
Session LF -- Liquid Fuels Technology

Session LF-2

Tar Sands

LF-2.1**University of Utah Oil Sand Research
and Development Program****CONTRACT INFORMATION**

Contract Number	DE-FC21-89MC26268
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Period of Performance	July 7, 1992 to July 6, 1993

ABSTRACT

An overview of the Oil Sand Research and Development Program at the University of Utah will be presented. It will include resource characterization of the Uinta Basin oil sand deposits and bitumens and bitumen-derived liquid recovery and upgrading technology and product utilization. The characterization studies will include the Whiterocks and Asphalt Ridge oil sands. The discussion of recovery and upgrading technologies will include aqueous separation, thermal recovery processes; solvent extraction, and thermal and catalytic upgrading of bitumen and bitumen-derived heavy oils. Product evaluation studies will include jet fuels, diesel fuel, asphalt and specialty chemicals. Plans for the future of the project will be discussed.

RESULTS AND DISCUSSION**Characterization of Bitumen**

The characterization of the Asphalt Ridge bitumen was continued and that of the PR Spring and Circle Cliffs oil sands were undertaken during the 1992-1993 contract period. Drum quantity samples of mined ore were obtained from the PR Spring oil sand deposit for process studies. The Sunnyside oil sand deposit was reconnoitered for sample acquisition during the 1993-1994 contract period.

The Circle Cliffs oil sand bitumen and mineral matter have been characterized. The effect of mineral composition on bitumen recovery, and the quality of the bitumen product that can be expected from

the modified hot-water process has been evaluated. The influence of chemical composition on bitumen viscosity has been examined with respect to an empirical relationship that has been established between the carboxylic acid content and the viscosity of the bitumen.

Aqueous Separation/Recovery of Uinta Basin Bitumens

The 1992/93 oil sand research program for water-based separation technology focused on the fundamental aspects of digestion/separation and on process engineering as required for process scaleup and pilot plant installation. The investigations have demonstrated the importance of surface and interfacial tension effects as well as colloid chemistry effects during modified hot-water processing. Based on the results from process development work and fundamental studies, it is evident that the modified hot-water process is now ready for pilot plant level operation. A complete flowsheet has been prepared with heat and material balances for the principal steps in the process.

Surface and interfacial tension data for bitumen recovered from the Whiterocks oil sands have been obtained. Experimental data from direct measurements of bitumen surface tension using the Wilhelmy plate method have been compared with surface tensions calculated from Neumann's equation-of-state using contact angle measurements and with Zisman's critical surface tension of wetting. Interfacial tension data, which were measured at several temperatures and for varying pH and electrolyte concentration (NaCl, $\text{Na}_5\text{P}_3\text{O}_{10}$) have been obtained. Zeta potentials at the bitumen/water interface have been determined for varying pH and electrolyte concentrations (NaCl, $\text{Na}_5\text{P}_3\text{O}_{10}$). These experimental data have been used to explain and understand the bitumen disengagement mechanism.

An experimental technique for the study of bitumen release from oil sand under stagnant digestion conditions has been developed and experimental data obtained. The new stagnant digestion laboratory setup allows simultaneous determination of physical and surface properties of the system, such as the oil sand natural porosity, the wetting ability of the aqueous phase based on the kinetics of air and bitumen displacement from the oil sand, the droplet size of released bitumen, the bitumen-bitumen droplet coalescence time, the extent of bitumen dilution (when diluent was used), the size and electrophoretic mobility of particulates released from the oil sand sample to the aqueous phase, and in-situ IR analysis.

The bitumen release from mineral particle surfaces under stagnant conditions was observed through a microscope for unconsolidated samples of the Whiterocks oil sand and the mechanisms of bitumen separation from the mineral surfaces have been related to surface/interfacial tension data. The spreading coefficient for bitumen at the water surface was determined from surface/interfacial tension data and was positive for all pH values of practical significance, and for all $\text{Na}_5\text{P}_3\text{O}_{10}$ and NaCl concentrations considered. The work of adhesion between bitumen droplets and coarse mineral particles of oil sands was calculated and found to depend on the concentration of reagents (Na_2CO_3 , $\text{Na}_5\text{P}_3\text{O}_{10}$, NaCl). The work of adhesion between bitumen/mineral particle surface and the spreading coefficient for bitumen at the air bubble surface, exhibited a strong dependence on the bitumen/water interfacial tension. Thus, in addition to bitumen viscosity considerations, interfacial tension plays an important role in hot-water processing of oil sands. Enhanced separation of bitumen from Whiterocks oil sands was achieved in hot-water separation experiments by control of the bitumen/water interfacial tension which should be less than $2\text{-}3 \text{ mNm}^{-1}$. A

somewhat reduced but satisfactory separation efficiency was found when the interfacial tension was from 4 mNm^{-1} to 7 mNm^{-1} .

High-speed photography was used to examine the nature of bubble formation in the swirl flow of the air-sparged hydrocyclone and the corresponding bubble size distributions. These fundamental measurements will help to establish design features and operating conditions for efficient flotation separation of dispersed bitumen from tailings water.

The bitumen concentrate produced in the hot-water process contained significant amounts of water along with residual sand particles. An organic solvent such as kerosene must be added to the bitumen concentrate to reduce the bitumen viscosity and facilitate separation of fine mineral particles and dispersed water. The Whiterocks oil sand bitumen concentrate obtained from the hot-water separation experiments was dissolved in kerosene prior to removal of dispersed water and fine mineral particles, and the kinetics of dissolution of bitumen concentrate in kerosene have been determined.

The process flowsheet for the hot-water separation process as well as preliminary mass and energy balances for both 100 and 2000 tpd oil sand pilot plants have been completed. A processing strategy which requires less energy and which leads to higher grade bitumen concentrates and higher bitumen recovery has been developed. The processing strategy is based on four basic features which are: 1) feed preparation, involving size reduction and pretreatment with diluent; 2) bitumen separation from sand, achieved by digestion, gravity separation, and flotation; 3) tailings disposal and water recycle; and 4) bitumen concentrate cleanup and diluent recycle. This water-based process development has been aided by fundamental research on the surface chemistry of bitumen-sand mixtures, the

natural porosity of the oil sands accessible by various hydrocarbon diluents, the identification of natural surfactants released from the bitumen during processing, and the FTIR microscopic studies of oil sands, as well as laboratory-scale experiments of bitumen separation from Utah oil sands.

Extraction of Bitumen by an Energy-Efficient Thermal Method

A mathematical model of a thermally coupled fluidized-bed oil sands extraction process has been developed. The model incorporates hydrodynamic considerations, mass transport phenomena, and reaction kinetics. A relationship for the superficial gas velocity has been developed to account for the pressure gradient through the bed as well as volumetric changes due to chemical reaction.

