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PILOT-SCALE DEMONSTRATION OF PEFI'S OXYGENATED TRANSPORTATION FUELS PRODUCTION TECHNOLOGY

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For
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Lakewood, Colorado

And
U.S. Department of Energy
National Energy Technology Laboratory
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

DISCLAIMER

ABSTRACT

During nearly three years of testing, the performance of a molybdenum sulfide based catalyst was studied in a bench-scale experimental program to support the design and later operation of a 500-gpd pilot plant. The purpose of the work was to generate design information for a pilot plant, optimize process conditions, and verify product composition and yields. Initial tests were focused on reactors in fluidized-bed and in dry, fixed-catalyst-bed configuration. Subsequent tests focused on reactors in slurry configuration. The performance of the catalyst measured in the experimental program was very strong, with alcohol selectivities and space-time yields meeting or exceeding all published values of located for similar catalysts. Product selectivities consistently were in the range of 90%, and alcohol space-time yields were measured as high as 500 grams per kilogram of catalyst per hour.

From a technical standpoint, the PEFI process appears to be very promising. Experiments have repeatedly demonstrated the capability to make ethanol and other alcohols from synthesis gas of varying compositions. To make further progress and generate information necessary to design a commercial plant, the technology still requires demonstration at pilot scale.

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EXECUTIVE SUMMARY

PowerEnerCat, Inc. (PECI) of Lakewood, Colorado, has developed a technology that can make mixed alcohols from synthesis gas produced from any carbonaceous source. This patent-pending catalytic process is licensed to Power Energy Fuels, Inc (PEFI). Earlier developmental testing at Dow Chemical Company, Brookhaven National Laboratories, and at PECI showed that the process produces predominately straight-chain terminal C1-C6 alcohols. The data also showed that manipulating the composition of the catalyst and processing conditions could control the ratio of ethanol and higher alcohols to methanol within a wide range. To facilitate commercialization, the technology needs verification at the pilot and demonstration scale.

A three-year, pilot-scale development and testing program was proposed to prepare the technology for commercialization using various feedstocks. During the first year a bench-scale reactor system was fabricated and is being operated at Western Research Institute's (WRI's) Advanced Technology Center (ATC). The system was tested for nearly three years to generate design information for the pilot plant, optimize process conditions, and verify product composition and yields. Initial tests were focused on reactors in fluidized bed and in dry, fixed-catalyst-bed configuration. Subsequent tests focused on reactors in slurry configuration. A 500-gal/day pilot plant was also designed and partially constructed by PEFI for installation at the ATC.

As of the writing of this report, PEFI has not been able to raise sufficient funds to complete construction of the pilot plant. From a technical standpoint, bench scale experiments have consistently shown that the technology is promising. Space-time yields of alcohols have equaled or exceeded published literature. Experiments have also demonstrated that the composition of alcohols in the produce is highly tunable by manipulating operating conditions. Results have also been duplicated using synthesis gas of widely varying compositions.

INTRODUCTION

Oxygenated hydrocarbons have received considerable attention for blends with gasoline to boost octane ratings and reduce engine emissions. Much of the motivation comes from the 1990 amendments to the Clean Air Act related to the development of reformulated gasoline (RFG). For some time methyl tertiary-butyl ether (MTBE) was one of the primary oxygenates used for RFG. However, recent well-publicized issues concerning MTBE contamination in drinking water have led to lawsuits and legislation to phase out its use (1).

Alcohols, ethanol in particular, may be an attractive alternative to MTBE. The Environmental Protection Agency (EPA) specifically mentions ethanol as an alternative to MTBE (1). Unfortunately ethanol, produced mainly by the traditional fermentation/distillation process, is also expensive and requires federal subsidies to produce a gasoline blend at a competitive price (2, 3).

An alternate method to produce ethanol (and higher alcohols) is via catalytic reactions from synthesis gas. Four categories of catalysts that can be used for this purpose include: soluble Ru complexes used as a homogeneous catalyst; modified ethanol catalysts such as alkali-doped ZnO/chromia or CuO; mixed metal catalysts such as supported Rh/Fe; and chalcogenide-based catalysts such as alkali-promoted MoS2 (4). Power Energy Fuels, Inc.'s (PEFI) proprietary catalyst is in the last category.

