concentrations of an oxygenate blend, even with ethers present. The effect is not as severe as with ethanol-only blends. The results, however, are predictable using the BV's of the ethers and the relatively high BV for ethanol at the reduced concentration.

- As with final blend RVP predictions, the final octane of a blend can be predicted very accurately using the octane blending values of the individual fuel constituents. Here again, the relative concentrations of the components are multiplied by the BVON's (Blending, Value Octane Number of the constituents) and the component values summed. The predictions are so close that no synergistic octane effect among these mixed oxygenates appears likely.

- ETBE was found to have the highest BVON of the ethers tested at 111. TAME and TAEE test about the same, between 102 and 104. There appears to be little difference in BVON relative to ether concentrations up to 12% in the blend.

- Approval to use ethanol/ETBE blends will likely increase potential ethanol markets. Allowing MTBE ethanol blends would extend both marketability of ethanol and increase the flexibility of mixing all oxygenates in the marketplace. This can be important for exchanges to handle temporary product outages, for independents having a broader choice of oxygenate blend terminals to choose from, and for the potential use of mixtures for the best performance properties balanced with environmental needs.

- In addition to exhaust emissions and materials compatibility testing now in progress, Sun has examined vapor pressure and water tolerance blending effects of MTBE/ethanol blends. Table VI shows 1) only minimal cosolvent effects of MTBE on these ethanol fuels, and 2) the reduced or lack of car tank commingling effects even as high as 70 °F actual tank temperature.

- The water tolerance of these blends is shown in Figure 4. At some temperatures, e.g., 50°F, water tolerance appears to blend more or less linearly. This result would indicate that dispenser, car tank, or tender/tank heel blending should not be a problem for haze or phase separation with MTBE/ethanol blends.

- Of special interest, the ethers do not appear to act as cosolvents for ethanol

in a two phase fuel/water system. The Nernst distribution coefficient for the ethanol was shown to remain essentially the same in such a system with or without high ethers present in the fuel. However, these data should be considered preliminary, and more extensive water extraction data need to be developed to provide quantitative information. The Nernst data concerning the ethers are somewhat erratic and judged to be inconclusive. More extensive laboratory work must be done to provide substantive results, but information developed to date supports the original premise that higher ethers can be blended with ethanol to offset the adverse effects of alcohol blending in gasoline.

Test Summary

The analytical work may be summarized in the following six tasks which were performed with input from AutoResearch Laboratories, Inc.

Task I - Assay Base Fuel. the selection of its base fuel was made from the Auto/Oil AQIRP(Air Quality Improvement Research Program). For completeness, tests conducted were PIANO analyses, RVP, T(V/L = 20), ASTM D-86 Distillation, RON/MON, water tolerance and other tests to show conformance with the ASTM D4814 specification. The Appendix Tables A-I and A-II summarize these data.

Task II - Assay Oxygenates. The compounds tests were commercial denatured ethanol, tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE), and tertiary-amyl ethyl ether (TAEE).

Primary analyses were made for purity, peroxides and water solubility/extraction. Appendix Tables A-III and A-IV give property data.

Task III - Oxygenate Blend Analyses. The blends, on a volume percent basis, earmarked for study were base fuel with:

- 5% ETOH + 12% ETBE
- 5% ETOH + 6% ETBE = 6% TAME
- 5% ETOH + 6% ETBE + 6% TAEE
- 5% ETOH + 6% TAME 6% TAEE
- 5% ETOH + 12% TAME

Tests conducted included RVP, ASTM D-86 distillation, T(V/L = 20), RON/MON, and water solubility/extraction. Tables A-V and A-VI show property data which will be discussed in more detail later in this report.

Task IV. The base fuel containing the oxygenates were also commingled to ascertain mixing effects and possible synergism regarding properties. Table A-VII and Figure A-1 illustrate the effects of commingling on the vapor pressure of the final mixture that will be addressed later in this report. Also Tables A-VIII and A-IX show water extraction and solubility data for the ethers and the mixed ethanol/ether blends, respectively.

Task V. Five and ten percent volume ethanol was blended with 12% volume UDEX Raffinate, a low vapor pressure hydrocarbon refinery gasoline blending stream to ascertain property similarities compared with blending higher molecular weight ethers. Data were added to Table A-VI.

Task VI. This task was reserved for contingency blending based on some of the major findings from the data developed. Examples of this were the vapor pressure and octane testing of two fuels: 10% by volume ethanol in the base fuel and 12% by volume TAEE in the base fuel. These data were included in Table A-VI.

Some of the initial blending of ethanol/ethers was erroneously done with a 3.2 volume % ethanol rather than a 5.0

volume % as designated. The data are useful, however, and are included here for analyses.

Table I combines the data for vapor pressure and octane quality of the oxygenates, primarily for comparison of neat values versus the actual blending values for the individual ethers/alcohol in the base fuel. For example, the neat value RVP may be compared to the actual blending value RVP, looking at the firs three columns in the table. Note specifically that ethanol does not blend on a linear basis. Figure 1 illustrates data plotted from Table I, and the curve is extended to extrapolate BV's at lower ethanol concentrations in the fuel. Also of interest, the BVRVP for ETBE and TAEE are about the same as their neat values. On the other hand, TAME blends significantly lower than its neat value. As previously mentioned, this phenomena is believed to be related to the purity of the product. Figures 2 and 3 illustrate the volatility data of the mixed blending.

The octane quality of the neat oxygenates blended into the base gasoline are also shown in Table I. The blending values (BVON) are calculated based on the octane improvement increase over the base gasoline. These calculations are shown in the Appendix. The R+M/2 values for ETOH (110-114) are about the same as for ETBE (111-112). Values for TAME and TAEE are significantly lower and are similar (102-104).

Table II illustrates the analyses of RVP and octane quality versus calculated values done of a linear basis from Table I. Of primary interest and importance, the calculated values are shown to be very accurate in predicting either the RVP or the octane value of the ether/alcohol fuel blends. Partial values based on percentage in blends and blending value are summed to obtain the final value of the total gasoline/oxygenate blend. Calculations are given in the Appendix. In particular, refer to the three equation method for maximizing oxygen content in the fuel with ethanol while using a higher ether to offset any vapor pressure effects.

Table III illustrates that the use of a low RVP hydrocarbon component is equivalent to blending with one of the low RVP oxygenates tested. Predicted values, as previously shown on Table II for the oxygenates, are essentially the same with the all hydrocarbon UDEX Raffinate. Moreover, no synergism with the oxygenate blends is discernable. Here again, calculated RVP is an excellent means of predicting the vapor pressure of the fuel blend.

Table IV is a summary of the Nernst coefficient data as determined from Tables A-VIII and A-IX. The ethers have high coefficients in favor of mixing with gasoline rather than water. However, the ether data developed with ethanol present is questionable and inconclusive. The Nernst data for the ethanol tends to indicate that the presence of ethers in the gasoline inconsequential. More data with an expanded analytical procedure need to be developed to confirm these results.

Figures A-2 through A-5 graphically display the water solubility limits of the base gasoline and the ethanol/ether blends. The procedure used to provide the graphs is included in Appendix X7.2.2 of a previous ASTM proposed specification for gasohol.

Conclusion

Laboratory and in-field testing has demonstrated technical attributes of ethanol/ether combinations at 3.7% wt. oxygen in gasoline. The ability to use such fuel blends will provide additional flexibility to marketers and refiners when attempting to meet new fuel standards. A proposed application for ethanol/ether combinations to 3.7% oxygen is entering a final stage of preparation. A waiver proposal to the U.S.

EPA will be submitted upon completion of final materials and emissions tests.

Acknowledgement

This work was supported by the United States Department of Agriculture and ARS with technical consultation by Mr. Walt Douthit.

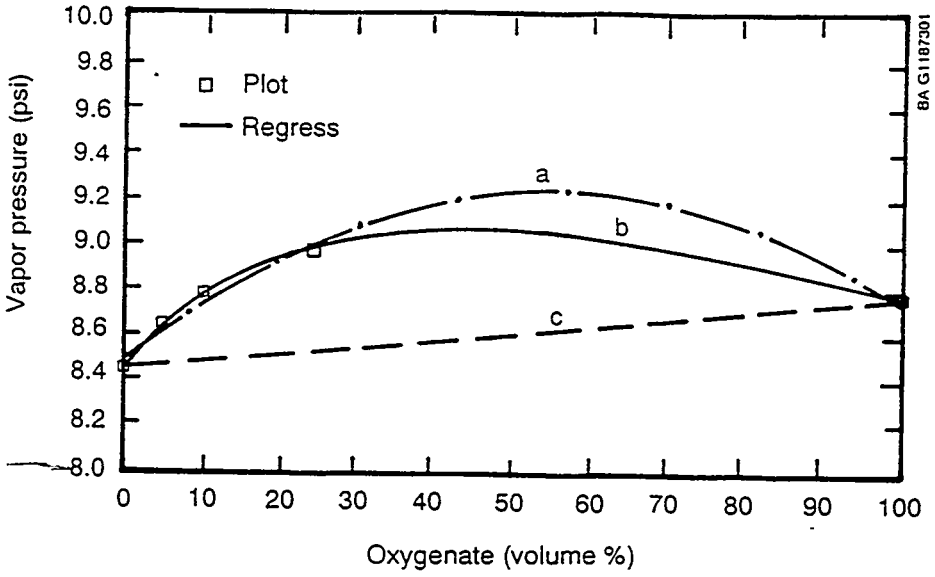


Figure A-1. Commingling vapor pressure effect - 5%V ethanol + 12%V ETBE

(a) second order polynomial equation
(b) based on experienced judgement
(c) linear blending line

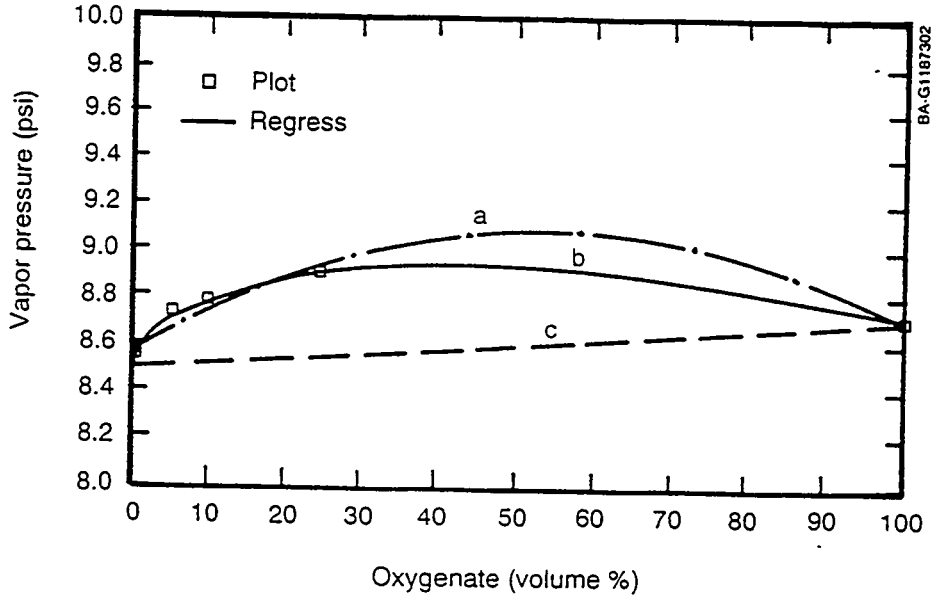


Figure A-1. Commingling vapor pressure effect - 5%V ethanol + 5%V ETBE + 6%V TAME

(a) second order polynomial equation
(b) based on experienced judgement
(c) linear blending line