A pyrolysis reaction scheme has been proposed to predict total bitumen conversion, coke production, light gas production, oil yield and oil density. Raw bitumen is characterized by the fraction of "heavy bitumen" that has a boiling point greater than 823 K and may be related to the fraction of asphaltenes present in the bitumen. The model predicts bitumen yields in general accord with trends observed experimentally. Maximum oil yields were observed at pyrolysis temperatures of approximately 733 K. Oil yield increases monotonically with average sand residence time at low temperatures, but at higher temperatures, first increases, and then decreases with residence time. This high-temperature phenomenon is explained by the increased gas-phase residence time, allowing gas-phase cracking reactions to become significant, which is not a consideration at lower temperatures. This model does not account for gas-phase reactions that may occur in the freeboard, which may be important at pyrolysis temperatures greater than about 500°C.

The fraction of heavy bitumen has a pronounced effect on pyrolysis products. If the bitumen consists of primarily light bitumen, then oil yield is maximized at long sand residence times and low pyrolysis temperatures. However, if the bitumen is dominated by a heavy fraction, then oil is recovered only by first cracking the heavy bitumen. This reaction has a modestly higher activation energy, so a higher temperature is required, and consequently, oil vapors may crack to light gas. To maximize oil yield from heavy bitumens, it may be necessary to use a higher fluidizing gas velocity, in order to limit the oil cracking reactions.

The kinetic model does not predict any dependence of oil density on bitumen quality. This seems to be a deficiency of the pyrolysis reaction model. This shortcoming may be addressed by making the product stoichiometry dependent on the source of the light bitumen (native or product of reaction).

The solution of the pyrolysis model determines the quantity of unreacted bitumen and coke that will enter the first combustion bed. The amount of coke burned in the first combustion bed (and in the second combustion bed) is determined in large part by the amount of coke entering which affects the thermal balance of the system. Thus, an iterative procedure is indicated, where at first, a pyrolysis temperature is assumed; the pyrolysis model is solved; the first-stage combustion model is solved; the heat-pipe temperature is found; and again, the pyrolysis model is solved and a new pyrolysis temperature. The second-stage combustion model would be solved after the coupled model has iterated to convergence.

Finally, the completed coupled model may be submitted to a rigorous optimization procedure. An objective function to be optimized might be oil yield, or revenues from oil sales, where oil quality is a concern, or perhaps operating or capital costs, or plant

profitability.

Fluidized Bed Pyrolysis of Oil Sands in a Large Diameter Reactor

A 15.2 cm diameter fluidized-bed reactor was designed, built, and operated to study the pyrolysis of oil sands at pressures slightly less than ambient. Fluidizing gas flow through the reactor was caused by reducing the pressure above the bed with a gas pump operating in the vacuum mode. The thermal energy for pyrolysis was supplied by a propane burner. The hot combustion gases from the burner, regulated to avoid excess oxygen, were used to fluidize the spent sand inventory in the oil sands pyrolysis reactor.

Operating the reactor at reduced pressure and pulling the combustion gases through the reactor significantly improved the quality of fluidization, thus equivalent liquid yields were obtained at lower temperatures than previously reported. At 723 K over 80 wt% of the bitumen fed was recovered as a liquid product and the spent sand contained less than 1 wt% coke. Maximum liquid product yields were obtained at a pyrolysis temperature of 748 K. There was no evidence to suggest that U/U_{mf} exerted an influence on product yields for the ratios investigated. In contrast to previous observations, residence times from 29 to 70 minutes were found to give similar yields and product distributions.

This work has verified the TGA pyrolysis observation that bitumen pyrolysis rates peak at temperatures below 775 K. It has also provided experimental evidence that, when coke formation is suppressed, increased liquid yields are favored over increased gas yields at pyrolysis temperatures below 775 K.

As a result of the pyrolysis experiments with Whiterocks oil sands, it was obvious that the reactor heating system required modification. A new two-

burner assembly, constructed from refractory materials, was designed and will be installed on the reactor.

Rotary Kiln Pyrolysis of Oil Sands

Continuous, reproducible solids feeding has been a problem associated with oil sands surface mining-recovery process development studies. Commercial Acrison bin-discharge feeders were tested for oil sand feeding in rotary kiln and fluidized bed pyrolysis reactors and for spent sands in a combustion reactor. Feeder calibration experiments were conducted using spent sands, oil sands and mixtures of fresh and spent sands. Three types of feeders, nine different sized augers, and three different auger types were tested. Experimental data included average feed rates and cumulative weight delivered from the feeder. The factors which were determined to affect oil sands feeding were: (1) bitumen content of the oil sand, (2) moisture content of the oil sand, (3) temperature rise in the auger and auger housings during the operation of the feeder, (4) auger rotation speed which was controlled by motor speed controller, (5) level of oil sand in the feeder hopper, (6) auger size and type, (7) ratio of spent sand to oil sand in the feed mixture, and (8) the effect of shear in the auger housing. A larger size auger running at low speed with a water jacketed auger housing gave the best feeding performance.

The successful application of an auger-type dry materials feeder for feeding oil sands to a process reactor or vessel requires careful consideration of the following findings:

1. Fast auger speeds did not give constant or reproducible feed rates.
2. Small diameter augers are less likely to give constant oil sands feed rates than large-diameter augers.
3. Dilution of the oil sands with spent sands improved feeder performance,

however, small diameter augers still did not give constant feed rates.

4. Compaction of oil sand feed in the hopper appeared to temporarily increase feed rates with small augers.
5. Oil sand feed rates are directly proportional to the oil sand moisture content (on an air-dry basis).
6. Reducing the clearance between the feed auger and auger housing with a sleeve did not improve the feeder performance with oil sands.
7. A helical auger offers no advantage in feeder performance using oil sands.
8. Augers with special coatings gave no significant improvement with regard to reducing the tendency of the oil sands to adhere to the auger flights.
9. Large diameter augers, running at slow speeds and low temperatures, are most likely to yield linear and reproducible feed rates.

Combustion of Carbonaceous Residues on Spent Oil Sands in a Dense Phase Transport Reactor

Based on the theory and practice of circulating fluidized bed combustors, a laboratory-scale dense phase transport reactor has been designed and constructed for the study of the combustion of carbonaceous residues on spent or coked sand. Hydrodynamic and combustion experiments have been conducted with the reactor. Both Type I and Type II curves were observed for the multisized coked sand under both fluidization or defluidization conditions. Fluidization and defluidization experiments gave a minimum fluidization velocity of 1.7 cm/s which is close to the predicted minimum fluidization velocity of 1.5 cm/s. The transition velocities were determined in flow regime transition studies: (a) plug slugging (U_{ms}) = 20 cm/s; (b) turbulent fluidization (U_c) = 50 cm/s; and (c) refluxing pneumatic transport (U_k) = 75 cm/s. Particle residence time distribution

experiments indicated that the fine particles tend to bypass the bed especially at higher superficial gas velocities which negatively impacts the combustion efficiency.

