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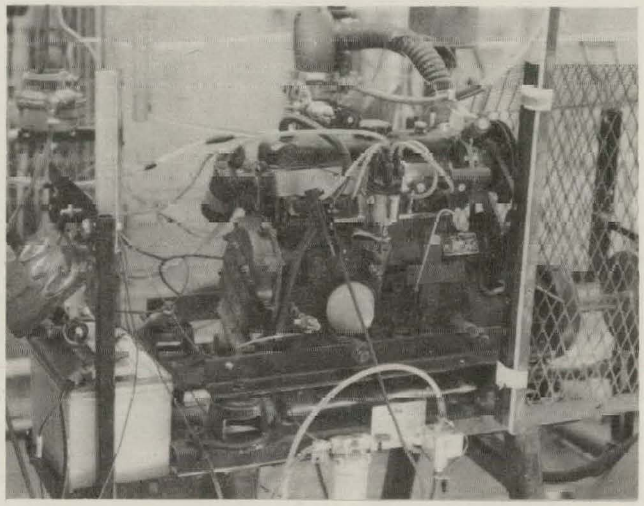
MASTER

# POWER-GRADE BUTANOL RECOVERY & UTILIZATION

TEST ENGINE
Renault Continental
840 ml.



by Randall Noon, P.E.

KANSAS ENERGY OFFICE

PREPARED BY THE KANSAS
ENERGY OFFICE WITH FUNDING
PROVIDED BY THE U.S. DEPARTMENT
OF ENERGY UNDER CONTRACT
DE-FG47-81AF93013-M001

DOE/AF/93013--T1

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# Power Grade Butanol Recovery and Utilization

by Randall Noon, P.E.
B.S., M.S. Mech. Eng.

Energy Research and Resource Development Division
Kansas Energy Office
214 West 6th Street
Topeka, Kansas 66603

Funding Provided by the U.S. Department of Energy, Alcohol Fuels Program, under Contract Number DE-FG47-81AF93013-M001

February 12, 1982

# Acknowledgements

I thank Jack Stacey and Jerry Landis, formerly with the Department of Energy, Kansas City, for their assistance in obtaining funding for the project. I also thank Joe King, former director of the Kansas Energy Office, for his support to allow the undertaking of the project. Special appreciation is due to Dr. William Griffith and Alicia Compere of Oak Ridge Laboratories for their useful advice and information. Lastly, I thank Cheryl Chick and Dr. Don Miller of Washburn University in Topeka, and Dr. Mark Schrock of Kansas State University in Manhattan, Kansas, for providing the hard laboratory data, without which there would be nothing to discuss.

Randy Noon, P.E.
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## I. Introduction

Besides ethanol fermentation, there are several fermentation processes which produce suitable substitutes for traditional, petroleum derived liquid fuels. In particular, the Weizmann Process produces normal butanol, acetone and ethanol via anaerobic fermentation.[1,2,3,4] These products may be used individually for fuel or together in a blend.[5,6,7]

While significant research is still continuing,[8,9] the fermentation of butanol is generally considered an accomplished, commerical technology. The recovery of n-butanol, acetone and ethanol via fractional distillation has also been accomplished commercially for some time. However, due to the increased emphasis in process energy conservation, new lines of research in alternate separation schemes are being pursued.[10,11]

To date, much of the work concerning butanol recovery has concentrated on producing technical grade, individual chemical feedstocks of n-butanol, acetone and ethanol. Some recent research has been done to extract n-butanol chemically using an absorbing alkane group hydrocarbon. The alkane is immiscible with the general aqueous solution, but is miscible with the solute n-butanol component.[12] This system produces an n-butanol/alkane fuel blend. However, the remaining aqueous solution of acetone and ethanol requires a separate recovery process.

**"Power Grade" Butanol**

As an alternative to the traditional recovery systems, it was proposed in a previous publication that the n-butanol/acetone/ethanol fermentation products could be recovered as a "power grade" fuel blend and used directly as a fuel.[13] This would affect a savings in process energy requirements because each chemical component would not have to be processed individually to technical grade purity. Further, some residual water could be tolerated in the fuel blend. It was estimated that such a "power grade" fuel blend could be recovered using only about 3730 joules of process energy per gram of fuel blend output (∽ 1607 BTU/lb). This compared well against the higher heating value of the fuel blend itself, estimated to be about 28,800 joules/gram (12,400 BTU/lb). This is a fuel output to process energy ratio of 7.72 to 1. As a comparison, ethanol recovery systems have an ratio of 3 to 1 or less.