Researchers at Dow and Union Carbide discovered that alkali-promoted MoS2 catalysts could be used to produce alcohols from synthesis gas (5, 6). Molybdenum sulfide catalysts have since been studied extensively for the production of alcohols (7). Santiesteban (8) studied the crystal structure of MoS2 and the effects of acid and base salts of a variety of alkali metal dopants. Among the dopants he studied, cesium exhibited the best promotional effects at approximately 15wt % CsOOCH. He identified the main mechanism for formation of higher alcohols as insertion of CO into the corresponding precursor alcohol. In a more recent report, Klier et al. (9) investigated a variety of doping methods for cesium-promoted MoS2 catalysts and a method for potassium-promoted MoS2. Their work also showed that prolonged exposure to air reduced the activity of the catalyst.

Recently, researchers have conducted bench-scale experiments examining the effects on alcohol synthesis of vapor-phase synthesized MoS2 catalysts (10), the influence of support acidity (11), and the effects of catalyst preparation and reaction conditions (4). Liu et al. (4) found only small effects of preparation procedure on the conversion and selectivity to higher alcohols. Their results indicated that both reactant flow rate and temperature affect the selectivity to higher alcohols. Similar effects of temperature and flow rate were noted by Li et al. (10). Bian et al. (11) found increases in activity and selectivity for supported MoS2 catalysts compared to unsupported MoS2.

Kinetic models have been developed by Smith et al. (12) and Park et al. (13). Park developed a rigorous model of the rate equations including the gas shift reaction. Although Park's model appeared to agree well with experimental data, it required regression of 15 independent parameters. Gunturu et al. (14) developed a simpler model using a set of statistically designed experiments. Their analysis suggested that the rate-limiting step in the chain growth of the alcohols might be the surface reaction of the corresponding precursor alcohol. Other steps, including CO insertion, hydrogen cleavage, and hydrogenation, did not affect the rate correlations in the range of temperatures and pressures tested.

Whereas the studies described previously refer to conventional bench-scale studies, Beretta et al. developed and operated a pilot-scale reactor to produce higher alcohols using a K-promoted Zn/Cr/O catalyst (15).

The goal of this project was also to develop, build, and operate a pilot-scale reactor system based on PEFI's catalytic process. Potential fuels for the technology include remote natural gas fields, municipal solid waste, landfill gas, coal, biomass, and other carbonaceous materials. After dewatering, the product is expected to be sold to gasoline producers/distributors for blending. Table 1 shows the target composition of Ecalene™.

Table 1. Target Composition of Ecalene™

Component	Weight %
Methanol	5-25%
Ethanol	45-70%
Propanol	15%
Butanol	5%
Pentanol	3%
Hexanol & Higher	2%

OBJECTIVES

The overall goal of the project is to verify and further define the catalyst performance, operating conditions, and yields of various alcohols in the PEFI process. Specific objectives for the project were:

- Design, fabricate, and operate a bench-scale reactor system to optimize process conditions and confirm product composition and yields
- Design and construct an instrumented and flexible 500-gal/day pilot plant to initially operate on pipeline natural gas
- Perform equipment shakedown and process optimization tests and plant modifications as warranted
- Perform steady-state "production" runs to produce sufficient quantities of product for gasoline blending evaluations by others
- Characterize process emissions and effluents for permitting requirements
- Operate the pilot plant for demonstration of the technology to potential commercial partners and investors.

EXPERIMENTAL

Figure 1 shows a simplified flow diagram of the bench-scale reactor system. A photograph is shown in Figure 2. The reactor was normally operated using CO and H2 from cylinders to simulate synthesis gas. N2 was used to purge the system for maintenance and extended shutdowns. The gases and the reactor were heated by 120-volt 1250-watt heat tapes with temperature controllers. Flow rates of CO and H2 were set by mass flow controllers. Pressure was increased by Whitey Laboratory Compressors. The main reactor was originally a packed bed fabricated from 3/8" OD high-pressure stainless steel tubing, which flared to ¾" OD high-pressure stainless tubing. Subsequent reactor designs increased the diameter for fixed bed reactors, but eventually a slurry reactor was fabricated. Lines between vessels were ¼" OD stainless tubing rated to 5500 psi. Temperatures were measured with type K thermocouples. Pressure was set and maintained by a regulator. Temperatures, pressure, and flow rates were read and logged by a PC-based system using Labtech control software. CO alarms (First Alert) were also installed to give a warning in the event of a leak. A combustible gas monitor (Matheson Inc.) was used to detect potential leaks of flammable gas.