The combustion efficiency was 54% at an equivalence ratio of 0.56 in the initial combustion experiment, which indicated that longer combustion residence times in the combustion zone were required.

Supercritical Fluid Extraction of Oil Sand Bitumen

The supercritical fluid extraction of bitumen from the PR Spring oil sand deposit (Utah) was studied using commercial propane as the solvent. The bitumen volatility was 36.3 wt% and its asphaltene content was 19.3 wt%. Experiments were performed at five different operating conditions which included three pressures (5.6 MPa, 10.4 MPa and 17.2 MPa) and temperatures (339 K, 380 K and 422 K).

The extracted phase yield increased as the extraction pressure increased at constant temperature. This effect was directly related to the increase in the pure solvent density with pressure. It was also observed that at higher extraction pressures, relatively heavier hydrocarbons were extracted. The asphaltene content of the residual fraction was higher than the asphaltene content of the bitumen, even on an absolute weight basis.

The extraction process was modeled using the Peng-Robinson cubic equation-of-state and the Lee-Kesler pseudocomponent characterization correlations. The experimental extraction results were in reasonable agreement with the predicted phase compositions based on a flash calculation using seven pseudocomponents. The following conclusions were drawn from these studies:

1. Pure solvent density was the governing factor for the extraction of PR Spring bitumen with propane. The extraction yield increased with an increase in pure solvent density.
2. The asphaltene content of the residual fractions was higher than the original bitumen on an absolute basis assuming all the asphaltene stayed in the residue. This indicates the depletion of cosolubilizing agents during the extraction process.
3. The H/C ratio of the residual fractions was lower than the original bitumen, thus, establishing that saturated hydrocarbons were preferentially extracted leaving the residue richer in unsaturated compounds.
4. Reasonable agreement between the experimental and predicted phase compositions was observed at the highest solvent density.

Catalytic Upgrading of Uinta Basin Bitumens over an HDM Catalyst

A Uinta Basin bitumen was hydrotreated over a sulfided commercial Ni-Mo on alumina hydrodemetallation catalyst. The catalyst was onstream continuously for over 1,000 hours. The extent of heteroatom removal, residuum conversion and molecular weight reduction were investigated as a function of process variables. The fixed bed reactor was operated in the upflow mode to ensure complete wetting of the catalyst and to maintain isothermal operation. The primary process variables studied were reactor temperature (620-685 K), weight hourly space velocity ($0.24-1.38 \text{ h}^{-1}$) and total reactor pressure (11.3-16.7 MPa). The hydrogen to oil ratio was fixed in all experiments at $890 \text{ m}^3/\text{m}^3$ (=5000 scf H_2 /bbl). The catalyst deactivation rate was $0.18 \text{ }^\circ\text{C}/\text{day}$ during bitumen hydroprocessing.

The effect of process variables on the extent of denitrogenation, desulfuriza-

tion, demetallation, residuum (>811 K) conversion and the product distribution and yields were determined. The HDM catalyst was effective for nickel and sulfur conversion during hydrotreating of the Whiterocks bitumen. However, it was ineffective for denitrogenation. HDN, HDS and CCR conversion of the Whiterocks bitumen over the HDM catalyst were correlated by first order kinetics. The apparent activation energies for desulfurization and denitrogenation were 91 and 98 kJ/mol, respectively. Sulfur removal appeared to be linked to residuum conversion because molecular weight reduction (i.e., residuum conversion) facilitated conversion of sulfur in higher molecular weight moieties. A molecular weight reduction-model for hydrotreating over the HDM catalyst was proposed using four reactant lumps.

Catalytic Upgrading of Uinta Basin Bitumens: HDM versus HDN Catalysts

The bitumen was also hydrotreated over a commercial hydrodenitrogenation (HDN) catalyst under varying conditions to determine the effect of catalyst on heteroatom conversion and molecular weight reduction. The process variables investigated included total reactor pressure (1600-2450 psi); reactor temperature (650-820°F), feed rate (0.29-1.38 h⁻¹; WHSV) and the catalysts employed (commercial HDN and HDM).

The hydrodenitrogenation (HDN) catalyst was more active for nitrogen, sulfur and residuum conversion than the hydrodemetallation (HDM) catalyst. Literature values for residuum conversion activation energies suggested that residuum conversion was thermal. However, residuum conversion was determined to be sensitive to the surface area and metal loading of the catalyst employed during hydroprocessing indicating that a portion of residuum conversion during hydrotreating was catalytic.

Catalyst selection influences the conversion of residuum: hydrotreating Whiterocks bitumen over a high surface area/high metal content hydrotreating catalyst enhanced residuum conversion. This is in disagreement with other workers who studied residuum cracking in dilute catalysts systems operating at higher temperatures. The reason for the disagreement is that in dilute catalyst systems, catalyst concentration is not high enough to cause a noticeable increase in global activity. This is particularly true at high temperatures when thermal cracking plays a significant role in residuum conversion.

The bitumen-derived liquid produced during oil sand pyrolysis was more susceptible to hydrotreating than the bitumen feed over the HDN catalyst. Therefore, it was concluded that molecular weight reduction should be accomplished prior to heteroatom removal for conversion of high nitrogen bitumens and heavy oils.

Residuum cracking is less sensitive to catalyst selection than heteroatom conversion because residuum conversion can proceed through a thermal pathway which, for the most part, is not available for heteroatom conversion. The segregation of residuum into a reactive or facile portion and a less reactive or refractory portion, is the result of a conversion pathway for residuum which is similar to asphaltene conversion. That is, facile residuum conversion consists of dealkylation of naphthenic/aromatic/polar nuclei forming a volatile or nonvolatile nucleus and a volatile alkyl fragment. Refractory residuum conversion consists of converting nonvolatile dealkylated nuclei through a series of ring opening/side-chain cleavage reactions.

CONCLUSIONS

- The Uinta Basin oil sand data base is evolving to a point where projections of site-

specific preferred recovery technologies are feasible.

- The aqueous separation process development has advanced to a stage where it is ready for a continuous pilot plant operation (~50 bpd).
- The upgrading sequence for the Uinta Basin bitumens for the production of refinery feedstocks should consist of a thermal process followed by hydrotreating of an HDN catalyst.
- The hydrotreated total liquid product for the sequence pyrolysis-hydrotreating produces a high quality aviation turbine fuel fraction.