**Project Objectives**

To develop such a "power grade" fuel recovery scheme beyond the conceptual stage, the Energy Research and Resource Division of the Kansas Energy Office undertook a two-fold program to demonstrate and test a "power grade" butanol/acetone/ethanol fuel recovery system, and further to demonstrate the feasibility of using the fuel blend in a standard type engine. With financial support from the Alcohol Fuels Grants Program of the U.S. Department of Energy, a development program was initiated to accomplish the following objectives:

*design and test an operational "power grade" butanol recovery plant that would operate at one liter per hour output using a recovery strategy similar to that proposed in reference 13.

*test and assess the performance of "power grade" butanol in an spark ignition automotive engine.

The first part of the program was accomplished in cooperation with Ms. Cheryl Chick and Dr. Don Miller of the Chemistry Department of Washburn University, Topeka, Kansas. The second part was accomplished in cooperation with Dr. Mark Schrock of the Agricultural Engineering Department of Kansas State University, Manhattan, Kansas. These individuals provided most of the pertinent laboratory work to support the program objectives. They also provided valuable professional assessments of the laboratory data.

## II. Recovery System Design Strategy

**Initial Design**

Initially, the recovery system design strategy shown in figure 1 was employed. However, it became apparent that the initial design parameters would require some modifications. The acetone still's initial overhead temperature occurred at 75°C instead of the expected 56°C. Also, the overhead contained larger fractions of water, butanol, and ethanol than was originally anticipated.

The butanol still's overhead appeared initially at 75°C instead of the expected 93°C. However, distillation operated generally smoothly between 85°C and 91°C without reflux. Between 85°C and 91°C the overhead condensate came over as a single phase. Between 91°C and 100°C, the overhead condensed into two phases due to a larger amount of water in the overhead. The single phase condensate was essentially similar in component proportion to the upper phase of the two-phase condensate. However, the overall amount of water in the phase intended for fuel use was too large, approximately 40%. This was caused by the increased amount of acetone and ethanol in the condensate solution "dragging" more water into the butanol solution phase.