The catalyst was normally used as provided by PEFI. Methods to dope the catalyst were found in the literature (4, 8, 15). For packed-bed configurations, 2.5 cm of 3-mm pyrex beads are loaded into the reactor followed by the doped catalyst mixed with smaller glass beads or helixes. Additional Pyrex beads are then added above the catalyst followed by glass wool. H_2/CO ratios were typically close to 1 (ratios of H2 to CO of .6 to 1.4 were tested), and gas hourly space velocities (GHSVs) varied from 2500 to 8500 liters per kg catalyst per hr. The catalyst was pretreated after loading (but not between experiments) with H_2/N_2 for 1 hr at 400 C. Pressures were tested as high as 10-11 MPa, and temperatures in the range of 290 C to 360 C. For each experimental condition, liquid products were condensed, stored refrigerated, and analyzed by gas chromatography. Off-gas samples were periodically collected and analyzed for CO, H_2, N_2/O_2 (an internal check), CO_2, H_2S, CH_4, C_2H_6, and C_3H_8.

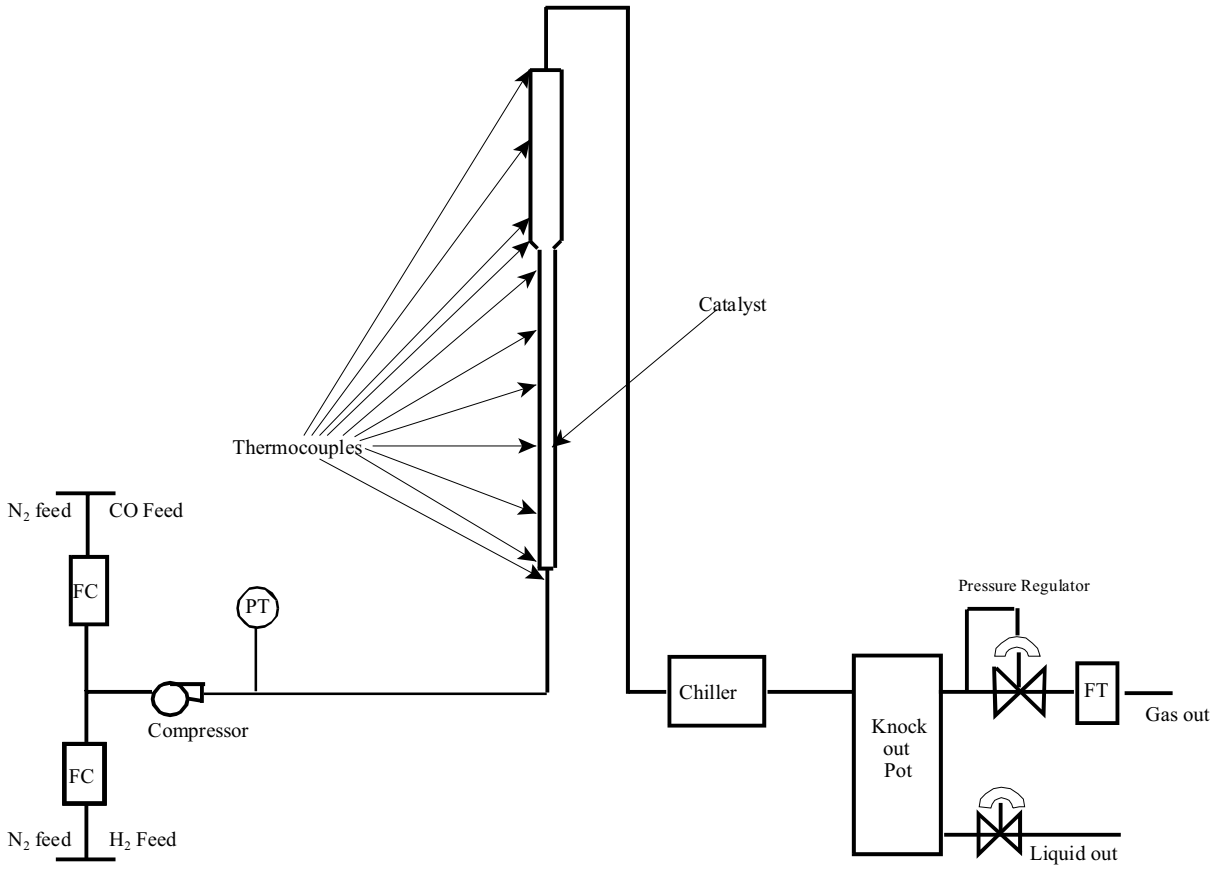

Figure 1. Flow Diagram for Bench-Scale Reactor System

Figure 2. Photograph of Bench-Scale Reactor System

RESULTS

Results from experiments conducted with the reactor in fixed-catalyst-bed configuration were presented at the Coal Technologies Conference March 4-8, 2001, the American Chemical Society National Meeting in Chicago, Illinois, August 2001, and at the American Institute of Chemical Engineers National Meeting in Reno, Nevada, November 2001. Results from the experiments conducted to date have duplicated or exceeded published literature, with space-time yields of alcohols up to 500 grams per hour per kilograms catalyst (see Figure 3), and CO_2-free selectivities' up to 90% (Figure 4). The composition of the alcohols in the product has been shown to vary greatly depending on the operating conditions and the feed composition. Figure 5 shows the product composition from a series of fixed-bed experiments. The variables adjusted during the experiments included total flow rate, H_2 to CO ratio, temperature, and pressure. For most of that series of experiments, the dominant alcohol in the product was methanol. Operation of the reactor in slurry configuration allows additional control of the composition of the products. Figure 6 shows the composition of the product for recent slurry reactor experiments. The dominant product was then consistently ethanol.