REFERENCES

Oblad, A.G., Bunger, J.W., Dahlstrom, D.A., Deo, M.D., Hanson, F.V., Miller, J.D., and Seader, J.D., "The Extraction of Bitumen from Western Oil Sand", Final Report, July 6, 1991 to July 5, 1992, Contract No. DE-FC21-91MC26268, August 1992.

Oblad, A.G., Bunger, J.W., Dahlstrom, D.A., Deo, M.D., Hanson, F.V., Miller, J.D., and Seader, J.D., "The Extraction of Bitumen from Western Oil Sand", Final Report, July 6, 1992 to September 29, 1993 Contract No. DE-FC21-92MC26268, December 1993.

Session LF -- Liquid Fuels Technology

Session LF-3

Mild Gasification

LF-3.1 Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products

CONTRACT INFORMATION

Contract Number

DE-AC21-87MC24116

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Period of Performance

September 30, 1987 to
September 30, 1994

		FY 1988	FY 1989	FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
		1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4
Task 1	Literature Survey & Market Assessment	■						
Task 2	Bench-Scale Mild Gasification Study	■	■					
Task 3	Bench-Scale Char Coking Study	■	■	■	■			
Task 4a	PDU Design		■	■				
Task 4b	PDU Construct/Shakedown			■	■			
Task 4.3.1	Modification of PDU Components					■	■	
Task 4.4.1	Parametric Variation Studies						■	
Task 4.4.2	Application Testing for Various Coal Types					■	■	
Task 4.4.3	Form Coke Testing with Chars from Various Coal Types					■	■	
Task 4.4.4	Long-Term Operation for Durability Testing of PDU System					■	■	
Task 4.5	Product Characterization					■	■	
Task 4.6	Final Report							■
Task 5	Design, Construct, Operate 1000 Lb./Hr. Briquette and Coke Equipment							■

OBJECTIVE

The objective of this project is to develop a continuous mild gasification process to convert highly caking coals to coal liquids, char and coke for near term commercial application.

Coal liquids after fractionation can be blended with petroleum and used interchangeably with conventional fuels without modifications in gasoline and diesel engines.

Char can be used as a carbon source in the production of ferroalloys and in mini-mills.

Coke can be produced by upgrading char through briquetting and calcining and for use in the steel industry foundries and blast furnaces.

In a step beyond the scope of the project, the plan is to finance, design and construct, in a partnership with others, a plant to produce coal liquids, char and coke in the initial range of 250,000 tons/year.

BACKGROUND INFORMATION

The process for converting coal to char and hydrocarbon liquids is relatively simple and was commercially practiced in the United States in the 1920s and 1930s to make smokeless fuel, a premium product in its day. Coalite, a coal derived smokeless fuel, is still being produced in the United Kingdom today in a batch mild gasification process. The Hayes process was self-sustaining in that approximately half of the non-condensable pyrolysis gases were used to supply the heat needed to operate the retort.

In 1984, Coal Technology Corporation (then called UCC Research Corporation) began work under an earlier DOE contract on coal mild gasification via a batch process. This work provided valuable knowledge, but it became

evident that a continuous process would be much better.

PROJECT DESCRIPTION

In the Coal Technology Corporation CTC/CLC® Process, coal is continuously moved by interfolded twin screws through a heated retort in the absence of air. The residence time of the coal in the Continuous Mild Gasification Unit (CMGU) is in the range of 20-30 minutes. The coal is heated to controlled temperatures between 800° and 1400°F and is converted into char, condensable hydrocarbon liquids, small quantities of water, and non-condensable fuel gases. The coal derived fuel gases could supply all the required process heat, but for convenience, natural gas is used in the experimental unit. The process concept is particularly suitable for highly caking coals which cannot be processed in fluidized bed or moving bed furnaces.

The present project to develop a continuous process began in September 1987 and consists of four main tasks. Task 1, Literature Survey and Market Assessment, and Task 2, Bench-Scale Mild Gasification Study, have been completed. Task 3, Bench-Scale Char Upgrading Study, has been underway since September 1989. In char upgrading studies, "green" char briquettes have been prepared and calcined in 20-pound batches to evaluate the effects of char, binders, and heating conditions on final coke properties. Since May 1990, 172 "green briquette" formulations have been tested thus far in this work.

Work on Task 4, PDU Mild Gasification Study, has been in progress since February 1991, with the completion of a CMGU with a design rate of 1000 lb./hr. Since start-up of the CMGU, there have been 132 runs, of which 60 were in the last 13 months, with a variety of

operating conditions and coal types.

A paper presented at a previous Contractor's Review Meeting describes the CTC/CLC® Continuous Mild Gasification Process, the key process items, and the initial operations. Since this information has already been published, it will not be repeated here.

RESULTS

At the time of the last Contractor's Meeting, the CMGU had been in operation for just over one year and 72 experimental tests had been completed. These tests on a variety of coals had produced much useful data: (1) the effect of coal feed rate, (2) heat input to the reactor, and (3) the residence time in the reactor needed to obtain the desired volatile matter in the char product.

Concurrently with the CMGU experiments, work was active on coke briquetting experiments. Here, the type and characteristics of the char's parent coal and the char volatile content affects the coke quality, along with the amount and type of coal binder used, and the amount and type of tar and pitch binder. The CMGU unit has been operated over a wide range of conditions within the parameters listed above for coals or different volatile matter content to consistently produce chars with the preferred volatile content.

Enough work had been done at this time a year ago to be confident that the twin screw process to produce char had the characteristics required for a good commercial process. It was already evident that we could make continuous coke that fully met industry standards. What needed to be done, and which has been done, was to firm up our understanding of the process, to eliminate problems as they become evident, and to improve the process where possible.

At the time of last year's meeting, two modifications to the CMGU system had been made but their effects had not yet been evaluated: (1) pulse-jet burners to replace the original electric heaters had been installed to furnish heat through the pyrolyzer screws internal shafts and (2) installation of a CTC designed and constructed natural gas heated enclosed screw conveyor to dry the feed coal.

The effect of these modifications was dramatic. The first run after these modifications averaged a feed rate at 922 lbs./hr. on October 11, 1992; this being almost double the previous high of 574 lbs./hr. A number of runs have since been made at feed rates of 1000 to 1100 lbs./hr. with ultimate top rate still to be determined.

The dryer greatly reduced the flow problems from the CMGU coal feed bin and reduced the amount of water vapor to the flare.

We now know very clearly that the CMGU works with any type of Eastern bituminous caking coal that we have tested to date. We believe it will work with Western coals but have not yet had an opportunity to test Western coals. We know now that free swelling index, normally a very important quality for coking coals, is of no concern in the CTC/CLC® Process. We know that we can operate the system to produce the desired volatile content of the char. We know there are clearly defined markets for the co-products.