# INITIAL DESIGN
# N-BUTANOL/ACETONE RECOVERY SYSTEM[13]

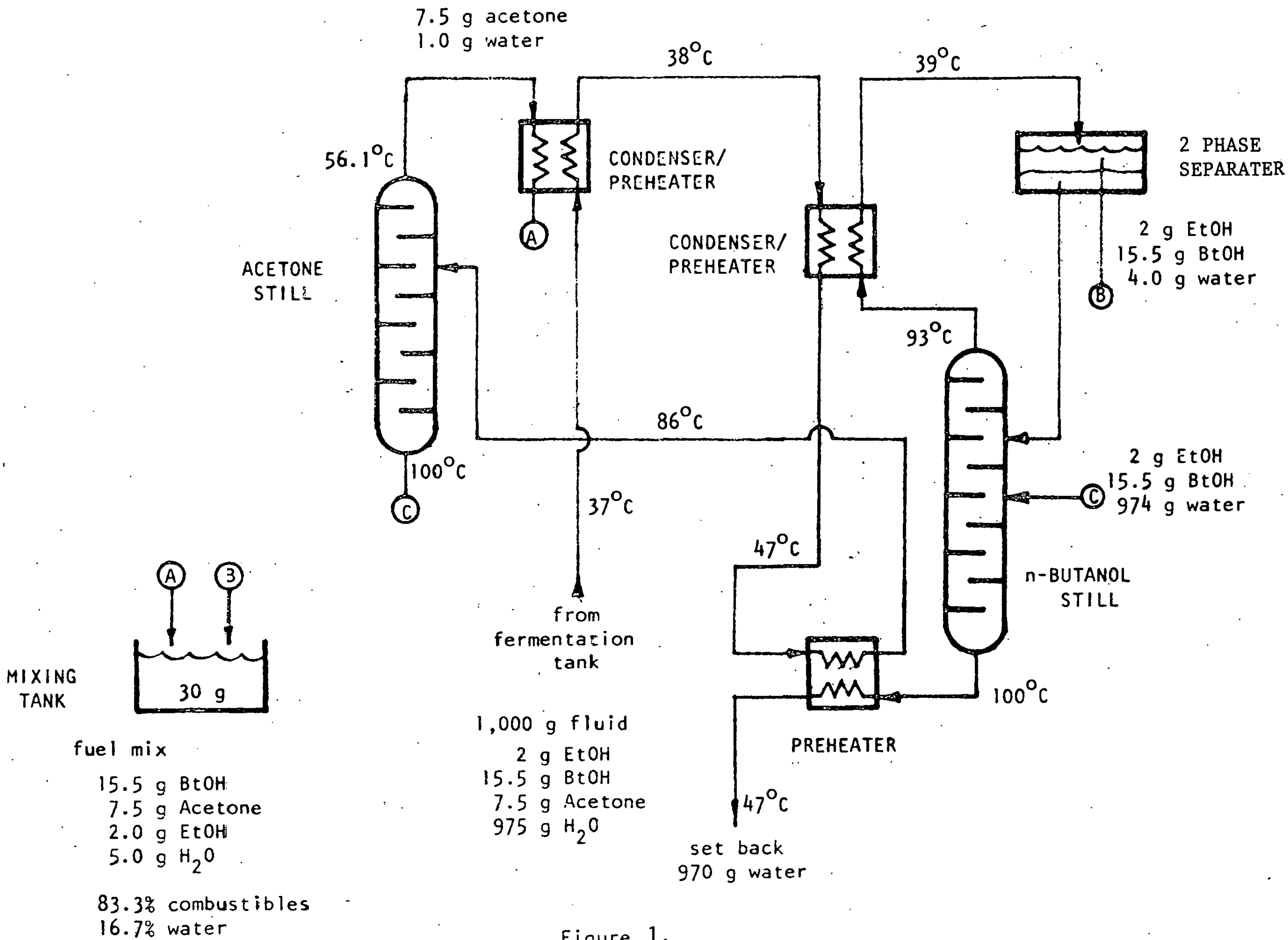


Figure 1.

The extra water problem could be solved by improving the efficiency of acetone and ethanol recovery in the first still. In other words, to decrease the water content in the butanol still's condensate, enough acetone and ethanol would have to be removed by the acetone still to affect an essentially binary butanol/water feed solution in the butanol still. To do this would require a level of recovery system complexity that would approach that of the conventional fractional column system. Because the initial design strategy was based upon the minimization of process energy input with a toleration of fuel grade purity rather than technical grade purity, it was decided to modify the initial recovery system design.

### Modified Recovery System Design

To preserve system symplicity, a combination of distillation and chemical extraction techniques was proposed. In experiments with a laboratory scale single column still composed of both a stripping portion and a rectification portion, it was observed that gross distillation of the post-fermentation quaternary solution of water, n-butanol, acetone, and ethanol (97.5%, 1.55%, 0.75%, and 0.2% by weight respectively) produced an overhead at 85°C to 91°C that condensed into a composition of about 45% n-butanol, 8% acetone, 2% etanol, and 45% water by weight. At higher overhead temperatures, a lower phase in the condensate forms containing 85% water, 6% acetone, 8% butanol, and 1% ethanol by weight.

It is notable that as the overhead temperature increases from 85°C to 91°C, water content in the condensate increased from 40% to 45%. At 91°C and above, more water continues to come over in the overhead. However, since the water solubility limits have been reached, the lower aqueous phase develops.

When unleaded gasoline is added to the condensate butanol solution, the gasoline absorbs the butanol and much of the acetone and ethanol, while pushing the water out of solution into a lower phase. Thus, the addition of gasoline can chemically dewater the condensate butanol solution. The acetone and ethanol will proportion themselves between the two phases roughly in direct proportion to the relative volumes of the two phases.

A schematic of the modified design is shown in figure 2.

## III. Modified Design Performance

### Preliminary Laboratory Scale Test Model

Using the modified design, a laboratory scale recovery system was first constructed, as shown in figure 3. This smaller system allowed quick experiments to be run on small samples to establish general performance characteristics. After sufficient experience was gained using the small system, the larger, one liter per hour recovery system was constructed.