A significant issue has been consistently encountered concerning temperature control for fixed-bed experiments. Figure 7 shows several temperature readings on the reactor on an early experiment. The exothermic reactions produced several hot spots and near runaway conditions. Since the catalyst tends to produce undesirable hydrocarbon side products at high temperatures, effective temperature control is critical. To combat this issue for subsequent tests, the catalyst was mixed with increasing amounts of glass helixes or beads, effectively lowering the spatial concentration of the catalyst, i.e. less catalyst per unit volume. This approach would likely have limited success as the scale of the reactor is increased, and would allow undetected hot spots in larger reactors. One solution used for this issue in Fischer-Tropsch reactors is to operate in a slurry configuration. Figure 8 shows a temperature profile during a preliminary experiment in slurry configuration. Temperature control was greatly improved.

Additional experiments have been conducted in which un-reacted synthesis gas was recycled into the feed for the alcohol reactor. Although the bench-scale setup does not allow precise control of the recycle rate, preliminary results indicated that overall synthesis gas conversion to alcohols was nearly doubled without significant effort.

CONCLUSIONS

From a technical standpoint, the PEFI process appears to be very strong. Experiments have repeatedly demonstrated the capability to make ethanol and other alcohols from synthesis gas of varying compositions. Preliminary economic evaluations from a 100-year old reputable engineering company, indicated that the technology is likely to be economically successful if the product qualifies for the renewable fuel tax credit. To make further progress and generate information necessary to design a commercial plant, the technology still requires demonstration at pilot scale.