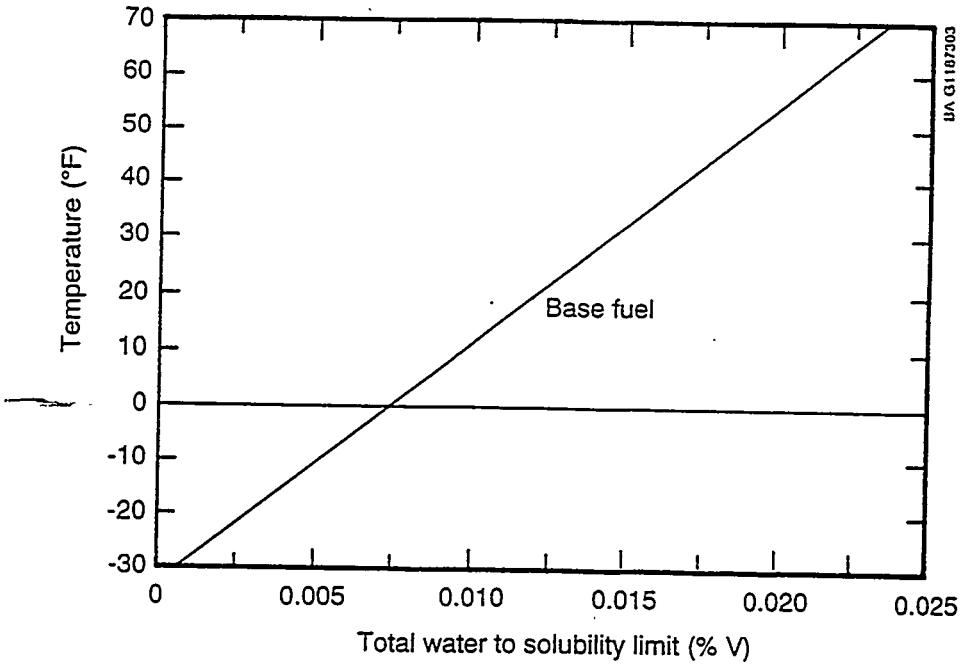


Figure A-2. Total water solubility of a base unleaded gasoline

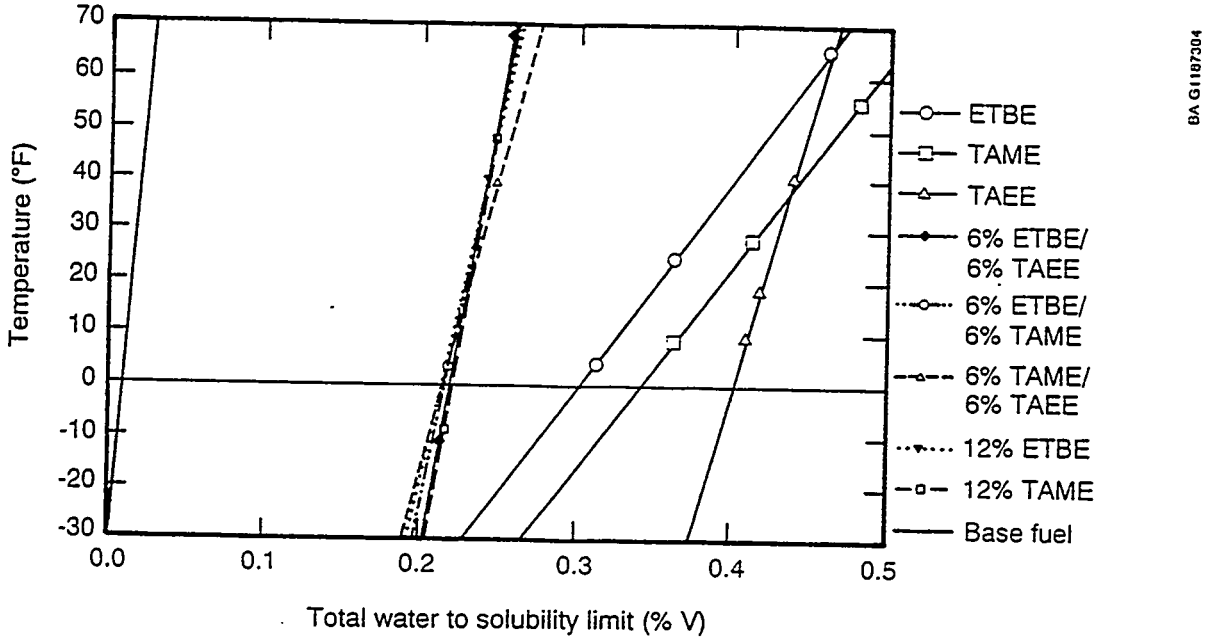
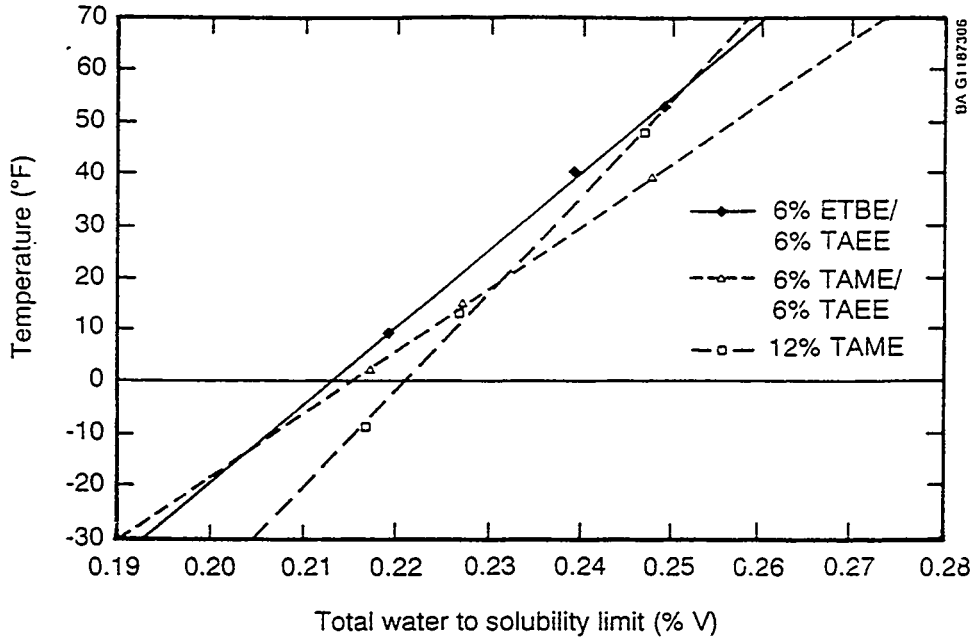


Figure A-3. Effects of oxygenates on water solubility of ethers and base unleaded gasoline



Source: Autoresearch Laboratories, Inc.

Figure A-4. Effects of ethers on water solubility of an unleaded gasoline containing 5%V ethanol

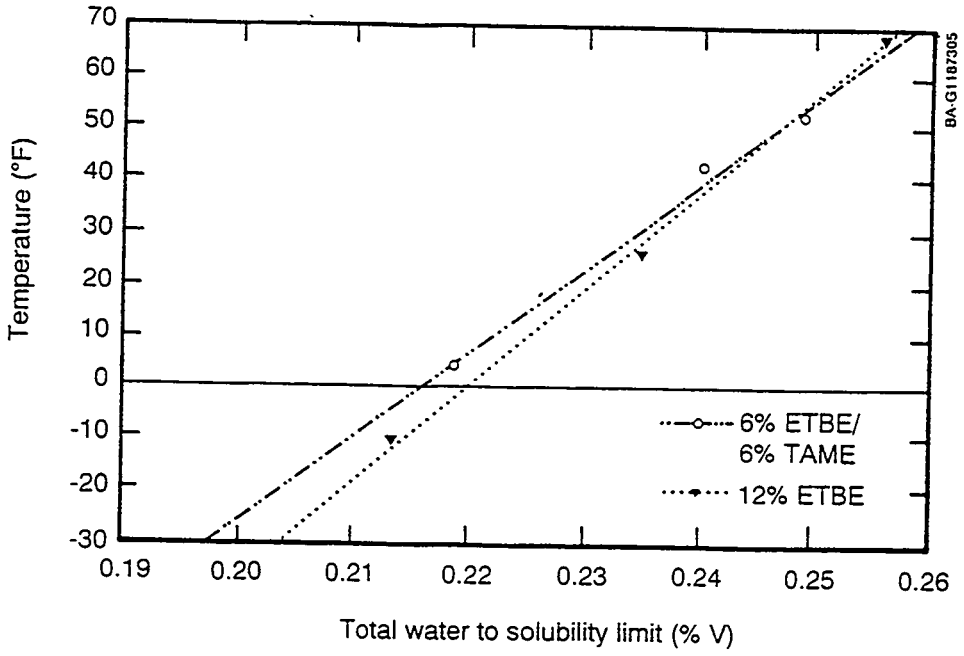
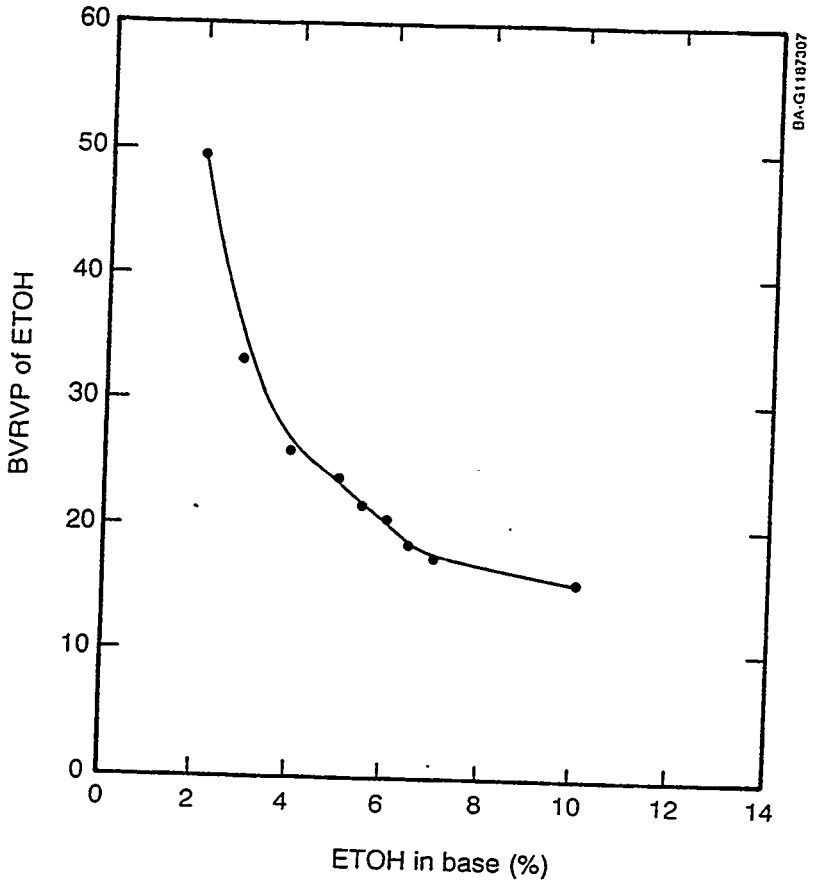
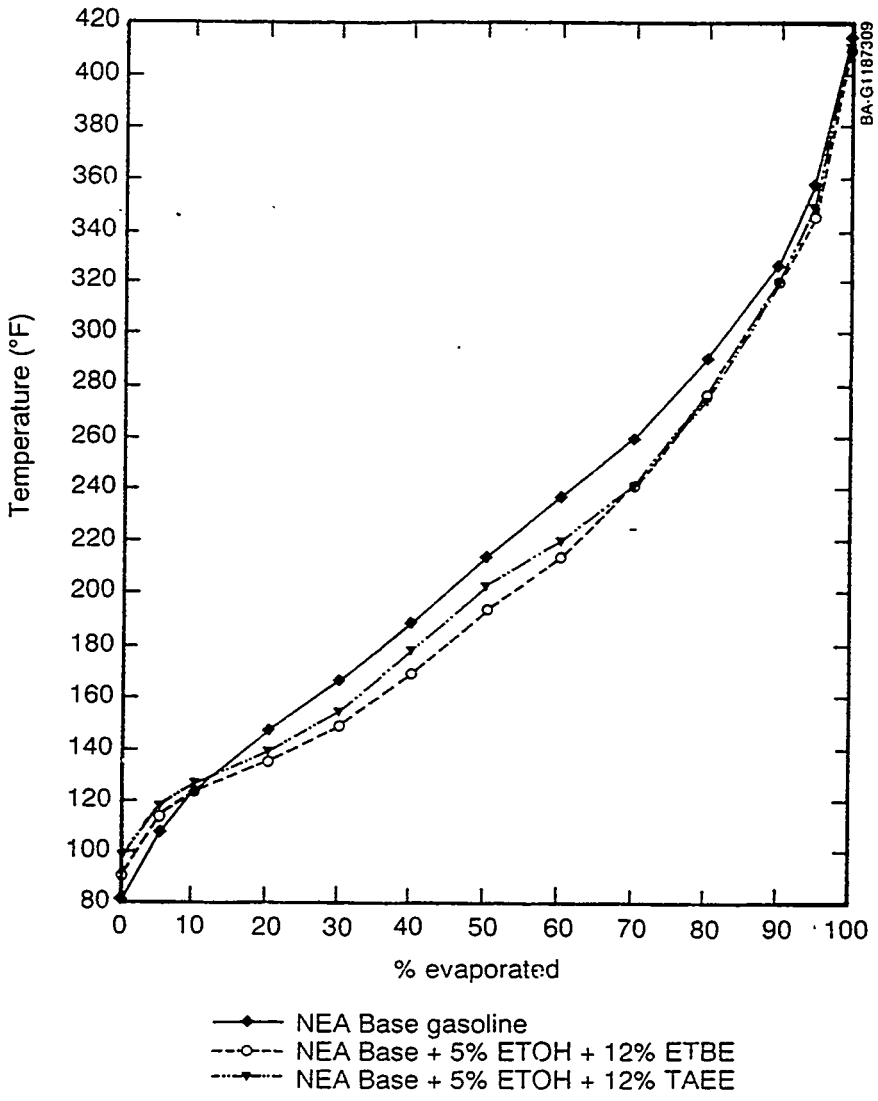


Figure A-5. Effects of ethers on water solubility of an unleaded gasoline containing 5%V ethanol



