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QUARTERLY TECHNICAL PROGRESS REPORT

CONTRACT TITLE AND NUMBER:

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Synthesis of Oxygenate Products for High Volume Fuels Applications
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CONTRACTOR NAME: Amoco Corporation
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CONTRACT PERIOD: 10-1-94 - 12-31-96

I. CONTRACT OBJECTIVE:

The Amoco Gas Transportation and Utilization Division (GTU) was formed as a dedicated group in the Amoco Exploration/Production Sector (E&P) for natural gas upgrading from a team of technologists out of the Corporate, Oil, and Chemical Sectors of Amoco Corporation. Since our group was formed in E&P, the emphasis on downstream natural gas processing is to move very large quantities of natural gas to market as transportable liquids for several large application areas including electric power generation, diesel fuel, gasoline substitutes or blending agents, and heating and cooking fuel.

We have assembled the elements of this project to include several new promising approaches toward the low-cost syntheses of specific oxygenate materials for some of these applications from a group of inexpensive chemical building blocks including synthesis gas optionally containing acetylene, methane, methyl ether, and methanol. Since our division is involved in a multicorporate venture plan for development of dimethyl ether (DME) or DME/methanol solutions as ultra-low emissions fuel for several applications, most of these oxygenates syntheses involve development of new technology based on DME (or methanol) as a starting material.

The objective of this project is to develop high yield syntheses of oxygenate products that are liquid at room temperature and which fit with Amoco's strategic business interests and technical strengths. The identified products include: Dimethyl Carbonate (DMC), 1,1-Dimethoxyethane (DMOE), C_2+ Alcohols/Ethers (C_2AE). The technical strategy is outlined below:

A.) Synthesis of DMC via oxidative carbonylation of DME instead of methanol. Since this synthesis would not coproduce water as a byproduct, there is a potential for very high DME conversions in contrast to the low (ca 20%) conversions obtained in conventional plants. We will compare this approach with the use of methanol in combination with various drying agents to achieve the same end. The business target for this product is primarily in gasoline blending applications where the desired intent is to raise oxygen content in gasoline.

Technical emphasis will be placed on development of a supported copper catalyst with a capability for cleavage of DME into its chemisorbed organic moieties. Amoco has extensive expertise in the area of catalyst design and development for oxidative carbonylation to DMC.

Proposed conversion: $CH_3OCH_3 + CO + 1/2\ O_2 \rightarrow CH_3OCOCH_3$

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B. Synthesis of 1,1-dimethoxymethane (DMOE) from acetylene/CO/H_2 process streams obtained from commercial methane oxidative pyrolysis processes. In the overall processing scheme the syngas would be converted to DME. The wet acetylene stream would be partially condensed to retain an equivalent of water and then condensed with DME to produce DMOE. (Alternatively, methanol could be used in place of DME/H_2O.) The business target for this product is also in gasoline blending applications.

Technical emphasis will be placed on development of a solid catalyst for gas phase synthesis with a capability for cleavage of DME. Amoco has extensive expertise in the development of modified zeolite catalysts for conversion of methyl ether/methanol to organic compounds and for conversion of acetylene to organic compounds.

Proposed conversion: $CH_3OCH_3 + HCCH \rightarrow CH_3CH(OCH_3)_2$

C.) Direct conversion of DME or DME/methanol to ethanol/propanol or their methyl ethers. Under the influence of functionalized alcohol condensation catalysts developed exclusively at Amoco it should be possible to achieve direct conversion of dimethyl ether (or methanol) to ethanol/propanol and/or the methyl ethers of these alcohols. Although this reaction is not currently known, a combination of key catalyst components from identified systems should result in a DME conversion catalyst to C_2+ oxygenates. The business targets for these products are in pure gasoline fuel or gasoline blending applications for the alcohols and in the corresponding diesel applications for the ethers.

Technical emphasis will be placed on catalyst screening of various modified magnesia-based catalyst systems for DME conversion. Amoco is a leader in the development of saturated alcohol condensation catalysts and processing technology.