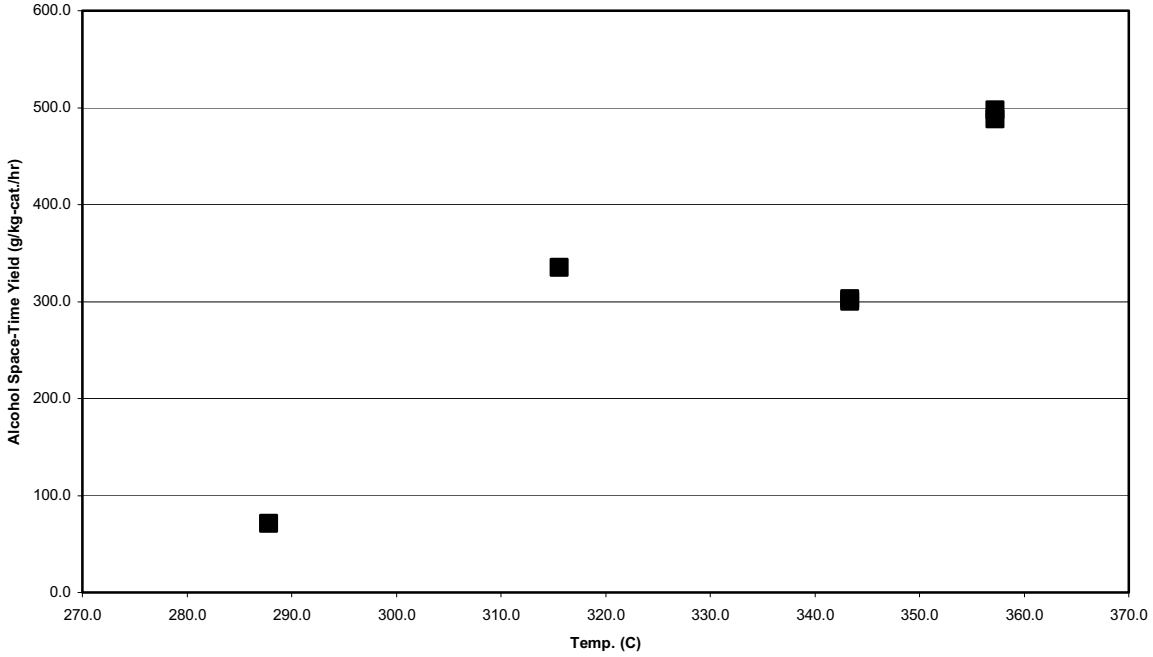

Figure 3. Alcohol Space-Time Yields as a Function of Temperature

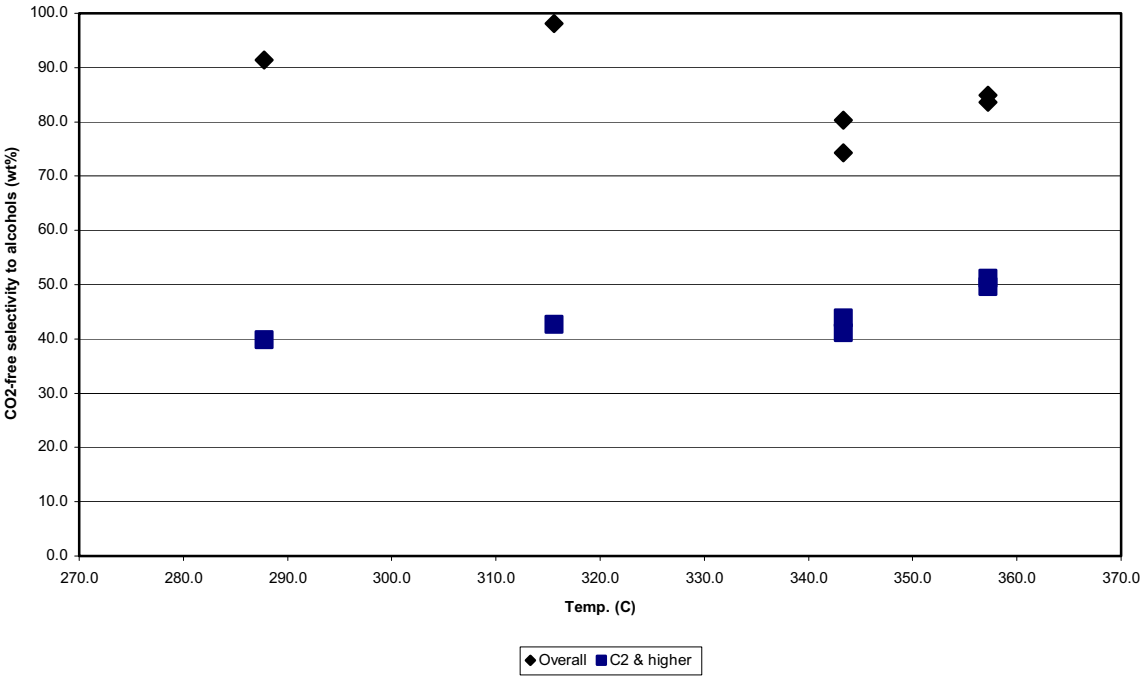

Figure 4. CO2 -free Selectivities in Fixed Bed Reactor as a Function of Temperature