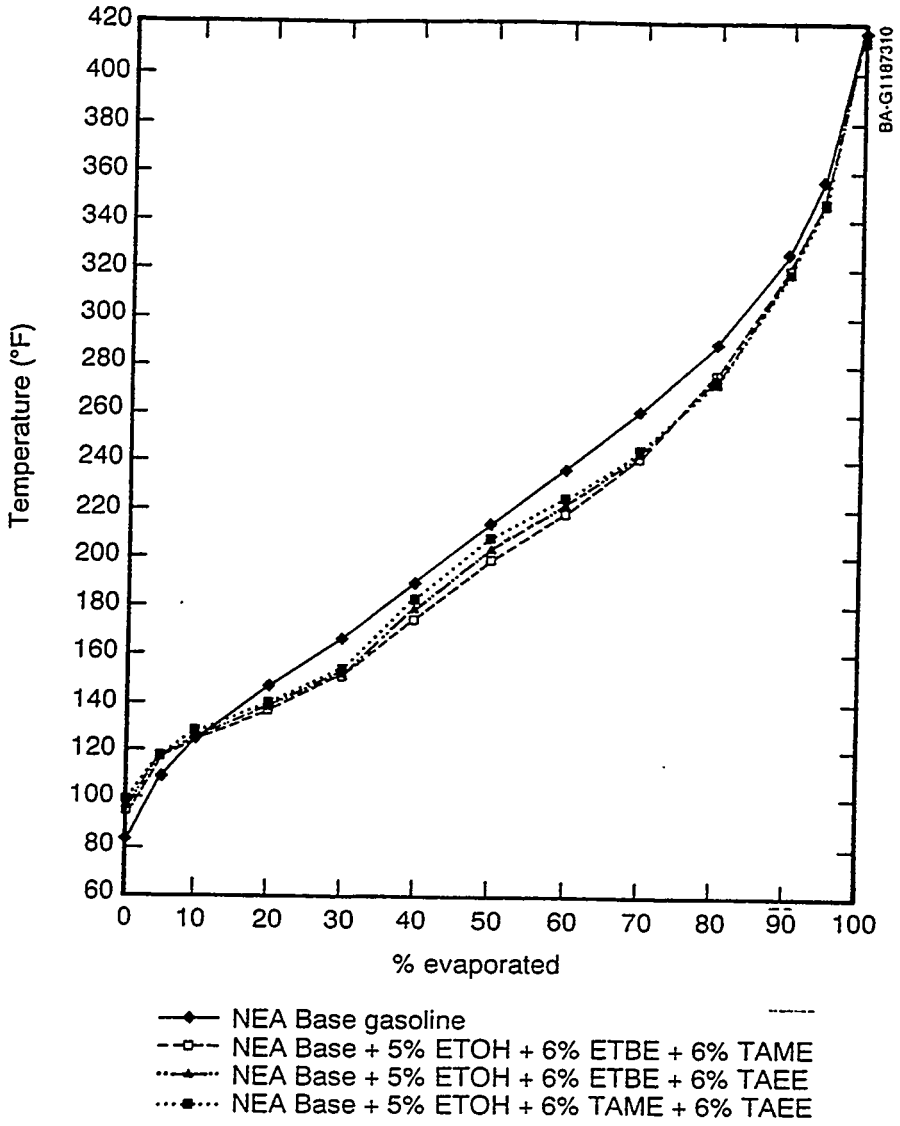
Source: Walter Douthit

Figure 1. ETOH vapor pressure blending values



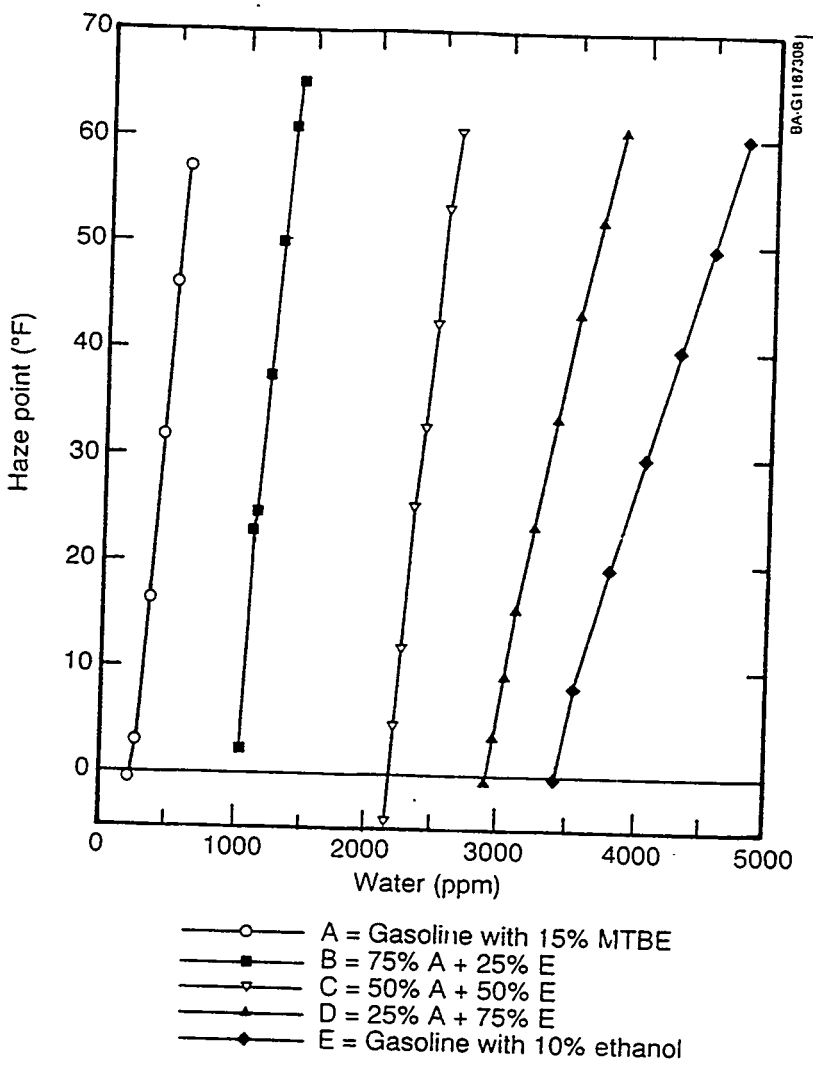
Source: Walter Douthit

Figure 2. Effects of oxygenate combinations on distillation



Source: Walter Douthit

Figure 3. Effects of oxygenate combinations on distillation



Source: Dr. Brian C. Davis

Figure 4. Haze point of MTBE/ethanol gasoline blends

Table I. Blending Vapor Pressure and Octane quality of Oxygenates

Blend	Neat RVP	Fuel RVP Analysis	Oxygenate Blending Value RVP	RON	MON	R+M/2	CALC BVON (R+M/2)
Base Gasoline	8.65			94.0	84.8	89.4	89.4 (89.2)
EtOH (Denat)	4.09						
-3.2% Blnd by Vol		9.42	32.8	95.0	85.3	90.2	114.4
-5.0% Blnd by Vol		9.43	24 (26)	95.9	84.8	90.4	110
-10%		9.38	16.8	96.9	85.7	91.3	110
ETBE	4.92						
-6%		8.38	4.17	95.5	85.7	90.7	111
-12%		8.18	4.78	97.2	87.0	92.1	111.7
TAME	2.77						
-6%		8.19	1.0	95.0	85.3	90.2	102.7
-12%		7.8	1.58	96.3	86.2	91.2	104.2
TAEE	2.19						
-6%		8.26	2.19	95.0	85.3	90.2	102.7
-12%		7.88	2.92	95.7	85.7	90.7	101.7

Source: Walter Dousthit

Table II. Analyses vs. Calculated Vapor Pressure and Octane Quality of Blends

Blend	RVP Analysis	CALC RVP of Blend	RON	MON	R+M/2	MIX BVON	CALC R+M/2
3.2% EtOH/ 12% ETBE in Base	8.85	8.96	98.1	87.9	93.0	113.2	92.9
5.0% EtOH/ " "	8.9	8.95	98.4	87.2	92.8	109.4	92.9
3.2% EtOH/ 6% ETBE/6% TAME	8.74	8.70	97.9	87.7	92.8	111.8	92.3
5.0% EtOH/ " "	8.76	8.71	98.2	86.9	92.6	109.4	92.3
3.2% EtOH/ 12% TAME	8.59	8.65	97.2	87.2	92.2	107.9	91.8
5% EtOH/ " "	8.66	8.57	97.9	86.4	92.2	107.0	92.0
3.2% EtOH/ 6% TAME/6% TAEE	8.59	8.58	97.3	87.4	92.3	108.6	91.8
5% EtOH/ " "	8.67	8.59	97.9	86.5	92.2	107.0	92.0
3.2% EtOH/ 6% ETBE 6% TAEE	8.72	8.77	97.9	87.8	92.9	112.5	92.3
5% EtOH/ " "	8.74	8.78	98.1	86.7	92.4	108.2	92.3

Source: Walter Douthit

Table III. Analyses vs. Calculated Vapor Pressure of Ethanol Blended With Low RVP Hydrocarbon UDEX Raffinate

No./Blend	Base Gasoline RVP	Analysis	BVRVP Ethanol	BVRVP Raffinate	Calc. RVP of Blend (See Below)
1. 5% EtOH/12% Udex Raffinate	8.56	8.86	24(a)	4.68	8.87
2. 10% EtOH/12% Udex Raffinate	8.56	8.92	16.8(a)	4.68	8.92

Calc.

Blend No. 1 .83 (BVRVP Base Gasoline) + .05 (BVRVP EtOH) + .12 (BVRVP Raff.) = .83 (8.56) + .05 (24) + .12 (4.68) = 8.87

Blend No. 2 .78 (BVRVP Base Gasoline) + .10 (BVRVP EtOH) + .12 (BVRVP Raff.) = .78 (8.56) + .10 (16.8) + .12 (4.68) = 8.92

(a) per Table I
Source: walter Douthit

Table IV. Distribution Coefficients Gasoline vs. Water Phases

Blend	C EtoH	C ETBE	C TAME	C TAEE
EtOH				
ETBE (NEAT)		85		
TAME (NEAT)			>200	
TAEE (NEAT)				>150
EtOH @ 10%	0.16			
5% EtOH/ 12% ETBE	0.14	8.0		
5% EtOH/ 6% ETBE 6% TAME	0.14	8.6	30(a)	
5% EtOH/ 6% ETBE 6% TAEE	0.14	7.5		60(a)
5% EtOH/ 6% TAME 6% TAEE	0.14		60(a)	10(a)
5% EtOH/ 12% TAME	0.14		120(a)	

(a) Accuracy Not Determined But Questioned
Source: Walter Douthit

Table V. Vapor Pressure Analyses vs. Calculated

Blend	NEAT VP, PSI		VP BLEND ANALYSES		OXY BLEND VP, PSI (EtOH)		CALCULATED VP OF BLEND	
	100'F	130'F	100'F	130'F	100'F	130'F	100'F	130'F
BASE	8.17	13.4						
MTBE	7.97	14.4						
-@ 14.5%			8.44	13.83	10.0	16.28		
-9.26% and 2.65% EtOH			9.06	15.22	(44.5)	(78)	9.32	15.38
ETBE	4.58	8.6						
-@ 12.5%			7.62	12.5	3.75	9.58		
-@ 21.9%			7.48	12.37	5.02	8.72		
-12.5% and 4% EtOH			8.6	14.67	(34)	(66)	8.64	14.99
MTAE	2.77	5.22						
-@ 12%			7.45	12.2	2.17	3.5		
-@ 21%			6.97	11.43	2.5	3.95		
-12% and 4% EtOH			8.35	14.17	(34)	(66)	8.48	14.32
ETAE	1.75	3.45						
-@ 13.8%			7.37	11.98	2.34	3.07		
-@ 24%			6.81	11.11	2.5	3.87		
-13.8% and 4% EtOH			8.18	13.88	(34)	(66)	8.13	14.1

Source: Walter Douthit

Table VI. Vapor Pressure Data for Ethanol/MTBE Blends

Gasoline A = 15% MTBE in unleaded gasoline base stock, RVP brought close to 9 psi with Butane addition.
Gasoline E = 10% Ethanol in an 8 RVP unleaded gasoline base stock.

Vapor Pressure by Automated SWRI Instrument, psi
November 1992

Gasoline A	9.62
Gasoline B (25% "E", 50% "A")	9.77
Gasoline C (50% "E", 50% "A")	9.65
Gasoline D (75% "E", 25% "A")	9.46
Gasoline E	9.45

Vapor Pressure by Labarator Grabner Instrument, psi
August 1992, Same Gasoline Components - Different Blend

Temp, °F	Gasoline A	Gasoline B	Gasoline C	Gasoline D	Gasoline E
30	1.91	1.76	1.91	1.62	1.65
40	2.46	2.34	2.48	2.20	2.17
50	3.13	3.03	3.11	2.84	2.79
60	3.91	3.87	3.94	3.64	3.61
70	4.87	4.85	4.90	4.58	4.53
80	5.98	6.07	6.09	5.75	5.71
90	7.30	7.51	7.45	7.10	7.07
100	8.78	9.13	9.07	8.73	8.70
110	10.50	11.02	10.99	10.63	10.58
120	12.45	13.21	13.19	12.84	12.86
130	14.60	15.62	15.67	15.35	15.40
140	17.08	18.37	18.57	18.30	18.39
150	19.78	21.46	21.79	21.63	21.78
160	22.75	24.81	25.36	25.33	25.58

Source: Dr. Brian C. Davis

Table A-1. Physical Property Data of Base Gasoline (a)
Phase I

DVPE, psi (D 5191)	8.64/8.66
T(V/L=20), °F (D2533)	141.6
Distillation, °F (D 86)	
Percent Evaporated	
1 BP	82
5	108
10	124
20	146
30	166
40	189
50	213
60	236
70	260
80	290
90	327
95	358
EP	416
Residue	1.4
Loss	2.1
Recovery	96.5
Specific Gravity, 60/60°F	0.7438
Octanes	
RON (D 2699)	94.0/94.0
MON (D 2700)	84.7/84.8
(R+M)/2	89.4/89.4
Water, ppm w/w (D 1744)	102
Oxidation Stability, Minutes (D 525)	1440+
Oxygenates, V% (D 4815)	0.0
Copper Corrosion, Rating (D 130)	1A(b)
Rust, Rating (D 665)	A
Sulfur, W% (D 4294)	<0.05
Phosphorus, g/gal (D 3231)	<0.0008
Lead, g/gal (D 3237)	<0.002
Gum, mg/100 ml (D 381)	
Unwashed	51.4
Washed	<0.1

(a) ALI 14766
(b) Slight tarnish
Source: Autoresearch Laboratories, Inc.