Proposed conversion: $CH_3OCH_3/CH_3OH \rightarrow CH_3CH_2OH$, $CH_3CH_2OCH_3$, etc.

D.) Reaction of DME or acetylene with synthesis gas (CO/H_2) or methanol. A variety of catalysts will be tested for conversion of acetylene/CO/H_2 or acetylene/methanol to propylene and conversion of DME/CO/H_2 or DME/methanol to dimethoxymethane (DMM) and/or other oxygenates. Propylene is readily hydrated to isopropanol, a superior gasoline blending agent. Dimethoxymethane is a superior diesel fuel.

In each of the above project categories intermediate milestone points exist such that a minimum 5% conversion of reactants to products must be obtained by specified dates in order to justify further work on the sub-projects. These dates are June 1, 1996 for DMC, August 1, 1995 for DMOE, and September 1, 1995 for C_2AE.

The initial phase of the project involves installation and construction of equipment necessary for DMOE and C_2AE experimentation. The reactor systems for each of these projects share common feed systems and G.C. analytical systems. The initial phase also involves initial proof of concept experiments for gas phase conversion of acetylene/methanol to DMOE. The most promising catalysts are to be tested for conversion of acetylene/DME/H_2O to DMOE.

II. Technical Report

B. Introduction

Acetals as a family organic compounds have been known since the 1800's to be produced via the reactions of alcohols with aldehydes catalyzed by anhydrous Bronstead acid catalysts. The synthesis of 1,1-dimethoxyethane (DMOE) from methanol and acetylene was first reported by Nieuwland, et.al., in 1923(1). The reaction is catalyzed by strong acids such as H_2S0_4 or BF_3 monohydrate in the presence of a mercuric salt such as $HgSO_4$ or HgO(2,3). High yields of DMOE were only obtained in the presence of the mercuric cocatalyst, and it has been suggested that an addition compound formed via the reaction of acetylene and the salt facilitate the subsequent reaction with methanol leading to DMOE(3).

Although yields of DMOE are high (>90%) it would be desirable in practical industrial applications to be able to carry out the synthesis with nonsoluble solid catalysts in order to minimize the cost of catalyst separation and recycle and to eliminate any potential environmental effects as the result of disposing of spent inorganic acids and mercuric salts. Solid catalyst systems for either gas or liquid phase synthesis of DMOE would be potentially useful in a modern large scale plant.

Although solid catalyst systems have been developed for the more conventional synthesis of DMOE from acetaldehyde and water, none have been reported in the literature for the acetylene-based synthesis(4). One reason for this is that a stronger acid is generally required for the activation of acetylene. Solid superacids and strongly acidic zeolites have been developed recently relative to the discovery of the acetylene-based route to DMOE, and many of these may not have been tested in the synthesis. Another reason may be related to the mechanistic role of mercury in the reaction. It is not known if solid forms of mercuric species incorporated into solid acids or ion exchanged onto zeolites are active in the activation of acetylene to the same extent as soluble mercuric salts in homogeneous liquid media.

Also unreported in the literature is the synthesis of DMOE from acetylene, dimethyl ether (DME), and water. This is not surprising in view of the relative ease in carrying out the methanol-based route in methanol solvent at room temperature in comparison to dispensing both dimethyl ether and acetylene as gases into a solvent based liquid system. However, modern economic studies have shown that in large scale production units the cost of making DME from synthesis gas is significantly less than the cost of making methanol(5). Thus, large scale production of DMOE for gasoline blending applications would be most economical with DME. This synthesis would be a good candidate for gas phase studies since none of the reactants are suitable solvents for homogeneous liquid phase studies.

We propose to design and test solid catalyst systems for the synthesis of DMOE or other interesting fuel oxygenate products from the reaction of MeOH and acetylene or DME, water, and acetylene The initial emphasis will be on gas phase reaction studies with pentasil zeolite acid catalysts at relatively low temperatures of 100 to 300°C to favor formation of addition products and minimize subsequent conversion of oxygenates to MTG type olefinic/aromatic products.