### Larger Test Model

The larger system employed heat recovery using counterflow, shell and tube copper heat exchangers. The inside pass was 1.25 cm in diameter; the outer pass had an outer annulus diameter of 1.9 cm. The "preheater" heat exchanger was 4 m. long; the "preheater/condenser" heat exchanger was about 1 m. long. The distillation unit was standard aluminum pipe utilizing a packed column configuration. The pipe was 0.5 m high and 7.6 cm in diameter (O.D.) packed with stainless steel "Chore-Girls". The boiler consisted of an electric heating wire wrapped around copper tubing, controlled by a rheostat. Figure 4 shows the general configuration.

## MODIFIED RECOVERY SYSTEM DESIGN

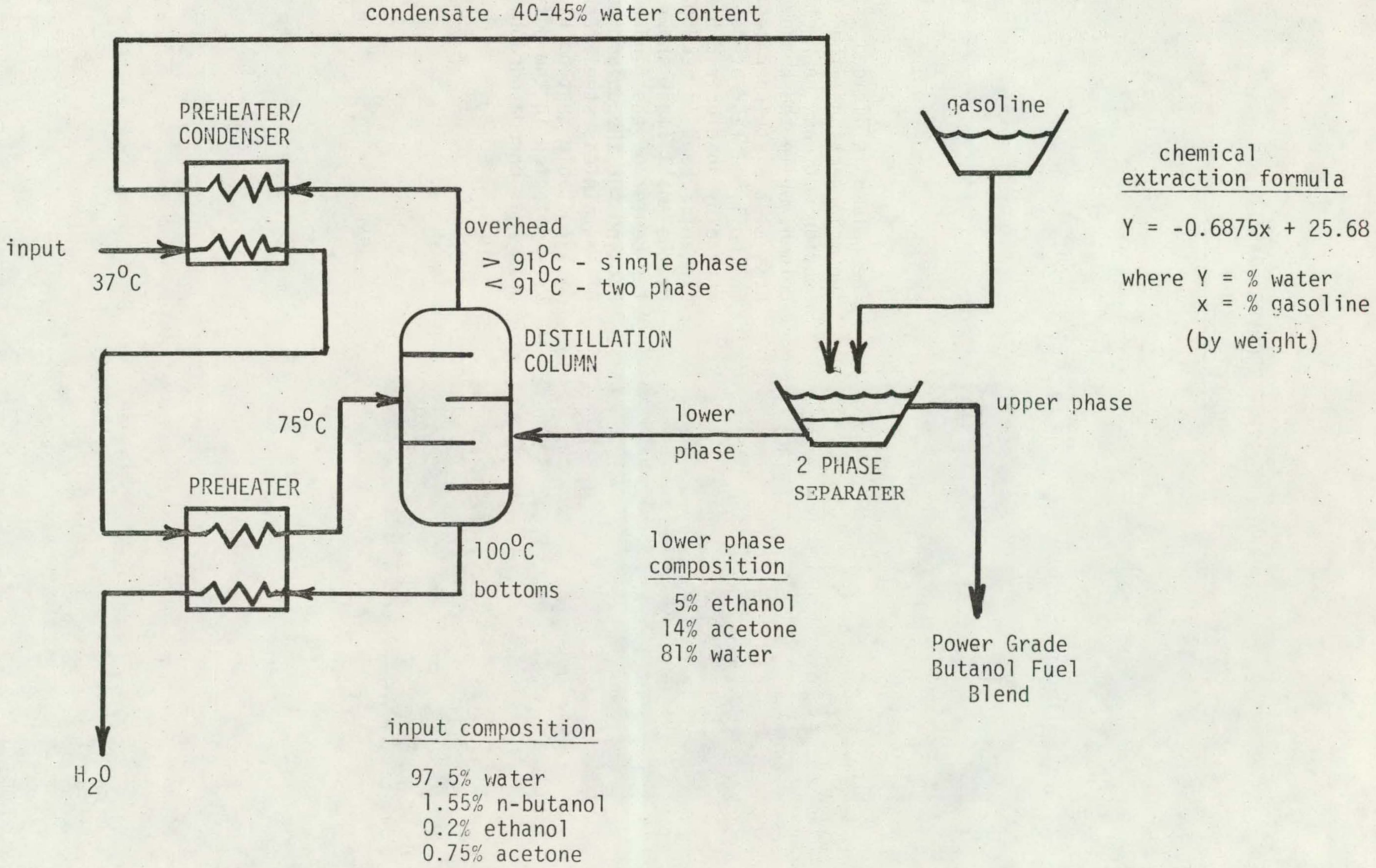
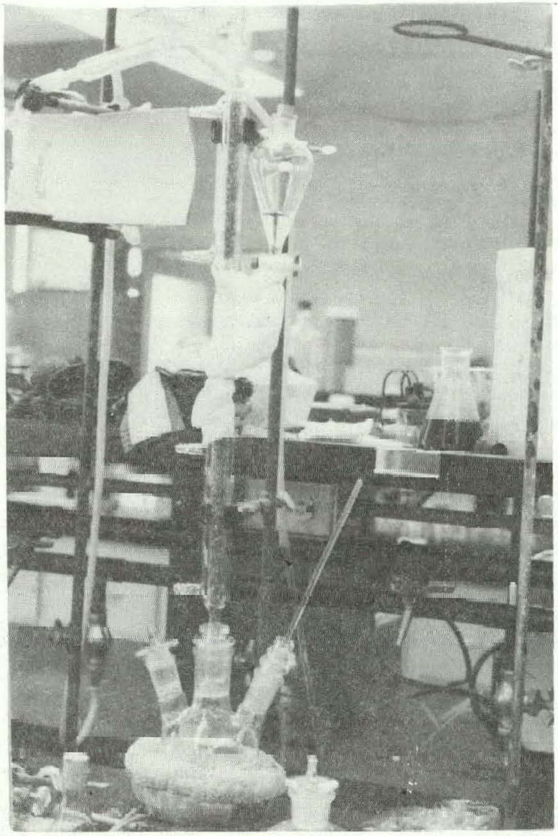