Table A-II. Piano Analysis

Customer's ID: NEA Reference Fuel
ALI's #: 14766

Note: Benzene and toluene values were determined using Alberta Research Council method GL-41 and the oxygenate values were determined using ASTM D-4815

Composite Report
Totals by Group Type and Carbon Number
(in Volume Percent)

Carbon #	n-Parrafins	Iso-Paraffins	Aromatics	Naphthenes	Olefins	Di-olefins	Unknowns	Totals
3	0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.016
4	4.275	0.312	0.000	0.000	0.443	0.000	0.000	5.030
5	5.347	7.639	0.000	0.273	3.930	0.062	0.000	17.251
6	3.471	7.449	1.486	1.670	2.650	0.039	0.001	16.766
7	0.661	5.035	6.790	1.277	1.545	0.000	0.171	15.479
8	0.237	14.241	9.928	0.793	0.177	0.062	0.450	25.888
9	0.029	1.678	8.077	0.081	0.085	0.000	0.768	10.718
10	0.021	0.211	3.367	0.055	0.019	0.000	0.569	4.242
11	0.006	0.000	0.686	0.000	0.000	0.000	1.041	1.733
12	0.108	0.096	0.407	0.000	0.000	0.000	1.002	1.613
13	0.096	0.000	0.000	0.000	0.000	0.000	0.906	1.002
14	0.034	0.000	0.000	0.000	0.000	0.000	0.115	0.149
15	0.000	0.000	0.000	0.000	0.000	0.000	0.111	0.111
HC Total	14.301	36.661	30.741	4.149	8.849	0.163	5.134	99.998
Oxygenates								0.000
Grand Total								99.998

Source: Autoresearch Laboratories, Inc.

Table A-III. Physical Properties and Composition of Oxygenates
Phase II

Oxygenate ALI Number	ETHANOL (DEN.) 14424	TAEE 14306	TAME 14310	ETBE 14425
DVPE, psi (D 5191)	4.09	2.19	2.77	4.92
Specific Gravity @ 60/60°F	0.7877	0.7698	0.7738	0.7448
Peroxide Number, ppm (D 3703)	<0.1	3.6	<0.1	2.8
Water, ppmw (D 1744)	7282	280	183	2851
Purity, W% (GC)				
C4	0.1	0.0	0.0	0.3
ETOH	94.8	2.3	0.0	0.2
C5	2.3	0.0	0.0	0.0
IPA	0.0	0.0	0.0	0.2
TBA	0.0	0.0	0.0	0.3
C6	1.0	0.4	0.0	0.0
AMYL ALCOHOL	0.0	1.7	0.3	0.0
TAME	0.0	0.0	99.2	0.0
ETBE	0.0	0.0	0.0	93.9
C7	1.2	0.5	0.4	0.0
TAEE	0.0	94.5	0.0	0.0
C8	0.5	0.5	0.1	4.5
C9	0.0	0.1	0.0	0.0
C10	0.0	0.0	0.0	0.3
C11	0.0	0.0	0.0	0.3
C12	0.0	0.0	0.0	0.0

Source: Autoresearch Labortories, Inc.

Table A-IV. Physical Properties of Single Oxygenate Blends
Phase IV

Fuel Composition (a)	BASE	BASE+ 5%EtOH	BASE+ 10%EtOH	BASE+ 12%ETBE	BASE+ 12%TAME	BASE+ 6%ETBE	BASE+ 6%TAME	BASE+ 6%TAEE	BASE 12%TAI
ALI Number	14766	15214	15493	14957	14958	14959	14960	14961	15492
Reblend	--	15360	--	--	--	--	--	--	--
DVPE, psi (D 5191)	8.64/8.66	9.25/9.28	9.38(b)	8.18/8.19	7.80/7.80	8.38/8.38	8.21/8.17	8.27/8.25	1.88(b
Reblend	--	9.43	--	--	--	--		--	--
T(v/L-20),°F (D 5191)	141.6	128.5	128.0						
Octanes									
ROM (D 2699)	94.0/94.0	95.9	96.9(c)	97.2/97.2	96.3/96.3	95.5/95.5	95.0/95.0	95.0/95.0	95.7(c)
MON (D 2700)	84.8/84.7	84.8	85.7(c)	87.1/86.8	86.2/86.2	85.7/85.7	85.3/85.3	85.4/85.2	85.7(c)
(R+M)/2	89.4/89.4	90.4	91.3(c)	92.2/92.0	91.2/91.2	90.7/90.7	90.2/90.2	90.2/90.1	90.7(c)
Distillation, °F (D86)									
Percent Evaporated									
IBP	82	92	94	89	94	86	91	85	86
5	108	111	113	116	119	114	113	112	115
10	124	120	122	131	133	129	129	128	132
20	146	131	134	149	153	148	150	150	155
30	166	143	143	166	172	167	170	171	177
40	189	176	152	183	190	186	190	193	197
50	213	207	184	200	206	206	210	214	275
60	236	231	226	220	223	228	229	233	231
70	260	255	250	246	245	253	253	253	248
80	290	287	283	281	278	286	286	283	277
90	327	326	324	323	323	325	328	325	322
95	358	353	352	350	350	352	355	352	350
EP	416	415	404	411	412	411	413	421	412
Residue	1.4	1.0	1.3	1.4	1.3	1.5	1.4	0.9	1.3
Loss	2.1	2.2	1.8	1.4	1.5	1.3	2.1	1.6	1.6
Recovery	96.5	96.8	96.9	97.2	97.2	97.3	96.5	97.5	97.1

(a) percentages are by volume
(b) Base DYPE = 8.53 psi
(c) Base RON = 94.0, MON = 84.4

Consultant: Mr. W. Douthit

Table A-V. Physical Properties of Ethanol/Ether Blends
Phase III

Fuel Composition (a)	BASE	BASE+ 3.2%EtOH+ 12%ETBE	BASE+ 3.2%EtOH+ 6%ETBE+ 6%TAME	BASE+ 3.2%EtOH+ 6%ETBE+ 6%TAEE	BASE+ 3.2%EtOH+ 6%TAME+ 6%TAEE	BASE+ 3.2%EtOH+ 12%TAME
ALI Number	14766	14951	14952	14953	14954	14955
DVPE, psi (D 5191)	8.64/8.66	8.85/8.85	8.73/8.85	8.69/8.75	8.59/8.59	8.57/8.61
T(v/L=20),°F (D 2533)	141.6	132.5	134.8	134.5	136.2	135.8
Distillation, °F (D 86)						
Percent Evaporated						
IBP	82	90	96	97	94	89
5	108	115	116	115	114	113
10	124	124	125	125	125	125
20	146	139	141	140	142	141
30	166	157	159	160	163	165
40	189	178	182	184	189	192
50	213	197	201	205	208	212
60	236	217	219	223	225	229
70	260	243	242	246	244	246
80	290	278	278	276	275	274
90	327	321	322	322	321	321
95	358	348	349	350	348	348
EP	416	411	411	410	411	412
Residue	1.4	1.3	1.3	1.4	1.4	1.4
Loss	2.1	1.1	1.5	1.7	1.7	1.8
Recovery	96.5	97.6	97.2	96.9	96.9	96.8
MON (D 2700)	84.8/84.7	88.1/87.6	87.9/87.3	88.1/87.5	87.6/87.1	87.3/87.0
RON (D 2699)	94.0/94.0	98.1/98.1	97.9/97.9	97.9/97.9	97.3/97.3	97.2/97.2
(R+M)/2	89.4/89.4	93.1/92.8	92.9/92.6	93.0/92.7	92.4/92.2	92.2/92.1

(a) percentages are by volume
Consultant: Mr. W. Douthit

Table A-VI. Physical Properties of Ethanol/Ether Blends
Phase IIIR

Fuel Composition (a)	BASE	BASE+ 5%EtOH+ 12%ETBE	BASE+ 5%EtOH+ 6%ETBE+ 6%TAME	BASE+ 5%EtOH+ 6%ETBE+ 6%TAEE	BASE+ 5%EtOH+ 6%TAME+ 6%TAEE	BASE+ 5%EtOH+ 12%TAME	BASE+ 5%EtOH+ 12%UDEX RAFFINATE(b)	BASE+ 10%EtOH+ 12%UDEX RAFFINATE(
ALI Number	14766	15216	15218	15219	15217	15215	15213	15494
Reblend	--	15362	15364	15365	15363	15361	15359	--
DVPE, psi (D 5191)	8.64/8.60	8.95	8.77	8.76	8.69	8.66	8.85/8.88	8.92
Reblend	--	8.85	8.75	8.72	8.66	8.66	8.98	--
T(v/L-20),°F (D 5191)	141.6	130.7	132.0	132.0	133.1	133.4	--	--
Distillation, °F (D 86)								
Percent Evaporated								
IBP	82	92	95	97	98	98	--	--
5	108	114	117	117	117	117	--	--
10	124	124	126	126	127	126	--	--
20	146	136	138	138	139	139	--	--
30	166	149	152	151	154	154	--	--
40	189	170	175	179	183	179	--	--
50	213	193	198	203	207	202	--	--
60	236	213	218	222	224	219	--	--
70	260	241	241	244	244	240	--	--
80	290	276	276	275	274	274	--	--
90	327	320	320	320	320	319	--	--
95	358	347	348	348	348	349	--	--
EP	416	411	412	414	413	412	--	--
Residue	1.4	1.2	1.2	1.0	0.9	1.1	--	--
Loss	2.1	1.4	1.2	1.2	1.3	1.5	--	--
Recovery	96.5	97.4	97.6	97.8	97.8	97.4	--	--
MON (D 2700)	84.8/84.7	98.4	98.2	98.1	97.9	97.9	--	--
RON (D 2699)	94.0/94.0	87.2	86.9	86.7	86.5	86.4	--	--
(R+M)/2	89.4/89.4	92.8	92.6	92.4	92.2	92.2	--	--
Oxygenates, V%								
(Modified D 4815) (c)								
EtOH	0.1	5.1	5.3	5.5	5.4	5.3	5.3	--
ETBE	<0.1	11.6	6.2	6.3	<0.1	0.1	<0.1	--
TAME	NO	NO	<0.1	<0.1	6.0	11.8	NO	--
TAEE	NO	NO	<0.1	6.6	5.5	<0.1	NO	--

(a) percentages are by volume
(b) UDEX Raffinate, 4.68 psi DYPE
(c) Semiquantitative data due to method development in progress
Consultant: Mr. W. Douthit

Table A-VII. Comingling Effect on Vapor Pressure
Phase V

Base Fuel	Base	Base
Oxygenate Blend (a)	BASE+5V% EtOH +12V% ETBE	BASE+5V% EtOH +6V% ETBE +6V% TAME
DVPE, psi (D 5191)		
Oxygenate Blend, V%		
0.0	8.44	8.47
5.0	8.64	8.70
10.0	8.77	8.75
25.0	8.98	8.89
100.0	8.77	8.70

(a) percentages are by volume
Consultant: Mr. W. Douthit

Table A-VIII. Water Extraction and Solubility Data
Phase II

Oxygenate	ETBE	TAME	TAEE
ALI Number	14425	14310	14306
Water Extraction (0.75% Water at 74°F) (a)			
Upper Phase			
Volume, mls	666.1	642.4	645.3
ETBE, V% (calculated) (d)	93.5	NA(c)	NA(c)
TAME, V% (calculated) (d)	NA(c)	98.7	ND(c)
TAEE, V% (calculated) (d)	NA(c)	ND(c)	93.9
Impurities, V% (calculated (d)	6.1	0.8	5.6
Water, V% (b)	0.44	0.51	0.47
Lower Phase			
Volume, mls	3.2	1.7	2.2
ETBE, V%	1.1	NA(c)	NA(c)
TAME, V%	NA(c)	0.1	NA(c)
TAEE, V%	NA(c)	NA(c)	0.6
Water, V% (calculated)	98.9	99.9	99.4
Total Water Solubility, V% (e)			
70°F	0.475	0.520	0.470
40°F	0.400	0.443	0.440
0°F	0.305	0.343	0.403
-20°F	0.255	0.290	0.383

(a) equilibrated by shaking intermittantly for 5 days at nominal 74°F.
(b) D 1744 weight percent converted to volume percent.
(c) NA = not analyzed
ND = not detected
(d) calculated based on blending volume percentages and lower phase data.
(e) includes water in the oxygenates.