B. Experimental

Construction

Two HP5890A gas chromatographs were set up and installed - one strictly for liquid samples and the other for gas and/or liquids. The liquid sample GC is equipped with an autosampler and will be run off-line. The column is suitable for separating alcohols and oxygenates. The gas sample GC operates with a two valve, three column, two detector system which can separate fixed gases and light hydrocarbons and oxygenates. It runs on-line and is capable of unattended, automated operation.

A VG Multichrom system for processing of GC analyses was installed and interfaced with the site VAX computer system. Methods for both on-line gas and off-line liquid analyses have been developed and instrument calibrations were performed. Gas analyses will quantitate fixed gases, light hydrocarbons, and light oxygenates such as methanol and dimethyl ether. Liquid analyses presently include C_1-C_4 alcohols and selected ethers and acetals, and will use THF internal standard with acetone solvent.

A double train quartz tube reactor system was designed and built. One reactor is to be used primarily for DMOE synthesis and has a capacity of 5 cc of catalyst. Another reactor is to be used for C_2AE and any needed scale up studies and has a capacity of 30 cc of catalyst. Heat is provided by a electric split-tube furnaces. Feed gases are monitored via mass flow controllers and liquids are injected with a syringe pump. Gases and liquids can be introduced to the reactor into a vaporization section, then onto the catalyst zone.

Products exit the reactor and liquids are condensed. A slipstream of gas product is diverted to the gas GC and liquid is collected for later analysis. Operability of the system was been demonstrated and the attached analytical system was tested and found to accurately analyze mixed gas and liquid product streams of the type described above.

Catalyst Preparation and Testing

For the initial catalyst testing and shakedown of the reactor system a 0.1% Hg/40% HZSM-5/60% PHF Alumina was prepared. To 10.00 g of 40% HZSM-5 molecular sieve supported on 60% PHF gamma alumina (Amoco-Hopkins, 11480-167, 1/16" extrudates) was added a solution of 0.16041 g $Hg(OAc)_2$ in 10 ml H_2O. The catalyst and solution was stirred until all of liquid was adsorbed and the extrudates exhibited a uniformly semi-moist appearance on the surface. The resulting catalyst was dried overnight in a 120°C vacuum oven and then calcined for three hours at 300°C. It was then crushed and sieved to 18/40 mesh granules and 3.57 g (5.5 cc) of the catalyst was charged into the small reactor tube.

A purge gas of pure nitrogen was passed through the reactor and the heater was set for an internal catalyst bed temperature of 108°C. As the reactor was approaching temperature the purge was replaced with a feed gas containing 10.2% N_2 by volume at a rate of 10.0 sccm. A feed of methanol was pumped into the preheat section of the reactor with a syringe pump at a rate of 0.003848 ml/m. After one hour TC and FID GCs of the reactor offgas were taken. No liquid was observed in the receiver. GCs were also taken in one hour intervals after achieving temperatures of 164°, 220°, 274°, 330°, and 381°C. Liquid samples were collected and analyzed by FID GC at the 165°, 274°, 330°, and 381°C temperatures.

In like manner the catalyst was evaluated for the conversion of DME, H_2O, and acetylene; DME and acetylene in the absence of H_2O; DME in the absence of acetylene or H_2O.

C. Results

Detailed results are shown in Tables I-IV and Figures 1&2. When acetylene (diluted with nitrogen) was co-fed with methanol, (1:2 mole ratio), the conversion of acetylene was low (<20%) at temperatures less than 300°C, but approached 100% above 300°C. Methanol dehydration to dimethyl ether occurred to a large extent at all temperatures up to 274°C but was greatest at 220°C. Small amounts of carbon oxides were produced, increasing with increasing temperature. Overall carbon selectivity to C_2-C_7 olefins became quite high (83%) at the 330°C temperature and aromatics were first observed in 10% selectivity at this temperature. At the highest temperature of 380°C aromatics selectivity increased to 44% and the balance of selectivity was largely to olefins. A trace of ethanol was seen at 165°C and a trace of dimethoxyethane was seen at 380°C.