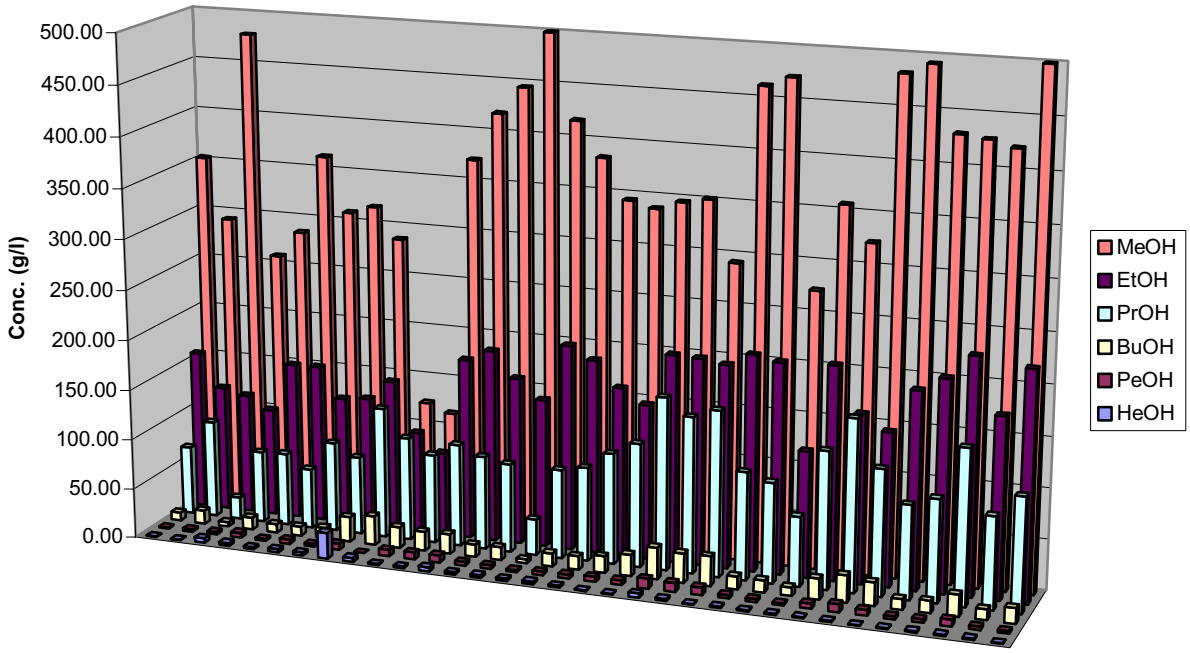

Figure 5. Distribution of Alcohols in Product for Fixed-Bed Experiments

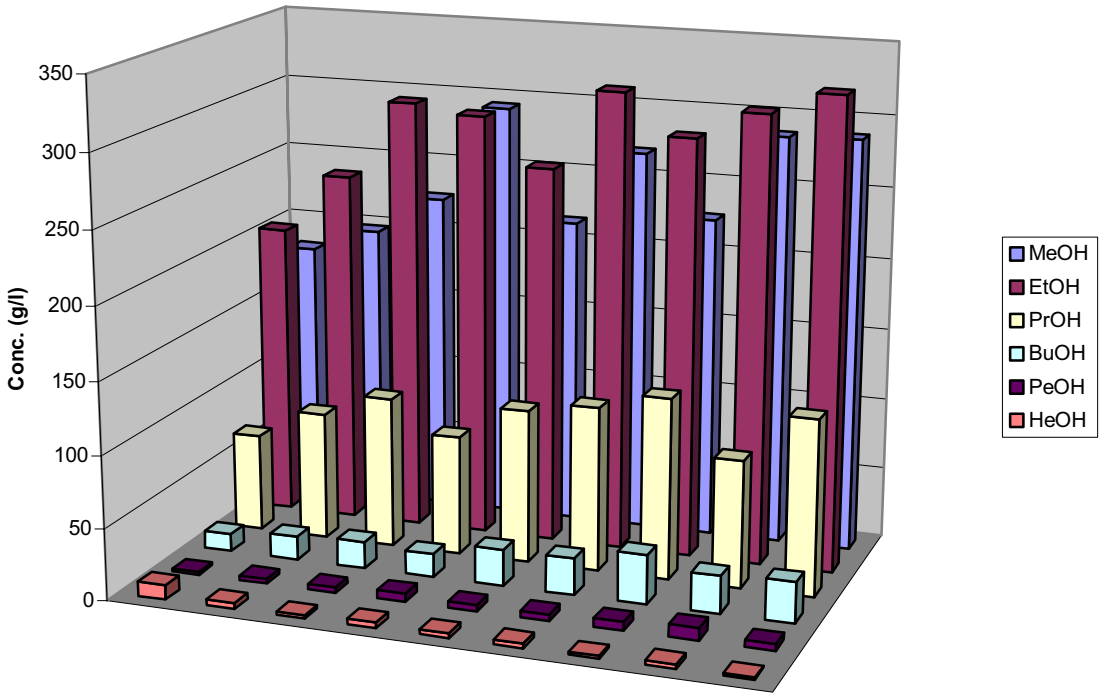

Figure 6. Distribution of Alcohols in Product for Slurry Reactor Experiments

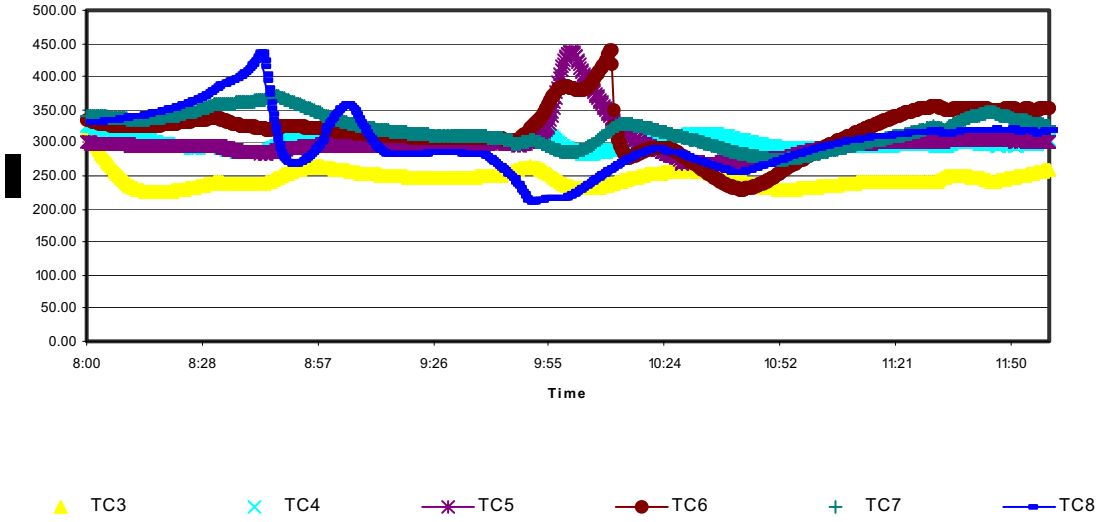

Figure 7. Thermocouple (TC) Readings During Fixed-Bed Experiment