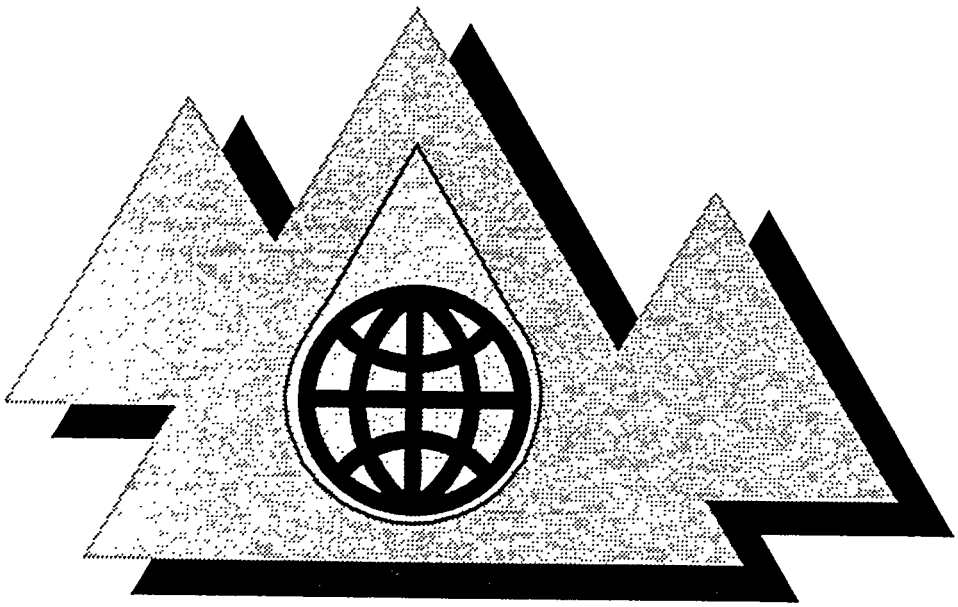
Consultant: Mr. W. Douthit

Table A-IX. Water Extraction and Solubility Data
Phase III

Fuel Composition (a)	BASE	BASE+ 5%EtOH+ 12%ETBE	BASE+ 5%EtOH+ 6%ETBE+ 6%TAME	BASE+ 5%EtOH+ 6%ETBE+ 6%TAEE	BASE+ 5%EtOH+ 6%TAME+ 6%TAEE	BASE+ 5%EtOH+ 12%TAME
ALI Number	14766	15216	15218	15219	15217	15215
Water Extraction (0.75V% Water at 74°F) (a)						
Upper Phase						
Volume, mls	--	656.5	656.5	656.2	655.3	655.4
EtOH, V% (calculated (d)	--	4.6	4.6	4.6	4.6	4.6
ETBE, V% (calculated) (d)	--	12.0	6.0	0.0	6.0	0.0
TAME, V% (calculated) (d)	--	0.0	6.0	0.0	0.0	12.0
TAEE, V% (calculated) (d)	--	0.0	0.0	6.0	6.0	0.0
Water, V% (b)	--	0.21	0.21	0.21	0.21	0.22
Lower Phase						
Volume, mls	--	8.9	8.5	9.1	9.0	8.1
EtOH, V%	8.6	32.0	31.0	31.0	30.0	31.0
ETBE, V%	<0.1	1.5	0.7	0.8	<0.1	<0.1
TAME, V%	ND(c)	0.2	0.2	0.2	0.1	0.1
TAEE, V%	ND(c)	ND(c)	0.1	0.1	0.6	ND(c)
Water, V% (calculated	--	66.3	68.0	67.9	69.3	68.9
Total Water Solubility, V% (f)						
70°F	0.023	0.257	0.238	0.260	0.273	0.258
40°F	0.017	0.241	0.240	0.240	0.248	0.245
0°F	0.008	0.220	0.216	0.213	0.215	0.221
-20°F	0.003	0.209	0.203	0.200	0.198	0.211

(a) equilibrated by shaking intermittantly for 5 days at nominal 74°F
(b) D 1744 weight percent converted to volume percent
(c) NA = not analyzed
ND = not detected
(d) calculated based on blending volume percentages and lower phase data
(e) percentages are by volume
(f) includes water in the base fuel and oxygenates

Consultant: Mr. W. Douthit



Fuel Cells, Stationary, and Other Applications

DEMONSTRATION TESTS FOR CONVERTING OIL FUEL TO METHANOL IN THERMAL POWER PLANTS

METHANOL ENGINE SYSTEM FOR POWER GENERATION

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Abstract

Methanol is now considered a clean oil-alternative energy source for electric power plants. NEDO has been conducting R&D on power generation from methanol in "Demonstration Tests for converting Oil Fuel to Methanol in Thermal Power Plants: since FY1981 by commission of the Agency of Natural Resources and Energy, Ministry of International Trade and Industry. In FY1988 NEDO began conducting "Demonstration Tests on a Reformed Methanol Gas Turbine Generation System:, with one of the main objectives being recovering waste heat by taking advantage of the reforming reaction of methanol. Since FY1989, NEDO has also been conducting "Developmental Research on Methanol Engine System for Power Generation", aiming at the low discharge of NO_x by methanol conversion of an oil-burning stationary diesel engine power generation system and a co-generation system. This paper reports the experimental results obtained in "Developmental Research on Methanol Engine System for Power Generation".

DEMONSTRATION TESTS FOR CONVERTING OIL FUEL TO METHANOL IN THERMAL POWER PLANTS

METHANOL ENGINE SYSTEM FOR POWER GENERATION

Introduction

Among existing heat engines, petroleum-fueled diesel engines have been widely regarded as the most outstanding motor because of their high thermal efficiency, reliability, durability, etc. However, there are two problems, i.e., recent environmental pollution problems due to exhaust gases and the petroleum energy resource problem. Because of these problems, the application of methanol fuel to diesel engines has been attracting much attention as a low-polluting alternative energy to petroleum.

In connection with the methanol engines for automobiles, research was started long ago and many experiments and fleet tests have been performed. Methanol engines for automobiles are now at a stage where they can be put into practical use. However, as far as diesel engines used for power generation or ships are concerned, little research has been done.

When methanol fuel is used, one of the major points to be improved is the stability of ignition and combustion. In the case of methanol fuel for automotive engines, the ignition of methanol is assisted in several ways, such as the use of a spark plug, a glow plug, dual fuel, etc.

It is possible to apply to stationary power generation engines the technology obtained from methanol engines for automobiles. Compared with automotive engines, however, stationary power generation engines have a lower compression ratio, larger cylinder diameter, and higher mean effective pressure. In addition, they require more reliability and durability. Thus, there still remains engineering problems which must be solved.

The authors adopted a heat surface ignition system by means of a glow plug, which is advantageous to a large combustion chamber. We went from there to develop a methanol engine system with multiple glow plugs, in which two or more glow plugs were mounted to one cylinder in order to ensure ignition and combustion.

This paper reports the test results on the combustion of methanol using multiple glow plugs. Points included are engine performance, exhaust emission reduction effect with the exhaust gas recirculation (EGR), water-added methanol fuel, and the durability of the glow plugs. Durability of the glow plugs is essential to the reliability of methanol engines.

Test Engine and Fuel Specifications

Table 1 shows the principal particulars of the test engine and Figure 1 shows a sectional view of the major parts. The test engine was a supercharged, direct injection single cylinder, Mitsubishi SR model. For the ignition assist system a glow-assist method, which can deal with the use of a larger cylinder diameter, was adopted. The multi glow-plug system in which two to four glow plugs were mounted to one cylinder was adopted. By increasing the ignition heat source and reducing the heat capacity of glow plug, effort were made to ensure stable ignition and combustion of methanol and improve the durability of the glow plug.

Table 1. Principal particulars of the test engine

Cycle & combustion systems	4 cycle, supercharged/direct injection
Number of cylinders	single cylinder
Bore X stroke	170 X 180 mm
Displacement:	4086 cc
Compression ratio:	14.0:1
.Rated output	85 kW/1800 revs/min
Fuel injection pump	Bosch type
Injection nozzle	Hole type, 8 ports
Ignition-assist system	Multi-glow plug system

In the EGR test, the exhaust gas was piped to the intake by cooling it to about 313 K (40°C) with a cooler and thereby eliminating the water content. The amount of EGR was calculated by measuring the concentration of CO_2 in the intake air at the inlet and exhaust gas at the outlet of the cylinder.

The fuel used was methanol for industrial use (purity over 99.6%). the water-added methanol of 7 to 20% was made by adding purified water directly into the methanol tank since methanol has a good compatibility with water.

Regarding durability of the low plug, actual results were obtained in various performance tests with the glow plug mounted on the engine. In addition, durability test for a longer period were also performed by using a glow plug testing device.

Experimental Results and Discussion

Engine performance of the multi-glow plug system

Methanol has extremely low self-ignitability (cetane number 3) due to its physical properties and therefore requires the ignition-assist device. In this research, the glow-assist system, using two to four glow plugs, was adopted.

Figure 2 shows a schematic view of the two glow-plug system and Figure 3 shows the four glow-plug system. As for the regular single glow-plug system, only one side of the two glow-plug system in Figure 2 was used.

Figure 4 shows the comparison in ignition delay when the number of glow plugs was changed. Little difference in ignition delay

is seen at low speed between a single glow plug and two glow plugs. At the high speed range, a difference of about two degrees is found.

In addition, when the compression ratio is increased from 14 to 16, improvement of about three degrees is made over the whole engine speed range and the difference between the two glow-plug system and the four glow-plug system is hardly seen.

Figure 5 shows the effect of the number of glow plugs on the rate of heat release. Since all of these glow-plug systems have the same fuel injection beginning, the difference in ignition time among them can be clearly seen. The rate of increase in heat release at high load is almost the same for all three systems. At low load, however, the rise of heat release of the four glow-plug system is quicker than the others. This shows the combustion stability of the multi glow-plug system.

Figure 6 shows the brake thermal efficiency of the engine and the exhaust emissions of each of the three glow plug systems when glow-plug temperature is constant at 1373K (1100°C).

As the rate of heat release in Figure 5 shows, the multi glow-plug system make the heat release time earlier and the peak value higher. This results in an increase of NO_x in the exhaust gas and a reduction of HC and CO.

The brake thermal efficiency of the engine with the multi glow-plug system is significantly higher compared with that of the single low-plug system. However, since there is only a very small difference in the brake thermal efficiency between two glow-plug systems and four glow-plug systems, it seems to be effective to use appropriately the two, three, or four glow-plug system, depending on the output, speed, etc. of the engine.

Influence of EGR

It has been known that the NO_x reduction effect can be obtained by recirculation of exhaust gas. With this in mind, we examined the effect of EGR on methanol engines. Figure 7 shows the relationship between the brake thermal efficiency and NO_x when the EGR rate is changed from 0 to 30%. The implementation of the EGR deteriorates the brake thermal efficiency slightly. However, it contributes to a great reduction in NO_x.

Figure 8 shows the cylinder pressure and the rate of heat release when no EGR, 10% of EGR, and 20% of EGR are performed. Although the ignition delay is prolonged by applying the EGR, the end of the combustion is almost the same. Therefore, the combustion period tends to be shortened.

Figure 9 shows the engine performances, including HC and CO, when the engine is operated by varying the output at a constant speed. NO_x is greatly reduced in the whole load range and the effect becomes larger with higher load. However, HC is hardly changed and CO increases almost constantly regardless of the load.

A catalytic device was not used in this research. Therefore, it is considered possible to improve greatly the exhaust emission problem by using both the EGR and an oxidation catalyst, because it is possible to reduce HC and CO with an oxidation catalyst without noticeably deteriorating the brake thermal efficiency.

Effect of water-added methanol fuel

It is known that in a diesel engine, water injection into a combustion chamber or water-added (emulsion) fuel is effective for improving engine performance or reducing NO_x. However, since that requires

installation of a water injection device or emulsification of the fuel, the number of cases in which they have been put into practical use is small.

However, since methanol has a good compatibility with water, a water-added fuel can be readily prepared by putting water directly into the fuel tank.

In this research, water-added methanol was prepared by putting purified water into a methanol fuel tank to obtain the mixing ratio set in advance. In the engine test using water-added methanol, the four glow-plug system was used.

Figure 10 shows the cylinder pressure and the rate of heat release when methanol fuel in which water of 7 to 17% by weight ratio is added. There is little difference in ignition delay and the rate of heat release is not greatly changed.

Figure 11 shows the brake thermal efficiency and the exhaust emissions when water-added methanol fuel is used. fuel injection quantity in axis of abscissa is converted to injection quantity of only methanol. As for the brake thermal efficiency, neat methanol (M100) is better at low load. For high load, however, water-added methanol is better. Methanol with a higher rate of water addition tends to have better brake thermal efficiency.

NO_x in the exhaust gas is reduced by water-added methanol. When the rate of water addition is 13% (13W), NO_x is about 100 ppm or less (converted into 13% O_2). As for HC and CO, however, little difference is seen between water-added methanol and M100.

These results were obtained using a combustion chamber compression ratio of 16 and the four glow-plug system. It has been confirmed that even if the same four glow-plug system is used, the brake thermal efficiency is reduced at compression ratio of 14, although a NO_x of 100 ppm or less is realized. Also, in the two glow-plug system the combustion fluctuation was large and therefore a stable operation of the engine could not be performed. Based on these facts, it was found that the surrounding conditions for the ignition is important in the combustion of water-added methanol.

Figure 12 shows the relationship between NO_x and the brake thermal efficiency using the EGR and/or water-added methanol fuel. The multi glow-plug system which was tested in this research is effective in achieving the stable ignition and combustion of methanol. With the multi glow-plug system, NO_x of 110 ppm or less is achieved while the brake thermal efficiency is maintained at 38% or higher.

Durability of the Glow Plug

One of the problems in methanol fuel engines is the durability of the ignition-assist device. It is said that in the glow-assist system, oxidation or cracks will occur in a glow plug surface due to several reasons, such as increasing the glow plug temperature in order to obtain satisfactory ignition characteristics or thermal fatigue caused by repetition of heating with the combustion gas and rapid cooling by vaporization latent heat of fuel spray. For these reasons, shields around the glow plugs were provided in some cases.

In this research, each of the glow plugs can be used at relatively low temperatures by the use of the multi glow-plug system. This is advantageous in terms of thermal fatigue.

Figure 13 shows the surface condition of the glow plug after 700 hours of operation of the test engine. Its surface is slightly rough, but shows no cracks, and the ceramic is not damaged. However, since

the engine performance deteriorated, it was necessary to replace the glow plugs. When the temperature of these glow plugs was measured, it was lower than the temperature which was set initially. That is, it was found that the internal resistance of the glow plugs increased.