Similar results were obtained when a 1:1 mole ratio of dimethyl ether: water was substituted for MeOH in the feed, but conversion of acetylene was comparatively lower. Dimethyl ether was hydrolyzed to methanol in addition to being converted to hydrocarbons and aromatics, especially at the higher 330° and 380° temperatures. Again, only traces of ethanol and dimethoxyethane were produced.

Feeding dimethylether and acetylene without the water gave similar results, except no traces of ethanol or dimethoxyethane were seen in the products. Very little liquid product was collected.

When dimethylether alone was fed to the reactor, no liquids were produced and only light hydrocarbons (including significant amounts of methane) with some COx were produced at the higher temperatures. Aromatics production was minimal. Overall levels of product detected as moles of carbon was significantly lower than the carbon introduced into the reactor as feed. We suspect this is attributable to extensive coke formation.

Figure 1 and Figure 2 show calculated conversions of DME and acetylene, receptively, as a function of temperature. Conversion patterns obtained with all of the feed systems are roughly similar. Indeed, with the exception of one data point, it can be observed that conversion of DME in DME-containing feeds seems essentially independent of the feed composition, i.e., of the coexistence of water and/or acetylene. In these cases conversion generally increased smoothly from a reaction temperature of 150-380°C and achieving 100% at 380°C. In contrast, conversion of acetylene was relatively low (<15%) until 329°C. These results suggest that DME underwent conversion independently of acetylene to typical olefinic, paraffinic, and aromatic DME conversion products. The methanol feed underwent the same reaction after producing DME in situ in the reactor.

Since total carbon accountability of hydrocarbon products and reactants was generally high (>90%, except with pure DME feed), it is apparent that acetylene also underwent conversion to some of the observed products.

D. Discussion

Based on initial experiments it appears that acidic mercury-containing HZSM-5 catalysts are not active for the conversion of DME/MeOH/acetylene feeds to DMOE or any other potentially useful light oxygenates. It is not surprising to have observed conversion of the various feedstocks to light olefins and/or aromatics at intermediate to high reaction temperatures since these conversions with methanol and dimethyl ether are well known with ZSM-5-type catalysts and other pentasil zeolites. Conversion of acetylene/H_2O mixtures of to olefins/aromatics/oxygenates is also known to occur with pentasil-based catalysts. Clean conversion of this feed to aromatic gasoline is reported to occur with a Zn-containing borosilicate pentasil zeolite (ZnAMS-1B), presumably via intermediate formation of oxygenate intermediates from the acetylene.

The inactivity of this catalyst for the synthesis of DMOE can be explained on the basis of several hypotheses. First, although DMOE might have formed in small amounts at the lower temperatures, the catalyst may have been too strongly active toward subsequent conversion to olefins/aromatics. Second, the supported mercury component of this catalyst may not play the same mechanistic role as mercuric salts in liquid phase systems in conversions of acetylene/MeOH to acetaldehyde/MeOH to DMOE or in direct conversions of acetylene/MeOH to DMOE. In these systems the presence of the mercuric catalyst component is essential to the synthesis.

In view of the unique role of zinc described in the above conversion of acetylene/H_20 to aromatic gasoline via oxygenate intermediates, we will focus future efforts on zinc containing zeolite catalysts.

E. Conclusion

Acidic pentasil molecular sieve catalysts containing low levels of mercuric components are not active for the conversion of acetylene/ MeOH or acetylene/DME mixtures to DMOE or other potentially interesting fuel oxygenate compounds. Near term work is in progress to test pentasil catalysts that are less acidic than HZSM-5 such as HAMS-1B and to test the catalytic effect of zinc instead of mercury. Early results indicate that a zinc-containing HAMS-1B is somewhat active for synthesis of DMOE, ethanol, and 1-butanol from acetylene/MeOH.