Of the 60 test runs made in the past 13 months, 17 were from the Red Ash coal seam with about 27% volatile matter; 15 were from the Sewell coal seam with about 30% volatile matter; 13 from the Pocahontas No. 3 seam with about 18% volatile matter; and the most recent 8 runs were made with Upper Cedar Grove coal with about 32% volatile matter. Our ability to regulate the temperature in Zone 1 and Zone 2

of the CMGU by control of the heat input and to regulate the retention time through the "plastic coal phase" by varying the forward-pause-reverse operation of the interfolded screws enables us to produce a char with the desired Volatile Matter (VM)-Fixed Carbon (FC) ratio. The desired final volatile matter content of the char is dependent on the market or process for which the char product is intended; i.e., ferro-metallurgical, "coke" briquetting, smokeless fuel or upgrading to other carbon products. Recent test runs using the higher volatile Upper Cedar Grove coal verify that the time for pyrolysis, irrespective of the volatile content of the feed coal and the volatile content of the product, is about the same 20 minutes from start of coal feed to the first char discharge indicating the final char volatile content is highly dependent on the Zone 2 temperature. An eight point data-logger, installed in July 1993, to continuously record selected temperatures in the system, the drive pressure under varying conditions of feed rate, and operating mode gives us improved data for analysis and better control of the process. Please see Figure 1 for an example of this data-logger output.

Of special interest were test runs conducted in December 1992 on 28 mesh x 100 mesh fines furnished by Penelec. The fines as received contained 40% moisture which was reduced to less than 4% by our dryer. The dried fines were routinely devolatilized from 25% volatile matter content to 6%-12% volatile matter at over 1100 lbs./hr. The char produced was used to make coke briquettes for evaluation by Penelec. This evaluation by Ralph Gray Services included analytical and petrographic analyses of the char, binder coal, coke and tar. Results of the coke tests are shown in Tables 1, 2, and 3. Photomicrographs of coals, char and coke follow in Figures 2, 3, 4 and 5.

To quote Mr. Gray's report, "This report... was planned with Penelec to determine an alternate use for fine size (28 x 100, 100 x 0 and/or 28 x 0) coal. This size coal contributes to a decrease in pulverized throughput at utility sites. It can definitely be used to produce coke briquettes that meet the requirements of quality metallurgical grade coke."

Mr. Gray further stated "... the process tar contained 8.4% solids (wet basis)."

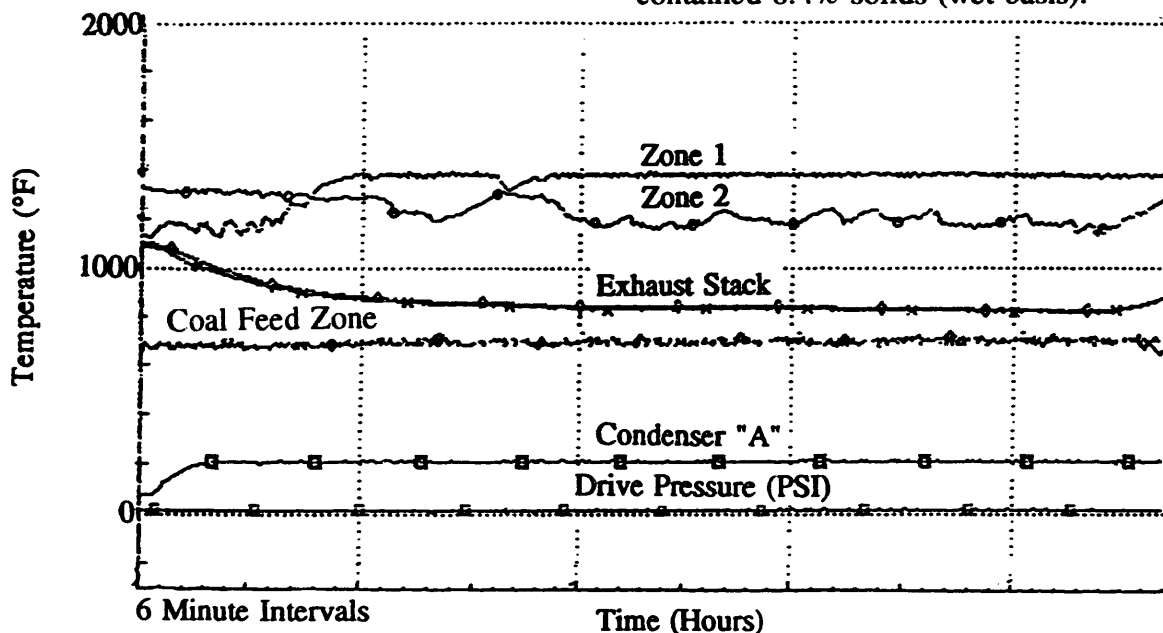


Figure 1. Data Logger Output

Table 1.
Proximate Analysis and Sulfur Content of the Indicated Green Briquettes and Cokes

SAMPLE I.D.	PROXIMATE ANALYSIS, WT. % (DRY)			TOTAL SULFUR, WT. % (DRY)
	VOLATILE MATTER	FIXED CARBON	ASH	
GREEN BRIQUETTES RJG# 16351	19.32	74.19	6.49	0.87
CTC COKED RJG# 16452	2.42	90.06	7.94	0.83
UEC COKED RJG# 16480	0.81	90.85	8.34	0.96
COMMERCIAL COKE RJG# 16357	0.36	90.72	8.92	0.83

Table 2.
Physical Properties of the Indicated Cokes and Briquettes

	MODIFIED		APP.SP GRAVITY	TRUE SP. GR.	POROSITY	CPA*	
	STABILITY	HARDNESS				AVG. WT. GMS	DENSITY G/CC
CTC COKED RJG# 16452	77.9	78.7	1.25	1.90	34.7	46.4	1.15
UEC COKED RJG# 16480	72.2	82.1	1.21	1.96	38.3	42.6	1.02/1.09
COMMERCIAL COKE RJG# 16357	79.0	85.0	0.93	2.06	54.9	--	0.98
GREEN BRIQUETTES	--	--	--	--	--	56.0	1.24
*COAL PETROGRAPHIC ASSOCIATES							

Table 3.
**Coke Reactivity Test Results from the Japanese "I" Test for Coke Strength
after Reaction (CSR) and Coke Reactivity Index (CRI)
for Indicated Coke Samples**

SAMPLE I. D.	COKE REACTIVITY INDEX (CRI)	COKE STRENGTH AFTER REACTION (CRI)
CTC COKED RJG# 16452	33.3	51.9
UEC COKED RJG# 16451	32.8	55.1
COMMERCIAL COKE RJG# 16357	28.4	55.6