Figure 2.

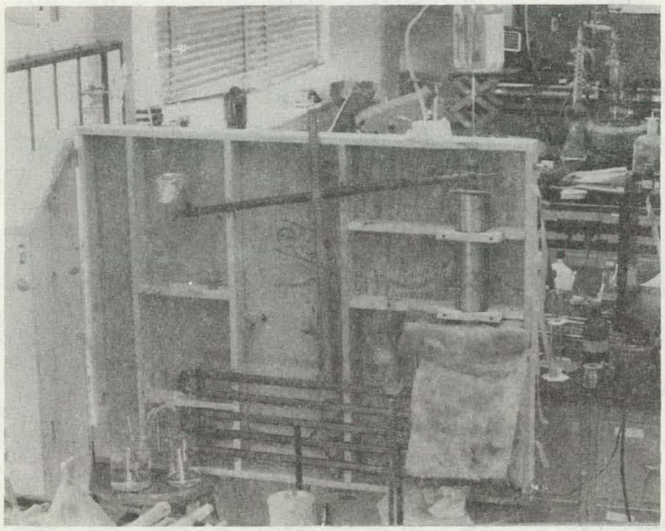
# LABORATORY SCALE RECOVERY SYSTEM
## MODEL



The column is divided into two main sections: the upper section acts as the rectification column, while the bottom section acts as the stripper section. The boiling flask at bottom is heated by an electric heating element. Feed is accomplished by the small flask shown at the top center of the figure. Packing for the column consisted of a stainless steel "Chore-Girl". It is notable that no hydocarbons were detected in the bottoms using gas chromatography analysis.

Figure 3.

# MODIFIED RECOVERY SYSTEM
# GENERAL CONFIGUATION



General configuration of the one liter per hour recovery system. Overhead condenser is located at the top of the still. The feed preheater is located at the bottom. The boiler is obscured by insulation.

View of the boiler obtained by removing the insulation.

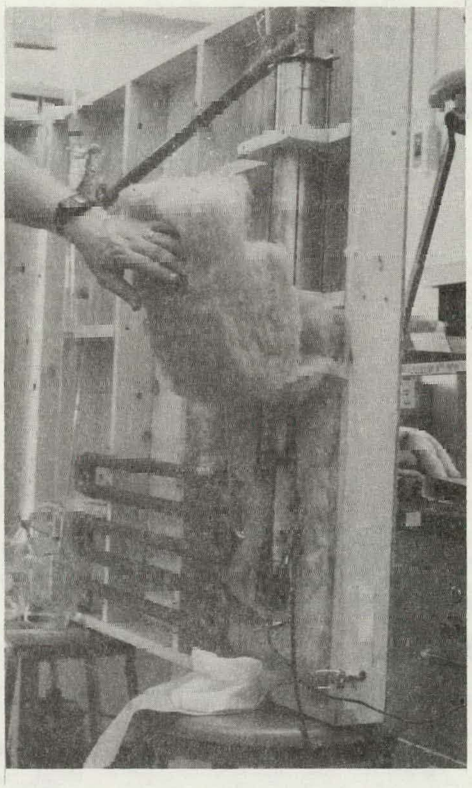


Figure 4.