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3. H.D. Hinton and J.A. Nieuwland, J. American Chem. Soc,. 52, 2892 (1930)
4. J. Andrade, et.al., German Patent DE 3403426
5. J.B. Hansen, et.al., SAE Technical Papaer 950063 (1995)

Figure 1

Various C1 Feeds
C2H2 Conversion

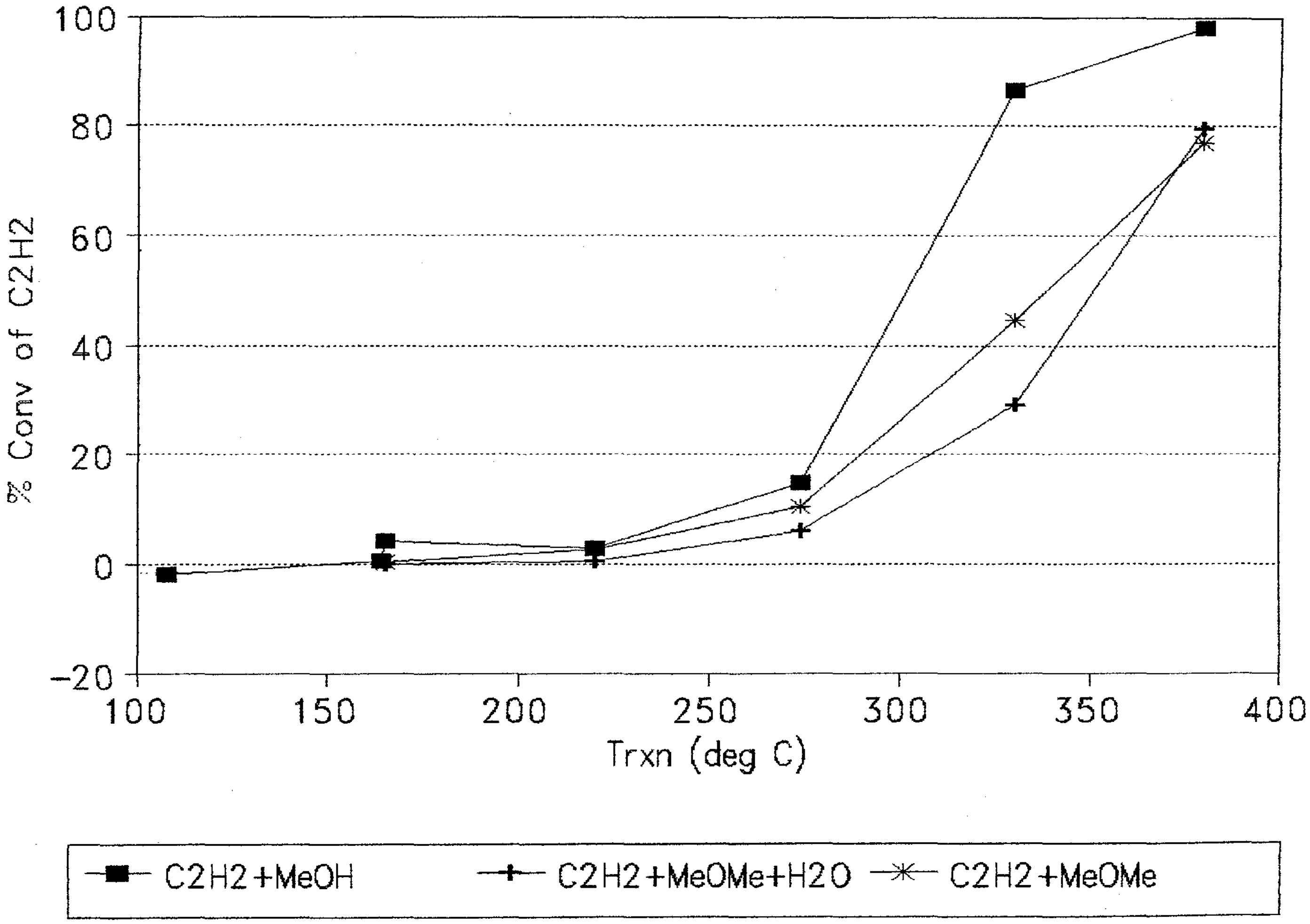

Figure 2

Various C1 Feeds
Est DME Conversion

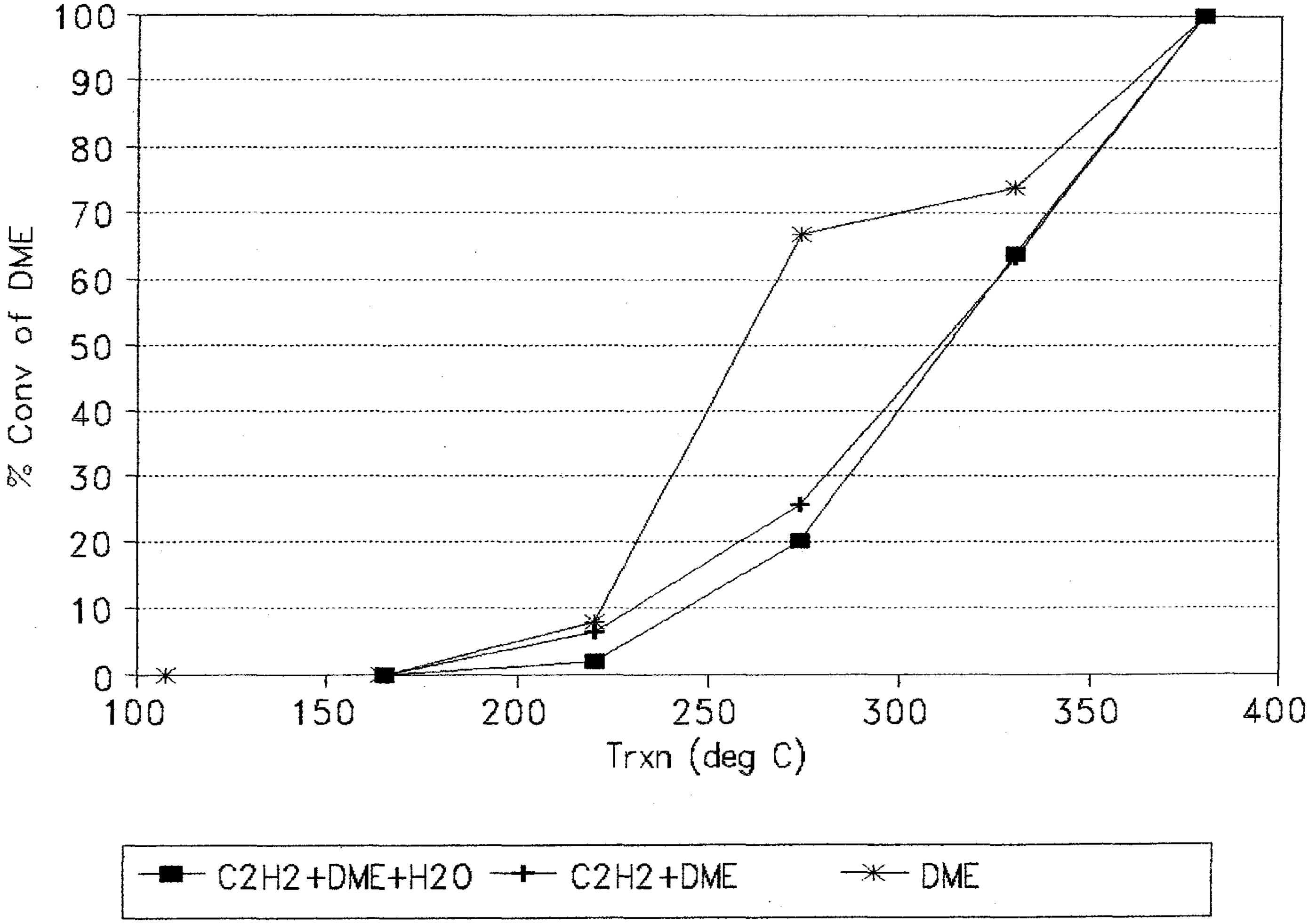

Table I - Conversions:

	C2H2 + MeOH ------>				C2H2 + MeOMe + H2O ------>		
Trxn	M% C2H2	M% N2	C2H2/N2	% Conv	M% C2H2	M% N2	C2H2/N2
RT	10.21	88.89	0.115				0.115
108.00	10.38	88.58	0.117	-2.05			ERR
164.00	9.82	85.94	0.114	0.48			ERR
165.00	9.19	83.43	0.110	4.12	8.37	72.80	0.115
220.00	8.70	78.00	0.112	2.85	9.39	82.06	0.114
274.00	7.96	81.27	0.098	14.69	8.89	82.19	0.108
330.00	1.37	86.93	0.016	86.31	6.90	84.82	0.081
380.00	0.20	86.97	0.002	97.98	2.07	87.57	0.024

Table II - Sel C2H2 + MeOH ------>

Trxn	Gas Prod-	%Sel -	norm=y				
	CO	CH4	CO2	C2H4	C2H6	C3H6	C3H8
108.00							
164.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
165.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
220.00	0.19	0.00	0.06	0.24	0.00	0.00	0.00
274.00	1.42	0.10	0.21	7.57	0.00	6.84	0.00
330.00	3.08	2.40	0.85	27.56	0.00	8.20	8.32
380.00	6.03	4.40	0.84	11.56	1.01	0.00	6.26

Table III - Sel C2H2 + MeOMe + H2O ------>

Trxn	Gas Prod-	%Sel -	norm=y				
	CO	CH4	CO2	C2H4	C2H6	C3H6	C3H8
165.00							
220.00	0.00	0.00	1.33	0.00	0.00	0.00	8.15
274.00	0.82	0.50	0.47	12.94	0.00	11.69	0.00
330.00	3.42	1.85	0.38	25.19	0.00	16.11	0.00
380.00	7.18	4.78	0.69	21.45	0.00	9.59	0.00

Table IV - Sel C2H2 + CH3OCH3 ------>

Trxn	Gas Prod-	%Sel -	norm=y				
	CO	CH4	CO2	C2H4	C2H6	C3H6	C3H8
165.00							
220.00	0.00	0.00	1.70	0.00	0.00	10.20	0.00
274.00	5.62	1.09	0.57	14.99	0.00	14.68	0.00
330.00	6.69	3.44	0.62	18.77	0.04	16.27	0.00
380.00	7.76	5.78	0.67	22.54	0.07	17.85	0.00

Table I - Conversions:

				C2H2 + CH3OCH3 ------>			
Trxn	% Conv	M% MeOMe	% Conv	M% C2H2	M% N2	C2H2/N2	% Conv
RT						0.12	
108.00	ERR					ERR	ERR
164.00	ERR					ERR	ERR
165.00	-0.02	8.13	0.00	9.21	80.15	0.11	0.09
220.00	0.53	7.97	1.93	9.01	80.47	0.11	2.65
274.00	5.93	6.50	20.09	8.34	80.66	0.10	10.08
330.00	29.24	2.94	63.86	5.34	84.20	0.06	44.85
380.00	79.48	0.00	100.00	2.34	87.74	0.03	76.81

Table II - Sel C2H2 + MeOH ------>

Trxn	Gas Prod-	%Sel -	norm=y				
	DME	AcAld	C4	C5	C6	C7+	MeOH
108.00							
164.00	96.03	0.00	1.44	2.53	0.00	0.00	
165.00	97.84	0.00	0.65	1.11	0.00	0.00	
220.00	98.07	0.00	1.37	0.08	0.00	0.00	
274.00	81.20	0.00	2.08	0.57	0.00	0.00	
330.00	1.52	0.00	6.91	16.05	10.32	5.27	
380.00	0.00	0.00	9.50	8.75	4.62	2.59	