Figure 14 shows the change of internal resistance of the glow plugs when a constant voltage is applied solely to the glow plug over a long period. As the figure shows, the resistance increases with the passage of time. The change of the internal resistance of the glow plug of 0.04 to 0.05 ohm corresponds to about 100 K in terms of the temperature of the glow plug. Therefore, the change of the internal resistance of the glow plug will also have an important influence on the engine performance.

The glow plug which had been used for a long period was cut and examined. It was found that many cracks occurred in the peripheral section of the ceramic-surrounded coil, as shown in Figure 15. In the case of a new glow plug, small holes are also recognized in the peripheral section of the coil. It is assumed that the size of these holes increased as the glow plug was heated. The extent of these cracks is more noticeable in the center and tip region of the glow plug.

Figure 16 shows the magnified peripheral section of the coil. With an elemental analysis of this peripheral section, the existence of carbon (C) was recognized. The main component of the coil is tungsten (W), which is assumed to have been changed in quality into tungsten carbide (WC) due to a pyrogenetic reaction of the glow plug. In terms of the material, tungsten and carbon react highly with each other and if they are maintained at high temperature, tungsten carbide is produced.

Tungsten carbide has a resistance about 10 times as high as tungsten, It is considered that this characteristic, together with the reduction of the sectional area of the coil due to cracks in the coil layer described above, caused the internal resistance to increase. The existence of carbon in the glow plug is considered to be a kind of contaminant which was added in the production of ceramics. When the manufacturing process of the glow plug was changed, the existence of tungsten carbide was not recognized. Thus, the problem of internal resistance change is expected to be solved in the future.

Reliability of Other Parts

In addition to the glow plug, several points about the durability of various parts with the use of methanol have been reported. In this research also, some troubles were anticipated. Up to the present time, however, no special problem that should be examined has occurred except for that of the glow plugs.

After engine operation, combustion chamber surfaces, such as the piston, are extremely clean. In connection with the fuel injection system also, a slight amount of rust was found in the feed chamber wall of the fuel injection pump, but it is not serious. In the future, the wear of parts, corrosion condition, etc. are expected to be checked and investigated by operation of the engine over a long period of time.

Conclusion

The EGR and water-added methanol fuel were applied to methanol engines using multiple glow plugs, and the improvement of the brake thermal efficiency and the reduction of NO_x were examined. The following points were found:

(1) The multi glow-plug system is extremely effective in achieving stable ignition and combustion of methanol.

(2) In the multi glow-plug system, the brake thermal efficiency is improved and HC and CO are reduced but NO_x tends to increase compared with those of the single glow-plug system.

(3) Reduction of NO_x emissions by the EGR or water-added methanol fuel was confirmed and by combining the above with the multi glow-plug system, NO_x of 110 ppm or less is achieved at brake thermal efficiency of 38% or higher.

(4) With regard to the durability of the glow plug, it is understood that one of the factors contributing to the deterioration of the glow plug is a change of the internal resistance.

In the future, performance tests, endurance tests, etc. are planned to be performed by using a six-cylinder 500kW class engine which has been put into practical use. An overall evaluation of the engine as a system for power generation, considering such points as starting and load response properties, is planned to be made.

Acknowledgement

This developmental research of methanol engine systems for power generation was entrusted to NEDO by the Ministry of International Trade and Industry, and is a part of the methanol conversion tests at petroleum fuel power stations. Goals included higher efficiency and lower NO_x emission of stationary diesel engines. We hereby extend our special thanks for the cooperation given by the persons concerned.

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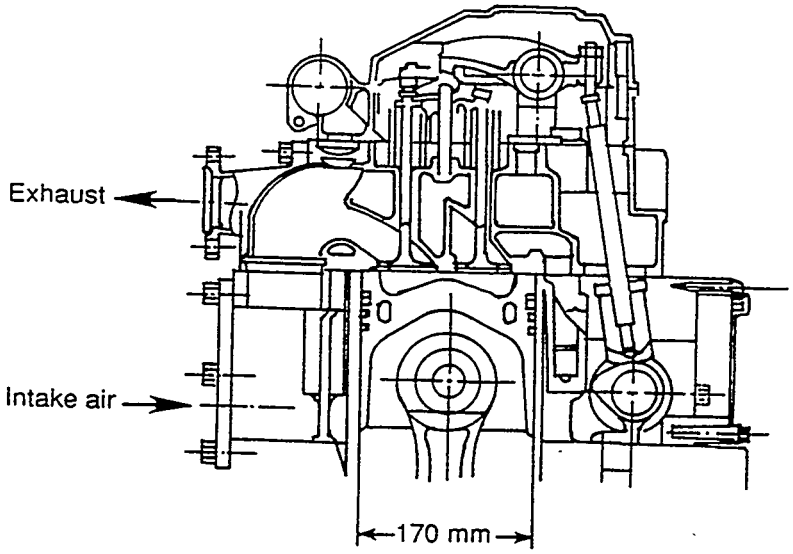

Figure 1. Sectional view of test engine

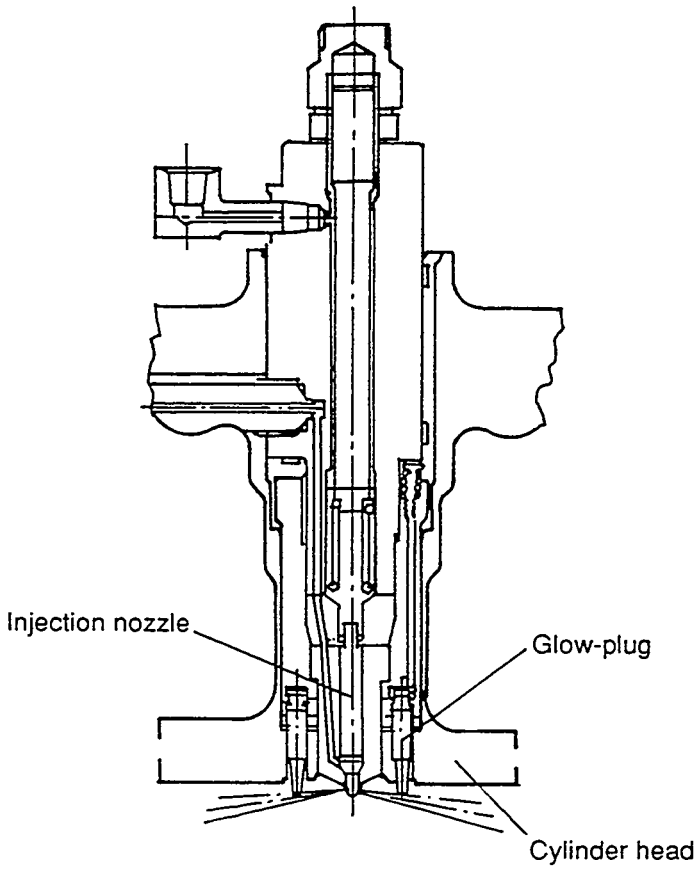

Figure 2. Methanol two glow-plug system configuration

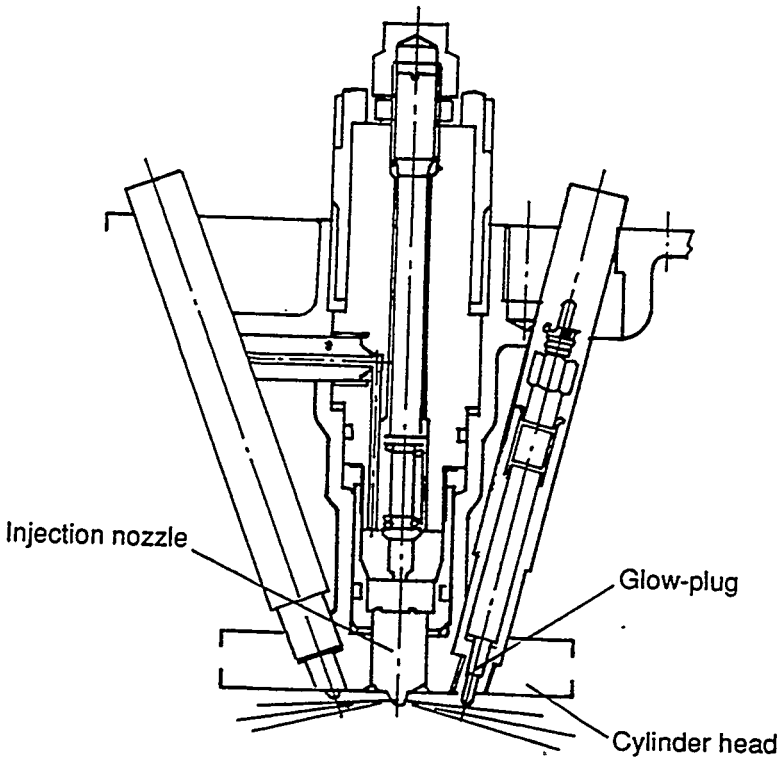

Figure 3. Methanol four glow-plug system configuration

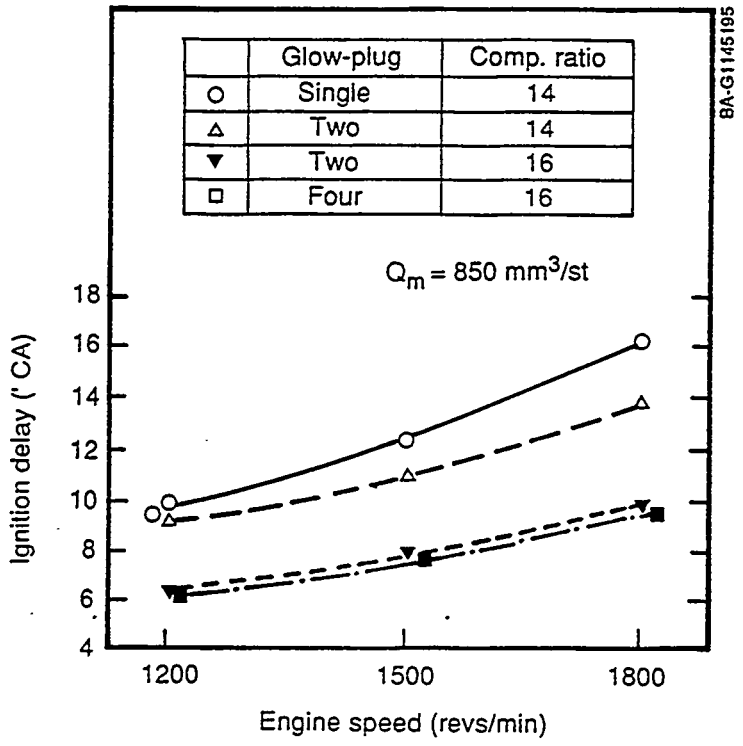

Figure 4. Comparison of ignition delay of number of glow plugs and compression ratios

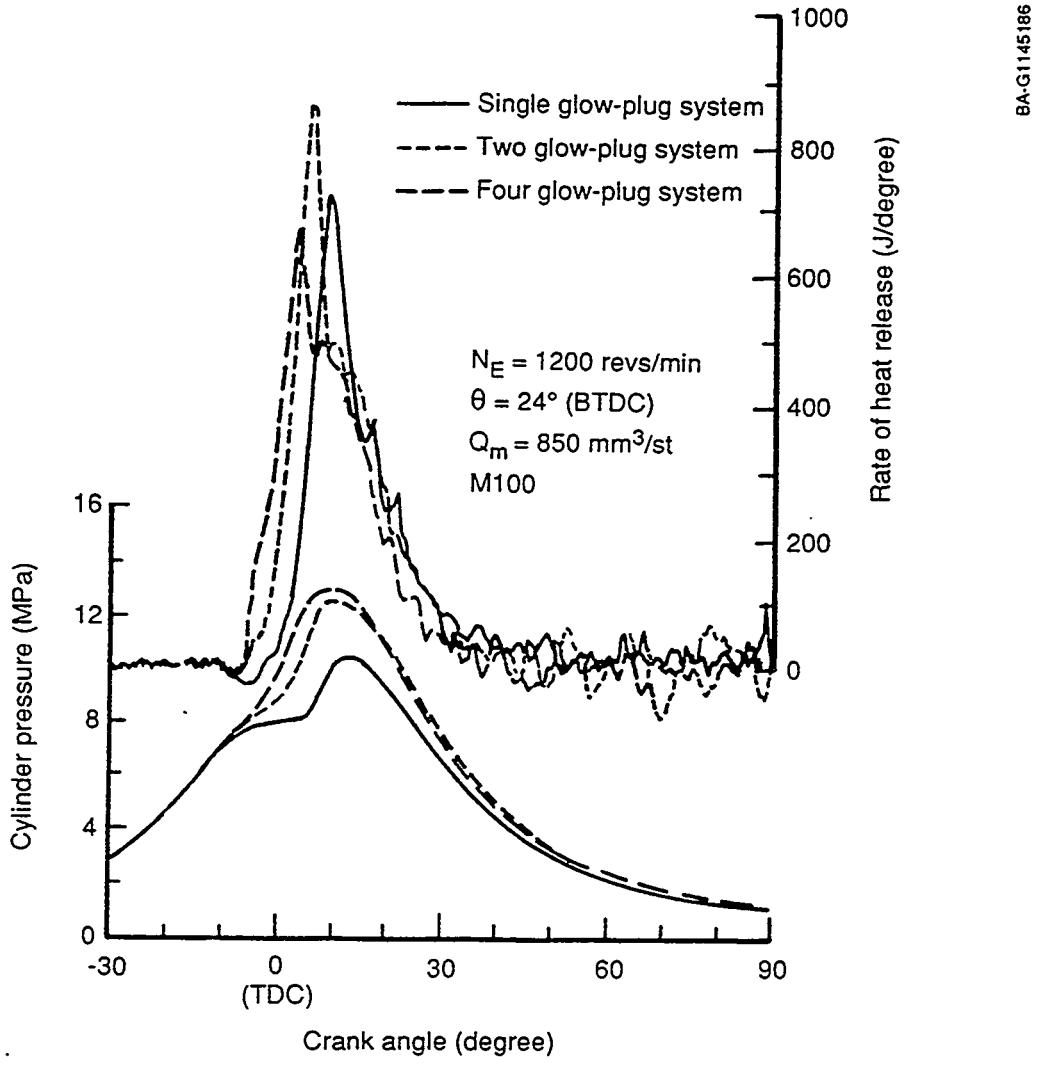

Figure 5. Comparison of number of glow plugs on cylinder pressure and rate of heat release