### Bottoms Purity

Generally, no hydrocarbons were detected in the still bottoms when proper feeds were observed, i.e., when the column operated stably. The actual processing rate achieved without overfeeding was 960 ml per hour. The fact that the still bottoms is essentially "clean", indicates that the bottoms can be extensively used as set back. It further indicates that recovery of the fermentation products is essentially complete.

### Heat Recovery

During the actual tests the "preheater" heat exchanger provided feed at 77°C to the distillation column (see figure 2). The setback water temperature was measured to be 60°C, having entered the heat exchanger at 100°C. The "preheater/condenser" heat exchanger cooled the overhead to about 70°C. Utilization of the two preheaters raised the feed temperature from 23°C to 77°C. This recouped 226,000 joules per kilogram of feed input.

### Process Energy Input

Measurements indicated that 730 watts, or 730 joules per second, of input energy was required at an input rate of 3.82 ml per second. This computes to an energy input of 191,000 joules per kilogram of feed input. In consideration that the still "preheater" heat exchanger hot water stream was exiting at 60°C instead of a desired 40-45°C, this value is essentially the same value as that estimated from data in reference 13. In fact, to achieve an energy rating of 144,000 joules per kilogram of feed would only require that the hot water exiting stream be lowered 12°C, to a temperature of 48°C.

### Dewatering

Figure 5 shows the experimental data concerning the dewatering of the condensate by the addition of gasoline. In general, the addition of 10% of gasoline by weight reduced the