Table III - Sel C2H2 + MeOMe + H2O ------>

Trxn	Gas Prod-	%Sel -	norm=y				
		AcAld	C4	C5	C6	C7+	MeOH
165.00							
220.00		0.00	0.00	0.00	0.00	0.00	90.52
274.00		1.85	4.70	2.37	1.65	0.00	62.86
330.00		0.00	6.11	6.25	4.95	2.52	29.71
380.00		0.00	8.32	7.17	4.26	2.88	6.98

Table IV - Sel C2H2 + CH3OCH3 ------>

Trxn	Gas Prod-	%Sel -	norm=y				
		AcAld	C4	C5	C6	C7+	MeOH
165.00							
220.00		0.00	20.39	3.92	0.00	0.00	63.79
274.00		0.00	11.56	8.46	6.40	3.46	33.16
330.00		0.00	11.59	7.19	4.91	3.91	17.91
380.00		0.00	11.61	5.91	3.42	4.35	2.65

Table I - Conversions:

Trxn	M% MeOMe	% Conv	M% MeOMe	% Conv
RT				
108.00			18.50	0.00
164.00			18.50	0.00
165.00	8.13	0.00	18.50	0.00
220.00	7.62	6.27	17.07	7.72
274.00	6.06	25.51	6.15	66.75
330.00	3.00	63.12	4.84	73.84
380.00	0.00	100.00	0.07	99.61

Table II - Sel C2H2 + MeOH ------>

Trxn	Gas Prod-	%Sel -	norm=y	Liq Prod-	%Sel	norm=yes	
	MeForm	EtOH	Acetone	MeAc	iPrOH	nPrOH	DMOE
108.00							
164.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
165.00	0.00	0.17	0.00	0.23	0.00	0.00	0.00
220.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
274.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
330.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
380.00	0.00	0.00	0.00	0.00	0.00	0.00	0.20

Table III - Sel C2H2 + MeOMe + H2O ------>

Trxn	Gas Prod-	%Sel -	norm=y	Liq Prod-	%Sel	norm=yes	
	MeForm	EtOH	Acetone	MeAc	iPrOH	nPrOH	DMOE
165.00							
220.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
274.00	0.00	0.15	0.00	0.00	0.00	0.00	0.00
330.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00
380.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19

Table IV - Sel C2H2 + CH3OCH3 ------>

Trxn	Gas Prod-	%Sel -	norm=y	Liq Prod-	%Sel	norm=yes	
	MeForm	EtOH	Acetone	MeAc	iPrOH	nPrOH	DMOE
165.00							
220.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
274.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
330.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
380.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table I - Conversions:

Trxn
RT
108.00
164.00
165.00
220.00
274.00
330.00
380.00

Table II - Sel C2H2 + MeOH ------>

Trxn	Liq Prod - %Sel		
	iBuOH	nBuOH	aromat
108.00			
164.00	0.00	0.00	0.00
165.00	0.00	0.00	0.00
220.00	0.00	0.00	0.00
274.00	0.00	0.00	0.00
330.00	0.00	0.00	9.53
380.00	0.00	0.00	44.24

Table III - Sel C2H2 + MeOMe + H2O ------>

Trxn	Liq Prod- %Sel		norm=yes
	iBuOH	nBuOH	aromat
165.00			
220.00	0.00	0.00	0.00
274.00	0.00	0.00	0.00
330.00	0.00	0.00	3.45
380.00	0.00	0.00	26.51

Table IV - Sel C2H2 + CH3OCH3 ------>

Trxn	Liq Prod- %Sel		norm=yes
	iBuOH	nBuOH	aromat
165.00			
220.00	0.00	0.00	0.00
274.00	0.00	0.00	0.00
330.00	0.00	0.00	8.69
380.00	0.00	0.00	17.37