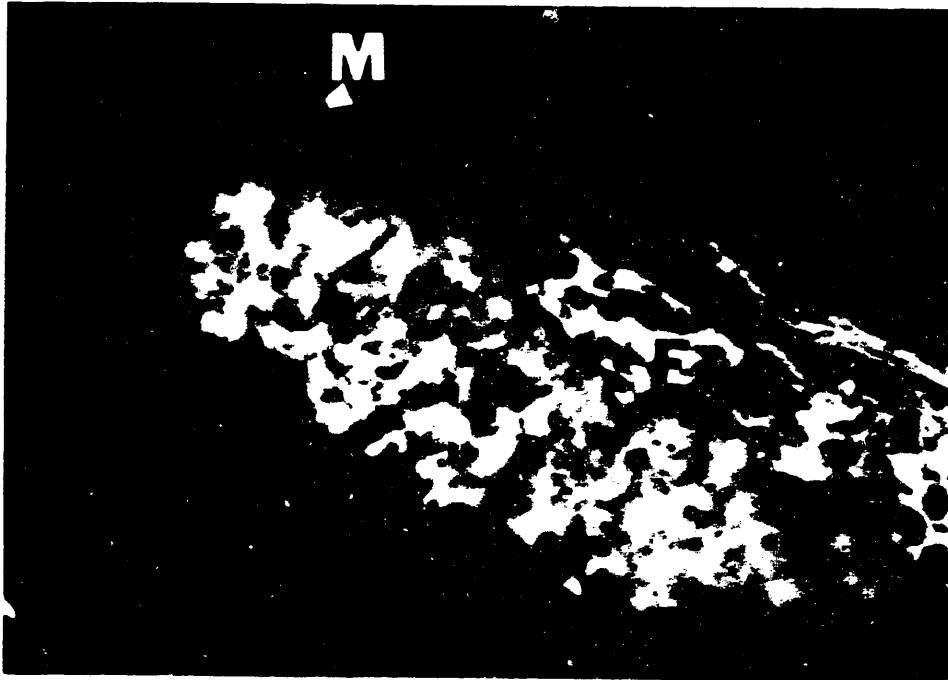


FIGURE 2 : PHOTOMICROGRAPHS OF MACERALS IN MEDIUM VOLATILE BITUMINOUS SEWELL COAL FROM COAL TECHNOLOGY CORPORATION SHOWING: V-VITRINITE, E-EXINITE, M-MICRINITE, SF-SEMIFUSINITE, F-FUSINITE AND P-PLASTIC MOUNTING MEDIA. REFLECTED LIGHT IN OIL, X 450.

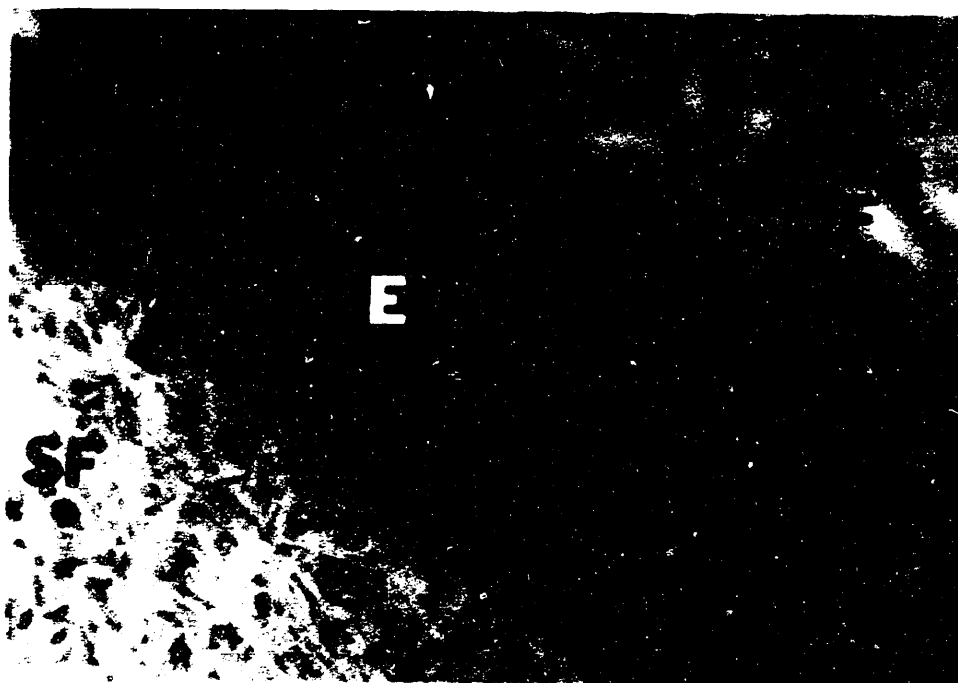


FIGURE 3: PHOTOMICROGRAPHS OF MACERALS IN HIGH VOLATILE BITUMINOUS KNOX CREEK COAL FROM COAL TECHNOLOGY CORPORATION SHOWING: V=VITRINITE, E=EXINITE, M=MICRINITE, SF=SEMIFUSINITE, F=FUSINITE AND P=PLASTIC MOUNTING MEDIA. REFLECTED LIGHT IN OIL X 450.

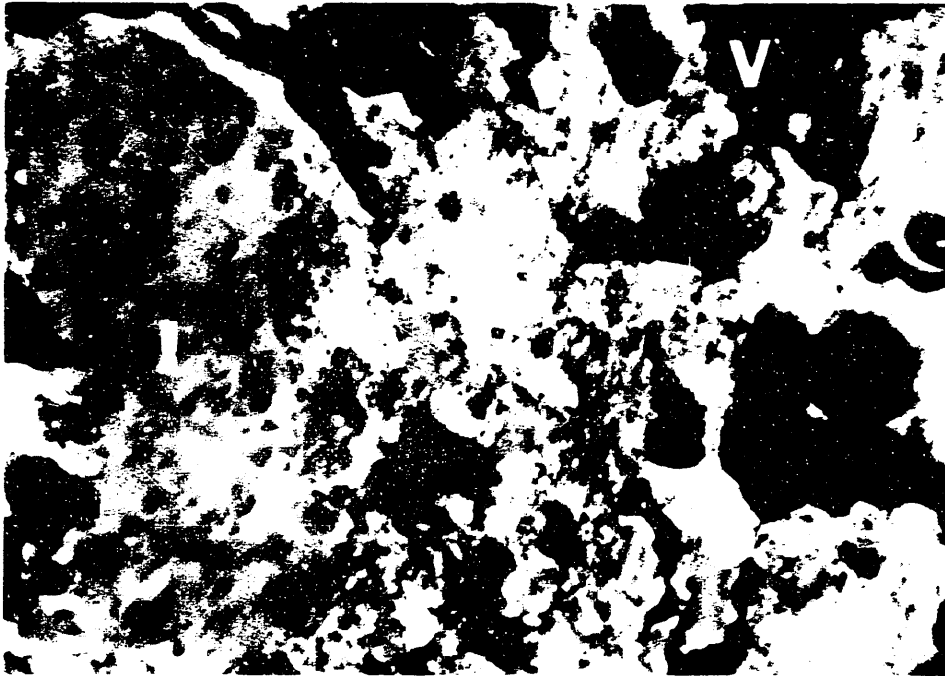


FIGURE 4: PHOTOMICROGRAPHS OF CHAR FROM COAL TECHNOLOGY CORPORATIONS' TWIN SCREW CARBONIZER SHOWING CHAR IN POLARIZED LIGHT WHERE A=ANISOTROPIC BINDER CARBON, I=ISOTROPIC INERT FILLER CARBON AND V=VOIDS. REFLECTED POLARIZED LIGHT WITH TINT PLATE IN OIL, X 450.