# DEWATERING of POWER GRADE BUTANOL FUEL BLEND by the ADDITION OF GASOLINE

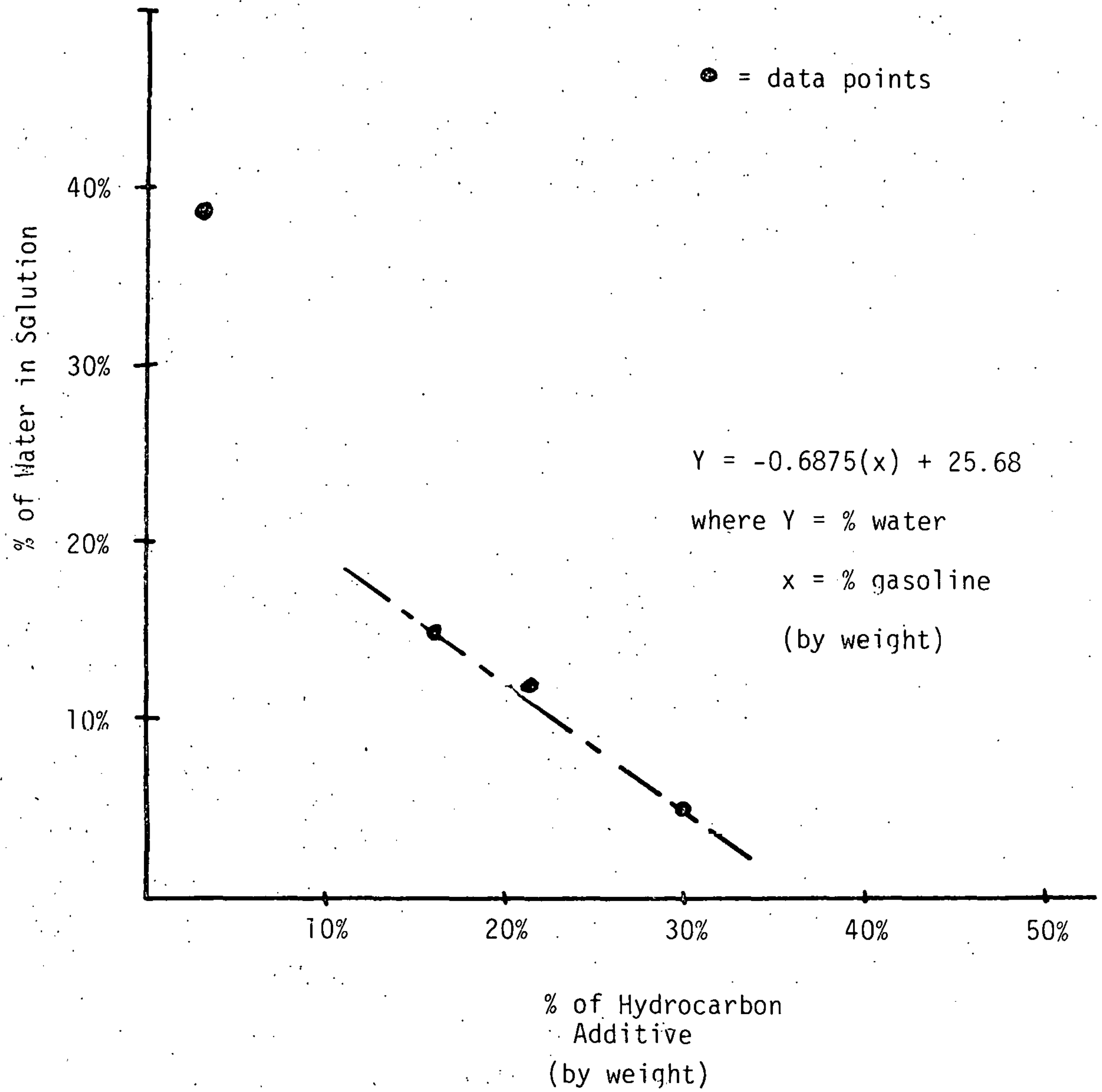


Figure 5.

overall solution water content to about 18%. Adding 30% gasoline would drop the water content to about 5%. Thus, the blending of the condensate with gasoline handily dewaters the condensate to acceptable fuel grade tolerance levels.

**Overall Energy Performance**

Overall, the process energy required to produce a "powergrade" butanol blend is the same for a 40% water content blend as it is for a 5% water content blend. The actual ratio of recovered fuel energy output to process energy was 35.0 Mj to 7.6 Mj per kilogram output of combined n-butanol, acetone and ethanol, or a 4.6 to 1 output to process energy ratio. This number excludes the added gasoline, and uses the higher heating values (HHV) of the components. The ideal ratio was previously calculated to be about 7.7 to 1, based upon ideal heat recovery conditions.[13] The test model performance ratio could have been easily improved to 6 to 1 by recovering more heat from the preheater (exiting at 48°C instead of 60°C) by lengthening it.

As a comparison, reasonably well designed anhydrous ethanol systems have an HHV output to process energy ratio of about 3 to 1. Thus, the experimental data indicates that this type of butanol recovery system has an excellent energy advantage over conventional ethanol systems.

## IV. Utilization

**Fuel Characteristics**

Table 1 shows the approximate first pass fuel blend output composition when various amounts of gasoline are used for dewatering. An approximate relative indicator of mileage can be derived from table 1 by comparing the lower heating value (LHV) of the fuel blend to that of plain gasoline.

**Table 1. "Power Grade" Butanol Fuel Properties Using Gasoline for Dewatering**

| % water | % gasoline | % BtOH | % acetone | % EtOH | HHV | LHV | LHV/HHV |
|---|---|---|---|---|---|---|---|
| 40% | -0- | 45% | 8% | 2% | 19.3 Mj/Kg | 16.8 Mj/Kg | 87% |
| 18% | 10% | 59% | 10.8% | 2.2% | 30.0 Mj/Kg | 27.4 Mj/Kg | 91% |
| 11.9% | 20% | 55.8% | 10.2% | 2% | 33.3 Mj/Kg | 30.6 Mj/Kg | 92% |
| 5% | 30% | 53.3% | 9.7% | 2% | 36.9 Mj/Kg | 34.2 Mj/Kg | 93% |
| -0- | 100% | -0- | -0- | -0- | 47.0 Mj/Kg | 43.9 Mj/Kg | 93.3% |

**Test Configuration**

Two power grade fuel blends were engine tested to demonstrate performance characteristics. The first blend consisted of 51% n-butanol, 25% acetone, 6% ethanol and 18% water by weight. The second blend consisted of 18% water, 11% unleaded gasoline, 44% n-butanol, 21% acetone, and 5% ethanol. The first blend represented the expected output from the initial recovery system design is; the second blend represented an approximate fuel output from the modified design using gasoline as a dewaterant.