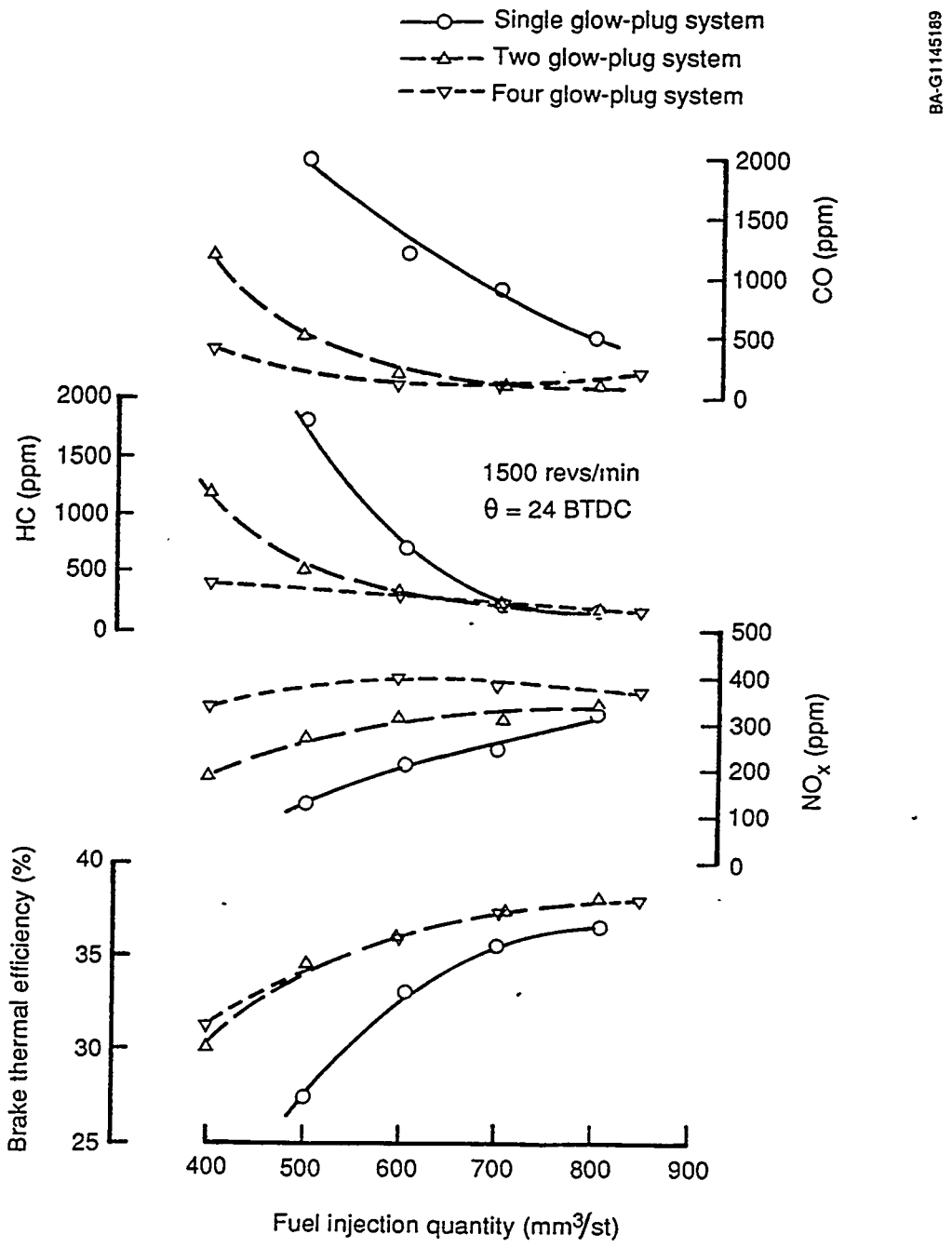

Figure 6. Influence of number of glow plugs on exhaust emissions and brake thermal efficiency