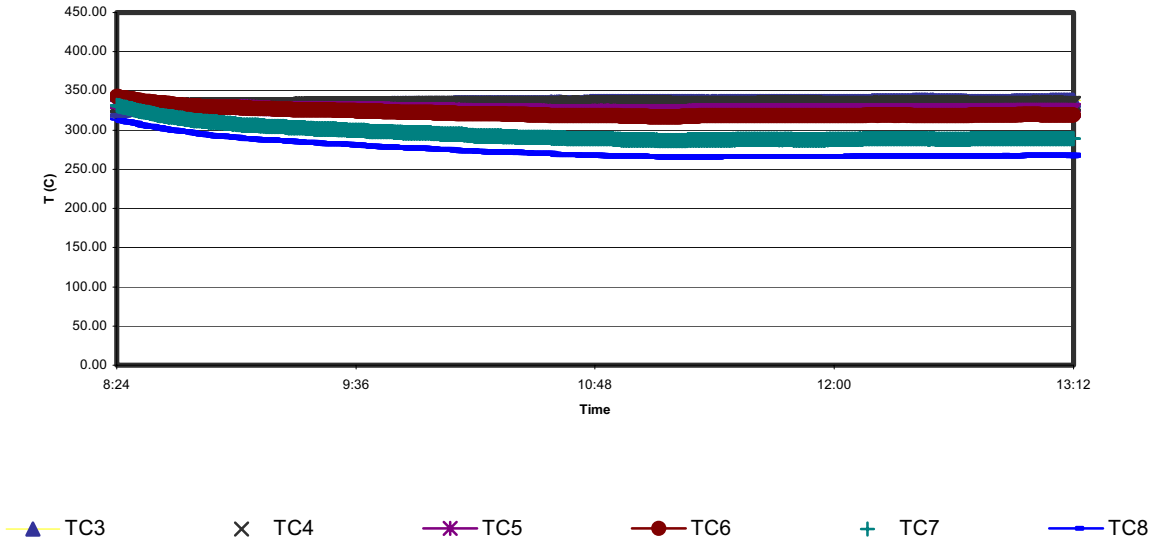

Figure 8. Thermocouple (TC) Readings During Preliminary Slurry Reactor Experiment

REFERENCES

1 Environmental Protection Agency 40 CFR Part 755, "Methyl Tertiary Butyl Ether (MTBE); Advance Notice of Intent to Initiate Rulemaking Under the Toxic Substances Control Act to Eliminate or Limit the Use of MTBE as a Fuel Additive in Gasoline."