The test engine was a water cooled, spark ignited, 4 cylinder Renault Continental which had a 840 ml. displacement. The compression ratio was 8.56 to 1. The carburetor was modified to allow for air/fuel ratio control. No spark advance adjustments were made from the standard setting.

The results of the tests on the first fuel blend are shown in table 2.

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**Table 2. Test Results on Fuel Blend #1***

| fuel | RPM | power output | thermal efficiency | mixture temp-erature | air/fuel ratio |
|---|---|---|---|---|---|
| gasoline | 3013 | 17.46 kW | 25.1% | 75$^{o}$C | 13.20 |
| gasoline | 3002 | 17.31 kW | 27.1% | 75$^{o}$C | 14.22 |
| gasoline | 2990 | 16.79 kW | 27.7% | 81$^{o}$C | 14.80 |
| blend #1 | 2989 | 16.79 kW | 25.1% | 34$^{o}$C | 7.84 |
| blend #1 | 2989 | 16.41 kW | 25.9% | 34$^{o}$C | 8.27 |
| blend #1 | 2985 | 14.32 kW | 25.3% | 35$^{o}$C | 9.26 |

* blend #1: 51% n-butanol, 25% acetone, 6% ethanol, and 18% water; 840 ml Renoult Continental engine

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## Engine Test Results

In comparison with gasoline, blend #1 performed well. Thermal efficiency and power output declined some, but not enough to pose a problem in normal operational situations. The air/fuel ratios are significantly different, as was expected due to the differences in combustion chemistry. The mixture temperature differences were very pronounced, caused by the relative difference in the heats of vaporization of the two fuels. Gasoline has a heat of vaporization of 330,000 joules per kilogram, whereas blend #1 has a heat of vaporization of 890,000 joules per kilogram. Some misfire problems at part-load operations were observed likely due to uneven fuel distribution to the cylinders. This effect was partially corrected by the use of extended, hotter spark plugs.

Table 3 shows the test results data of the second fuel blend, compared with gasoline test data and blend #1 test data.

**Table 3. Test Results on Fuel Blend #2***

| fuel | RPM | power output | thermal efficiency | mixture temperature | air/fuel ratio | exhaust gas temperature |
|---|---|---|---|---|---|---|
| (max. eff.) gasoline | 3500** | 18.2 kW | 26.7% | 57°C | 15.14 | 762°C |
| (max. power) gasoline | 3500 | 19.2 kW | 24.5% | 50°C | 13.13 | 733°C |
| (max. eff.)*** blend #1 | 3500 | 16.7 kW | 27.1% | 26°C | 9.68 | 739°C |
| (max. power) blend #1 | 3500 | 19.0 kW | 23.5% | 24°C | 7.29 | 704°C |
| (max. eff.) blend #2 | 3500 | 17.3 kW | 26.7% | 26°C | 9.93 | 737°C |
| (max. power) blend #2 | 3500 | 19.6 kW | 22.8% | 22°C | 7.61 | 693°C |

* blend #2: 18% water, 11% gasoline, 44% n-butanol, 21% acetone and 5% ethanol; 840 ml Renault Continental engine

** ± 1%

*** see table 2

The addition of gasoline into the butanol fuel blend (blend #2) showed a modest but significant power gain when operating at maximum efficiency as compared to the first butanol fuel. In general, while some operating characteristics are different than gasoline, the power output and thermal efficiency data indicate that power grade butanol fuel blends function well in standard spark ignition engines with only modest equipment adaptations. Some selected material changes may be necessary over the long term due to possible corrosion effects of the acetone. This should not pose as a serious impediment, however. Since blends #1 and #2 contained relatively large doses of water, it is a fair assumption that further dewatering by additional gasoline can only enhance general engine performance.

## V. Conclusions and Remarks

This project has demonstrated that recovery of a "power grade" butanol fuel blend is simple and can be accomplished at a considerable energy advantage over ethanol. It was further demonstrated that such a power grade blend works well in a typical spark ignition engine. Because of the ability to blend n-butanol with gasoline and water without the same type of phase separation problems which plague gasohol, and because of the ability of bacteria to ferment n-butanol from both hexose and pentose sugars,[14] butanol fuel blends offer useful advantages as compared to fuel ethanol recovery and utilization systems.

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