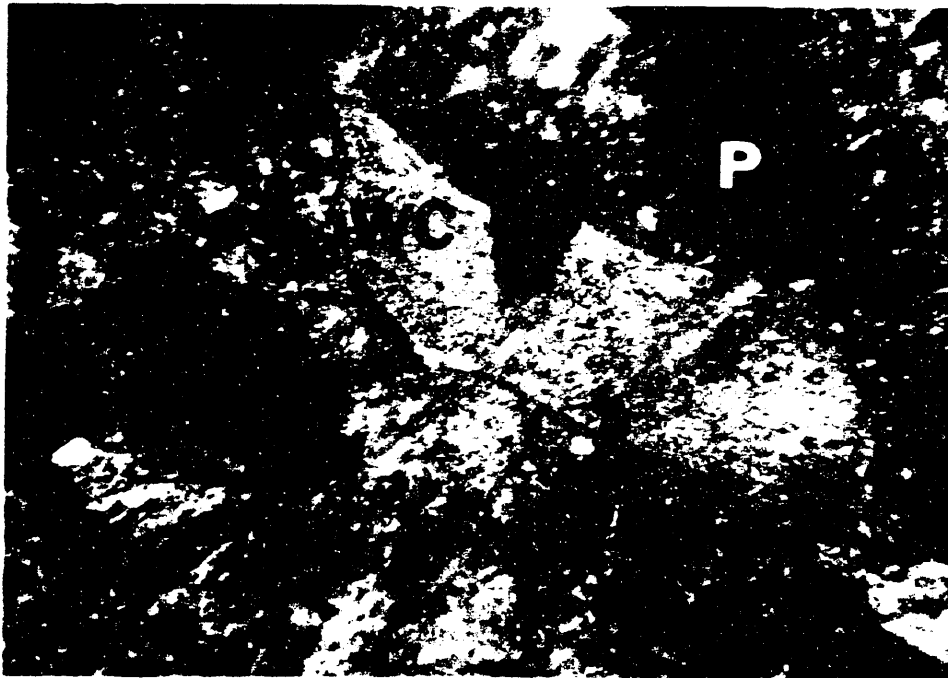
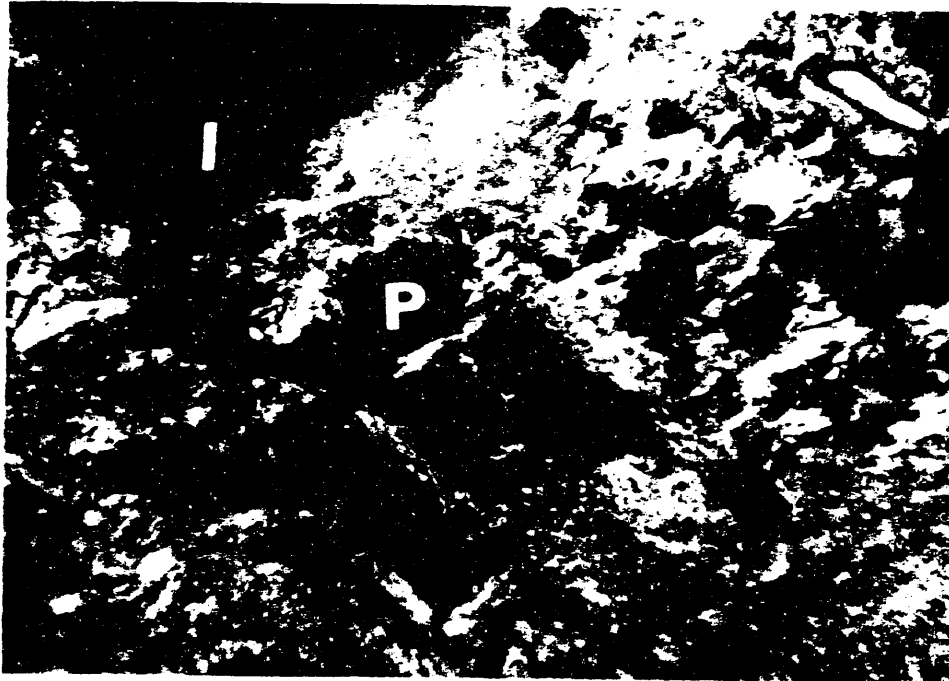


FIGURE 5: PHOTOMICROGRAPHS OF COKE BRIQUETTE FROM COAL TECHNOLOGY CORPORATIONS' FORMCOKE PROCESS SHOWING: WC=ANISOTROPIC CHAR IN COKE WALLS, WB=ANISOTROPIC BINDER CARBON IN COKE WALLS, I=ISOTROPIC INERT FILLER CARBON AND P=PORES. REFLECTED POLARIZED LIGHT WITH TINT PLATE IN OIL, X 450.

"The fine size solids are very low in ash-forming minerals and add to the coke yield from coal tar pitches. The coarser solids contain ash-forming materials from the coal and are an objectionable constituent of pitch."

"Your process tar sample contained very little coarse solids. . . The Normal QI content of the tar is 97.5% with only 2.5% of coal carry over. Most of the particles are spherical and appear to consist of concentric layers. The fine solids which total 84.5% are 0.25 to 1.5 microns with 13% of 1.5 to 4 micron solids. The carry over solids range from 5 to 15 microns which is on the fine size for these materials."

"Your process tar should be desirable for use in producing contract pitches for the electrode industry."

Also, a 70 lb. sample of CTC coke sized 3" x 2" was sent to Koppers Industries for an ASTM D3402-81 coke stability test. The result of the stability test was 70.2.