2 Congressional Research Service Report for Congress 98-290, "MTBE in Gasoline: Clean Air and Drinking Water Issues," James E. McCarthy and Mary Tiemann, Specialists in Environmental Policy Resources, Science, and Industry Division, Updated October 2, 2000.

3 Congressional Research Service Issue Brief for Congress RL30369, "Fuel Ethanol: Background and Public Policy Issues," Brent D. Yacobucci, Environmental Policy Analyst Resources, Science, and Industry Division; Jasper Womach, Specialist in Agricultural Policy Resources, Science, and Industry Division, Updated June 27, 2000.

4 Liu, Z., Li, X. Close, M. R. Kugler, E. L., Peterson, J. L., and Dadyburjor, D. B., "Screening of Alkali-Promoted Vapor-Phase-Synthesized Molybdenum Sulfide Catalysts for the Production of Alcohols from Synthesis Gas." *Ind. Eng. Chem. Res.*, 1997, 36, 3085-3093.

5 Stevens, R. R., Eur. Pat. Appl. 84116467.6 (1984), Conway, M. M., Murchison, C. B., Stevens, R. R., U. S. Patent 4,675,344 (1987), assigned to Dow Chemical Co.

6 Kinkade, N. E., Eur. Pat. Appl. 84116468.4 (1984), assigned to Union Carbide Corporation.

7 Klier, K., Herman, R. G., Simmons, G. W., Lyman, C. E., Santiesteban, J. G., Najbar, M., Bastian, R., "Direct Synthesis of Alcohol Fuels over Molybdenum-Based Catalysts," Final Technical Report DOE/PC/80014-F, 1988.

8 Santiesteban, J. G., Ph.D. Dissertation, Lehigh University, Bethlehem, PA, 1989.

9 Klier, K., Herman, G., Deemer, M., Richards-Babb, M., and Carr, T., "Ethanol Synthesis and Water Gas Shift over Bifunctional Sulfide Catalysts," Final Technical Progress Report DOE/PC/91301-T2, 1995.

10 Li, X., Feng, L., Liu, Z., Zhong, B., Dadyburjor, D. B., and Kugler, E. W., "Higher Alcohols from Synthesis Gas Using Carbon-Supported Doped Molybdenum-Based Catalysts." *Ind. Eng. Chem. Res.* 1998, 37, 3853-3863.

11 Bian, G., Fan, L., Fu, Y., and Fujimoto, K., "Mixed Alcohol Synthesis from Syngas on Sulfided K-Mo-Based Catalysts: Influence of Support Acidity." *Ind. Eng. Chem. Res.* 1998, 37, 1736-1743.

12 Smith, K. J., Herman, R. G., Klier, K., "Kinetic Modeling of Higher Alcohol Synthesis over Alkali-Promoted Cu/ZnO and MoS2 Catalysts." *Chem. Eng. Sci.* 1990, 45, 2639-2646.

13 Park, T. Y., Nam, I., Kim, Y. G., "Kinetic Analysis of Mixed Alcohol Synthesis from Syngas over K/MoS_2 Catalyst." *Ind. Eng. Chem. Res.* 1997, 36, 5246-5257.

14 Gunturu, A. K., Kugler, E. L., Cropley, J. B., and Dadyburjor, D. B., "A Kinetic Model for the Synthesis of High-Molecular-Weight Alcohols over a Sulfided Co-K-Mo/C Catalyst." *Ind. Eng. Chem. Res.* 1998, 37, 2107-2115.

15 Beretta, A., Micheli, E., Tagliabue, L., and Tronconi, E., "Development of a Process for Higher Alcohol Production via Synthesis Gas." *Ind. Eng. Chem. Res.* 1998, 37, 3896-3908.

16 Gang, L., Chengfang, Z., Yanqing, C., Zhibin, Z., Yianhui, N., Linjun, C., Fong, F., "Synthesis of Mixed Alcohols from CO2 Contained Syngas on Supported Molybdenum Sulfide Catalysts." *Appl. Catal*. 1997, 150, 243-252.