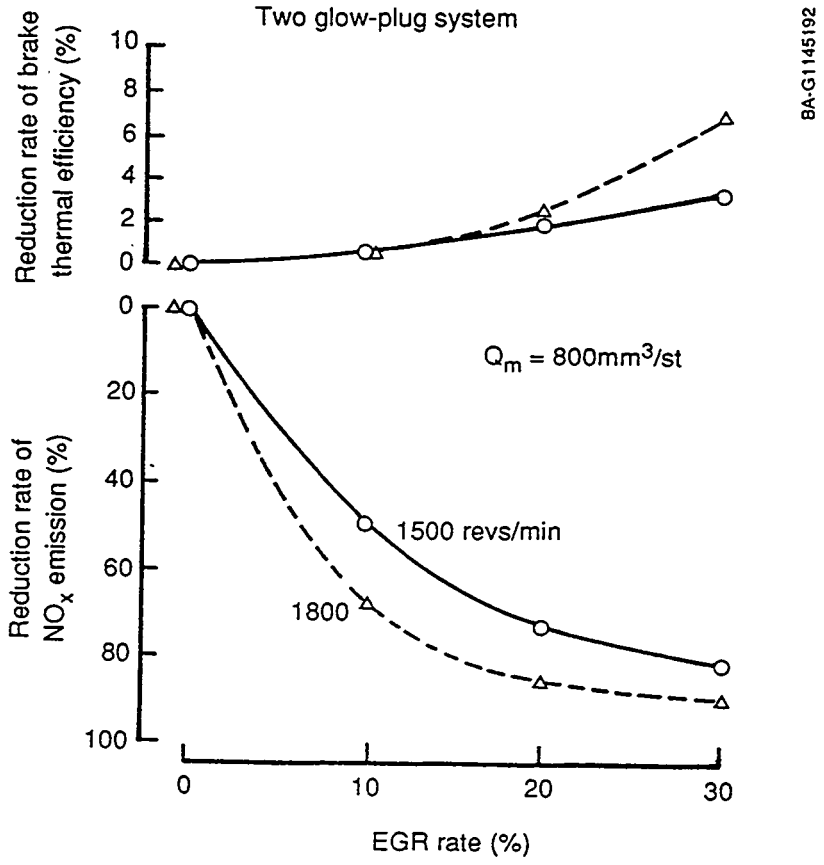

Figure 7. Influence of EGR on NO_x emission and brake thermal efficiency

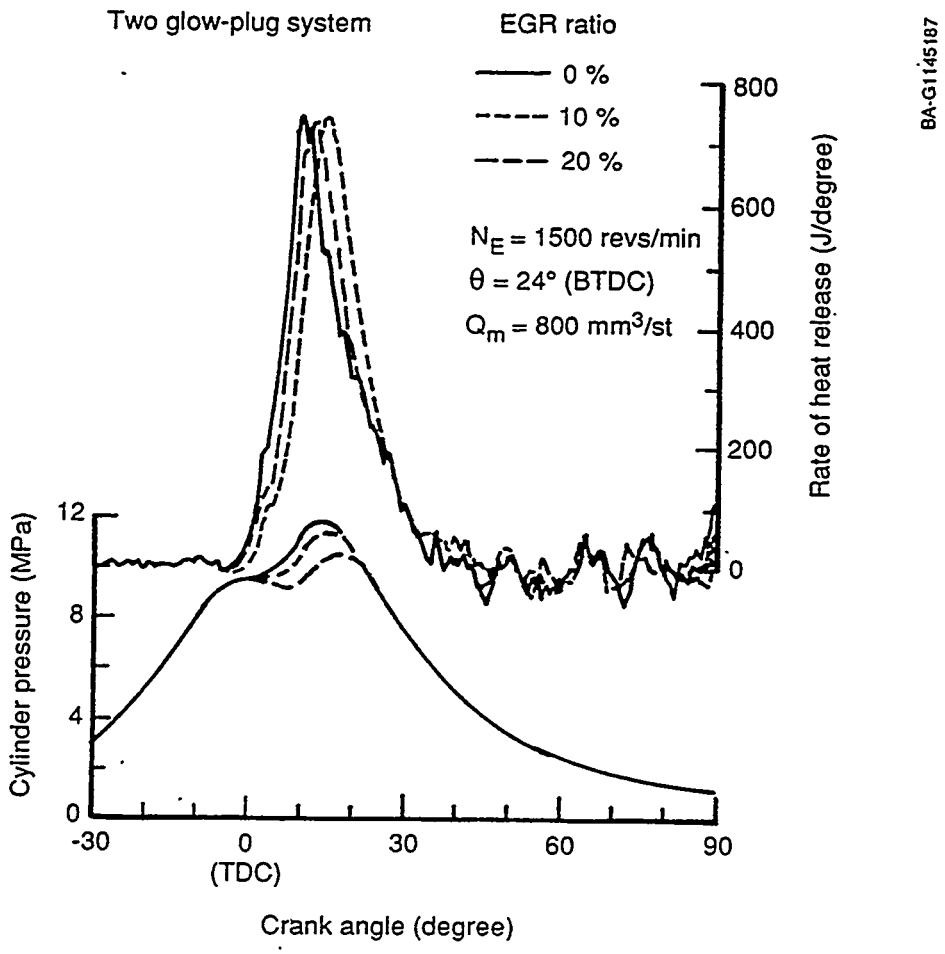

Figure 8. Comparison of EGR on cylinder pressure and rate of heat release

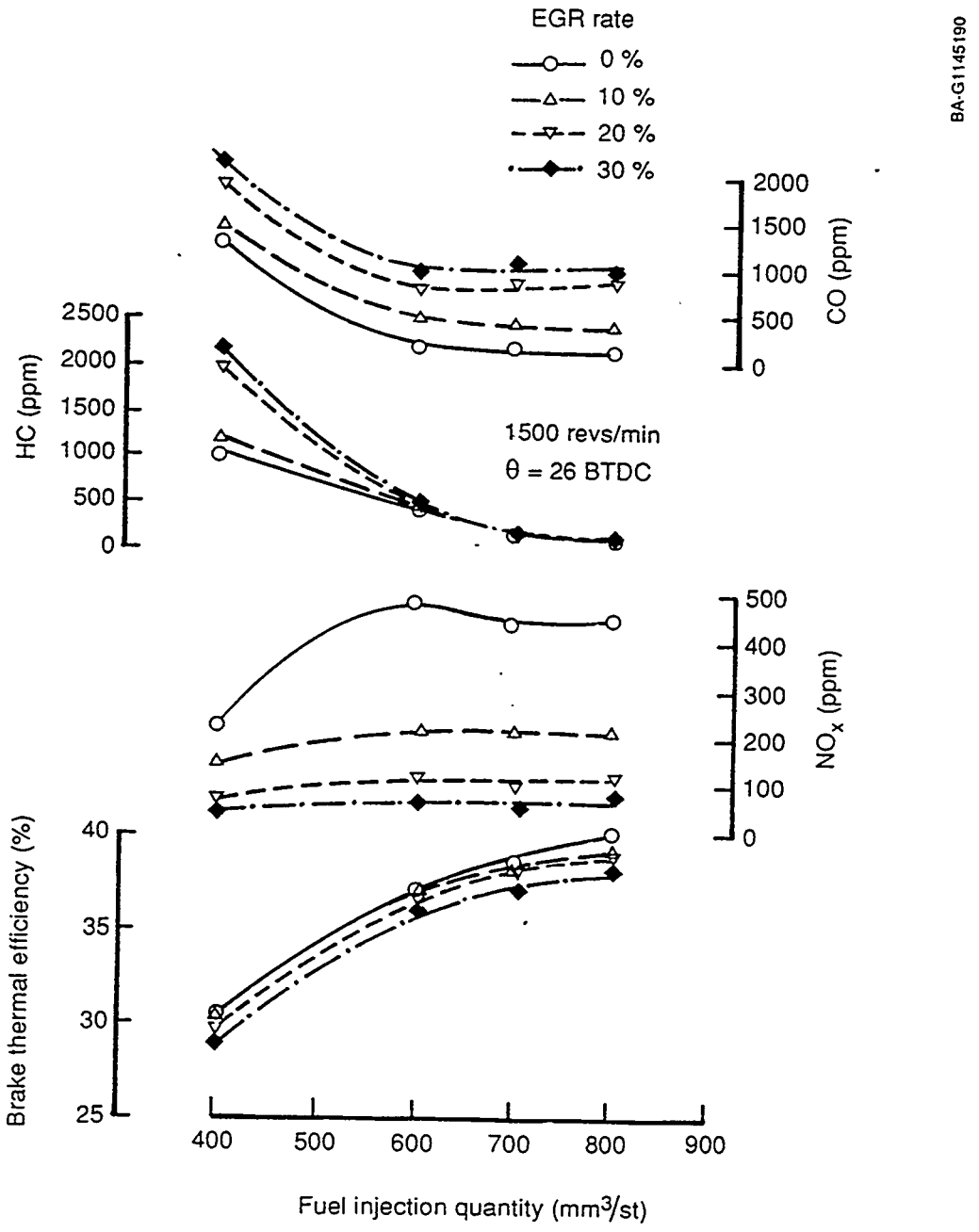

Figure 9. Influence of EGR on exhaust emissions and brake therm efficiency

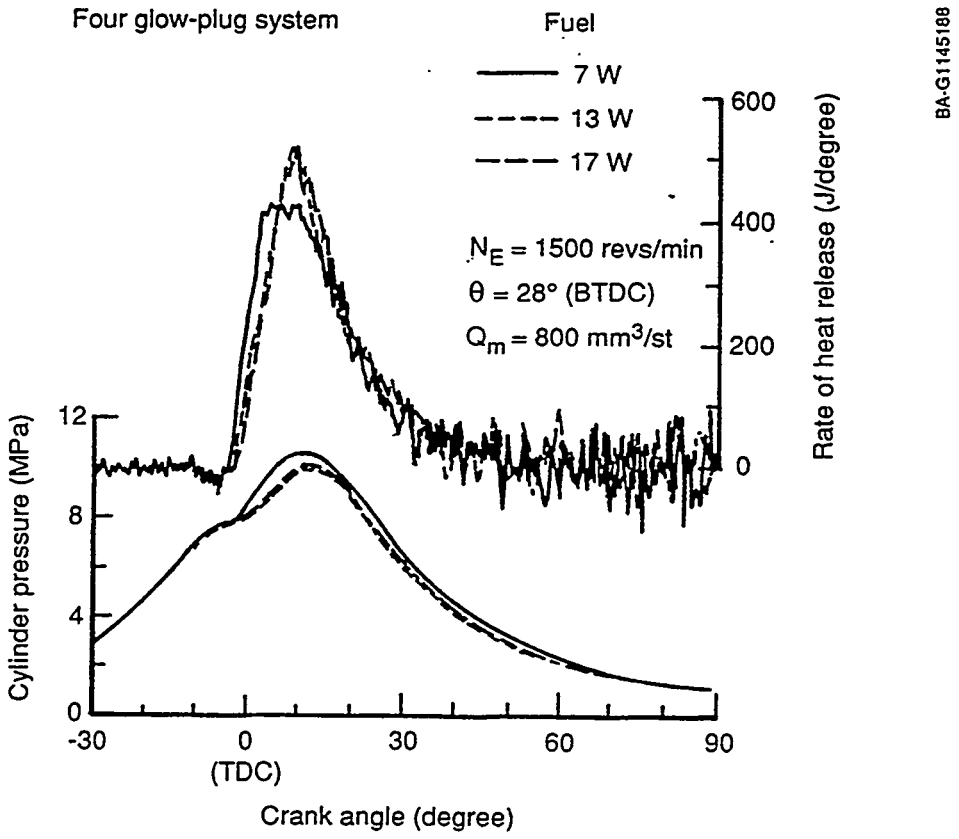

Figure 10. Comparison of water-added methanol fuel on cylinder pressure and rate of heat release

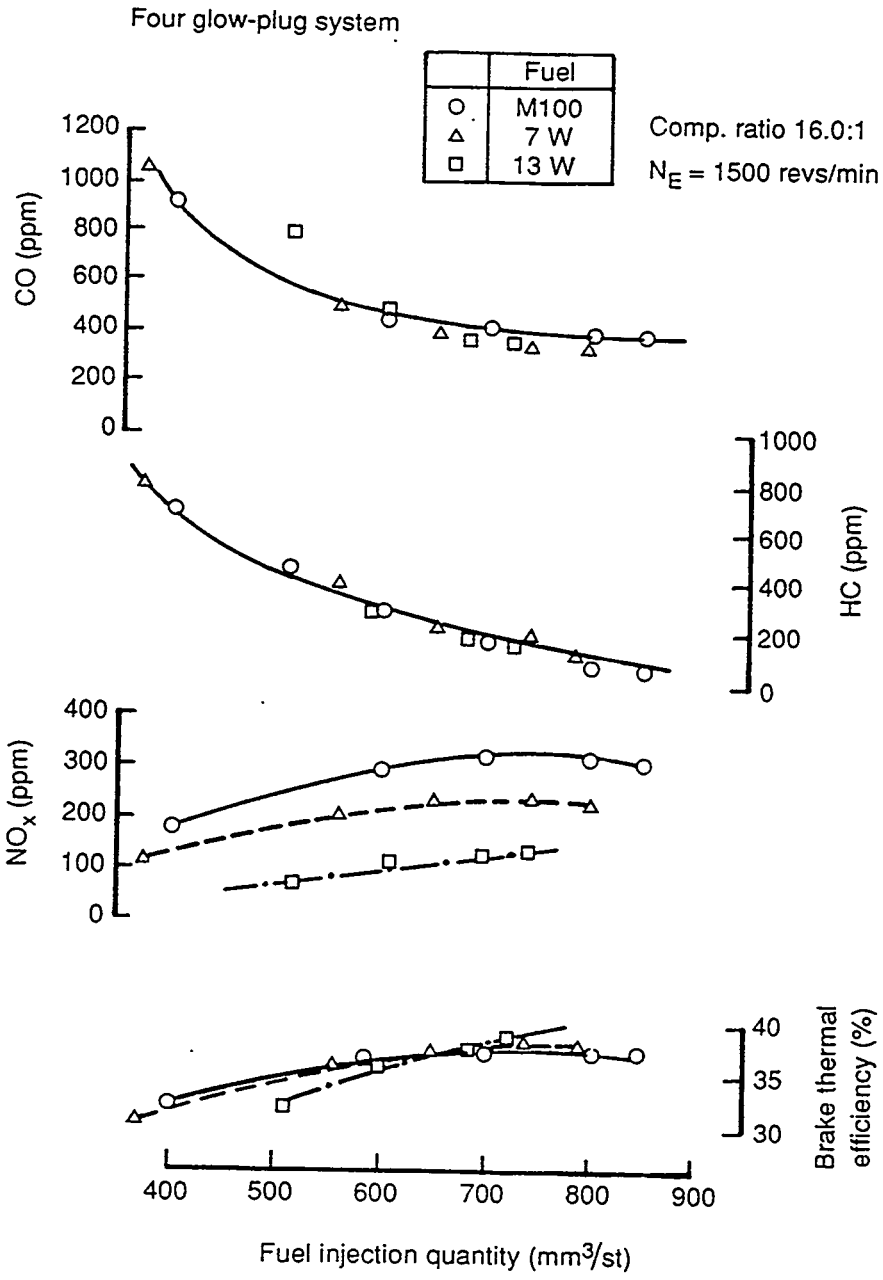

Figure 11. Influence of water-added methanol fuel on exhaust emissions and brake thermal efficiency

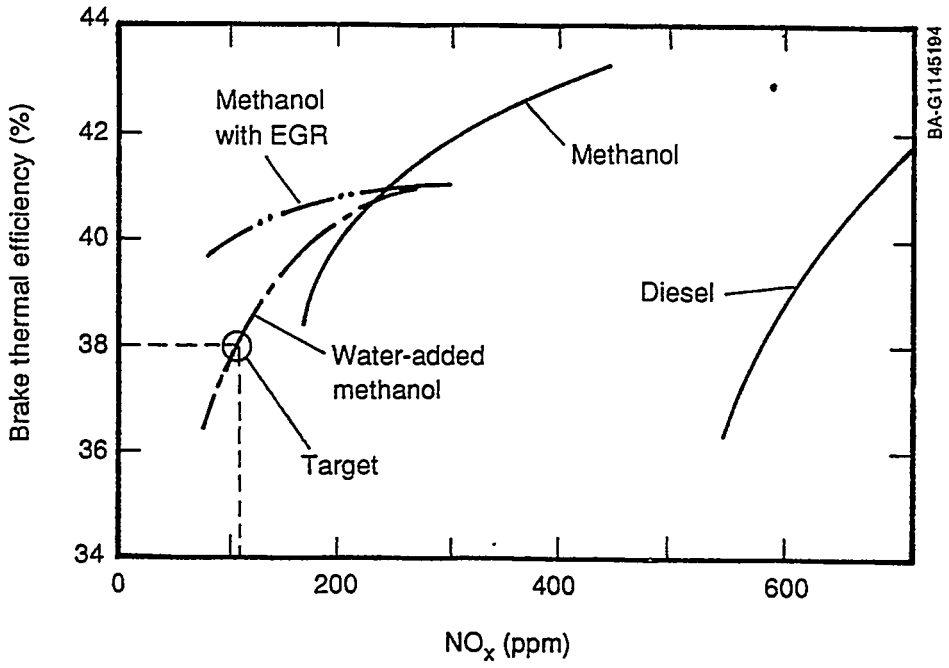

Figure 12. Relationship between NO_x emission and brake thermal efficiency

Figure 13. Used glow plug

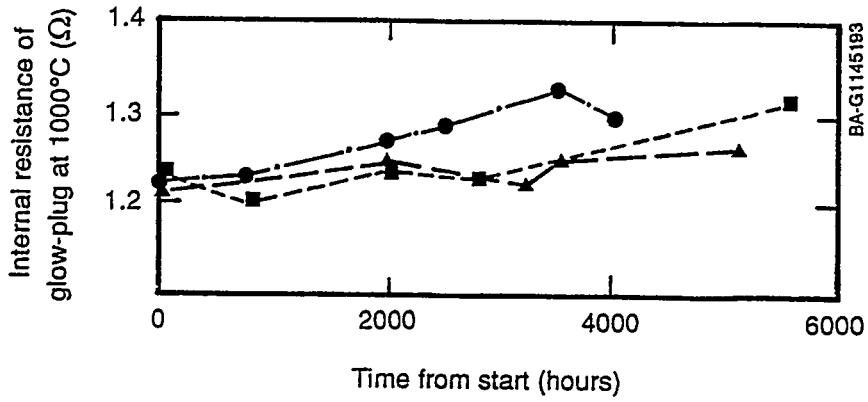

Figure 14. Change of internal resistance of glow plugs

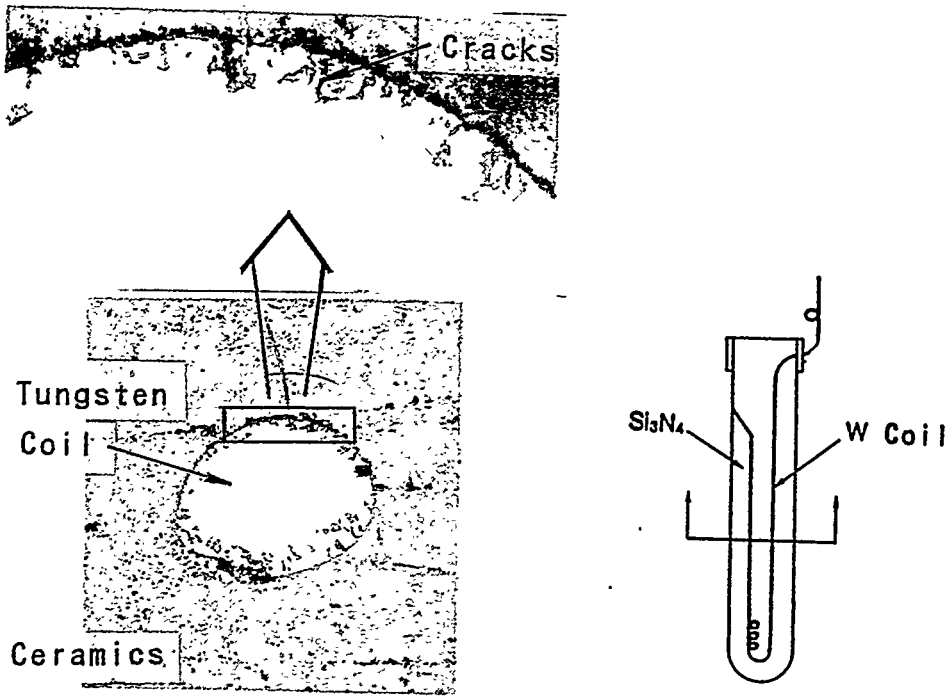

Figure 15. Peripheral section of coil in glow plug

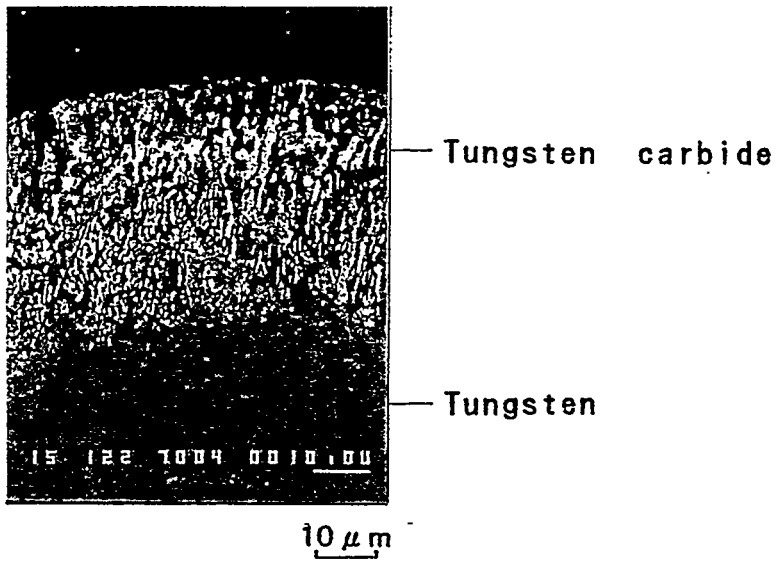

Figure 16. Elemental analysis of coil in glow plug