Koppers Industries then supplied enough of their proprietary "coke blend" for one test run in the CMGU which was made in February 1993. The char produced was then blended with the "binder coal," also supplied by Koppers, and coal tar from the CMGU was briquetted, calcined in the batch oven and the "coke briquettes" returned to Koppers for testing. The results of this test, as shown below, were excellent, actually exceeding their best conventional coke results for reactivity.

Volatile Matter	0.54
Fixed Carbon	91.48
Ash	6.98
Sulfur	0.59
Stability	65.90
Hardness	69.10
Reactivity	7.00

A comparison of test results for typical CTC/CLC® continuous briquetted coke with conventional coke industry standards is shown in Table 4.

Table 4. CTC/CLC® Coke Quality Comparison

Physical Characteristics	Standard Coke Specifications ¹	CTC/CLC® Continuous Briquetted Coke
CRI (Nippon Steel Method), %	32 Max	24-31
CSR (Nippon Steel Method), %	55 Min	65-74
Coke Stability, %	58	61-66
Coke Hardness, %	67	69
CRI (Bethlehem Steel Method), %	<15	7-13
Moisture, %	5-7	2 Max ²
Ash (Dry Basis), %	8	7
Volatile (Dry Basis), %	1.0 Max	0.5-1.0
Fixed Carbon (Dry Basis), %	91	92
Sulfur (Dry Basis), %	0.7	0.6
Bulk Density, Lbs./Cu. Ft.	29	40

Notes:

¹Standard Coke Specification is given by Ralph Gray Services

²Due to dry coke cooling, not water quenching

Co-mingled with work to increase the capacity and run duration of the CMGU, increased emphasis was placed on more complete control for the collection of the CMGU vapors and a simpler, but efficient, method(s) for separation of the tars, oils and non-condensable gases for cleaner environmental emissions.

While the modifications of the previous year to the condensing system had been effective at lower CMGU operating levels, the increasing levels of operation returned the problems of increased vapor pressure within the CMGU and tar and fines fouling of the vapor lines and coal feed system. The coal feed screw was modified to form an effective vapor seal by means of a "coal plug." This successfully eliminated vapor plugging at the coal feed point.

The installation of a secondary condenser and a subsequent "demister," both water cooled, in the flare line increased the collection of liquids from the vapor stream. Occasional carbonization of liquids and tars near the flare resulted in vapor pressure back through the condenser system.

In June 1993 a different approach to collect the tars was tried. Devised and built in May and installed in June, this unit did a good but incomplete job of collecting tar from the pyrolysis gas stream. This tar solidified to a hard, brittle solid with a glassy texture resembling commercial pitch although with about 50% higher volatile content. Subsequent runs were conducted with this "tar trap" connected to the pyrolyzer via an inspection port and the original three (3) condensers still connected. An additional "mass transfer" condenser installed to receive the off-gases from the tar trap collected a lighter (thinner) tar at its collection pockets. These units appear to be very effective but there were still condensation and accumulation of material near the flare.

An experiment using a "bubble scrubber" on a portion of the flare gases appeared effective, so a bubble scrubber to handle 50% of the flare gas stream was built and installed in July 1993. Our analysis indicates this unit increased the combustibles (CH_4 , H_2 , CO) content of the gas from 75% to 95% and reduced the N_2 and O_2 content of the gas from 24% to 5% when compared to the bubble scrubber feed gas stream. These units, the tar trap, and the packed column condenser appear very effective at this point and could greatly simplify the tar collection system while yielding better products.

Analyses of a tar sample and coal tar liquids sample collected from this system are shown in Table 5.

Table 5.
Heavy Coal Oil Liquid

Specific Gravity	60°F	1.108
Water	Vol. %	9.0
Quinoline Insolubles	Wt. %	4.4
Ash	Wt. %	0.089
Ammonium Chlorides	lb./1000 gal.	300

Pitch

Softening Point, Mettler	C	54.40
Toluene Insolubles	Wt. %	16.40
Quinoline Insolubles	Wt. %	10.10
Coking Value	Wt. %	28.60
Ash	Wt. %	0.36
Sulfur	Wt. %	0.45
Distillation to 360 C	Wt. %	10.50

Notes:

- (1) The oil sample appears to be useful only as a fuel. The material is too dirty for use in creosote blends and is too low in gravity to contain a recoverable quantity of pitch. The material had to be heated to about 150°F before it appeared to be pumpable.
- (2) The second sample appears to be a typical soft pitch.

Analyses of the non-condensable gases that presently go to the flare are shown in Table 6.

Table 6. Fuel Gas (Non-Condensable from Pyrolysis)

Gas	Volume ¹ %	Wt. (#/Ft ³)	Btu/Ft ³	Air Required
CH ₄	38.16	0.0171	366.3	3.66
C ₂ H ₆	1.46	0.0012	24.8	0.24
C _x H _{2x+2}	2.25	0.0038	38.3	0.09
H ₂	30.66	0.0017	89.5	0.89
O ₂	4.95	0.0044	--	--
N ₂	19.13	0.0150	--	--
CO	2.76	0.0022	22.0	0.07
CO ₂	0.65	0.0008	--	--
H ₂ ^c COS SO ₂	0.0037	0.2x10 ⁻⁶	1.1	0.01
Totals	100.0237	0.0462 #/SCF	542.0 Btu/SCF 11,700 Btu/Lb	4.96 SCF/SCF

Note: ¹From METC Analysis CTC #60, Run 40-92

Based on our pilot plant observation, the volume and heat content of these gases would be sufficient to fuel the CMGU unit. However, it should be noted here that in a commercial plant, this stream would be used to supply supplemental heat, as needed, to maintain pyrolysis temperatures to the hot air exhaust stream from the calcining unit with the excess to a flare or possibly for co-generation of electric power.

Although our attempts to collect a good sample of the "calcining gases" exhausted from our 20 lb. batch oven have not been successful, the results of such a sample could be

misleading. A comparison of the results of "green briquettes" calcined in our 20 lb. batch oven with its long "ramp temperature" time to "green briquettes" calcined in the UEC 30 lb. oven charged at 1350°F and increased to 1850° in 3-1/4 hours indicates that although the coke test data are very close, the sulfur liberated by our 20 lb. batch oven is higher probably due to the low initial temperature and slow heating rate. In the CTC/CLC® Process the ambient loading of "green briquettes" would be eliminated, greatly reducing the amount of SO₂ emissions indicated by our current material balance calculations.

After review of the CTC/CLC® Process, the United States Environmental Protection Agency Region III Air Enforcement Branch notified the West Virginia Division of Environmental Protection that our proposed commercial plant in West Virginia would not be a coke oven battery and should be classified as a fuel conversion plant for the conversion of caking type coals into three distinct new fuel forms of enhanced value. The West Virginia Division of Environmental Protection, Office of Air Quality, subsequently issued the permit for construction of a commercial plant in Mercer County, West Virginia on September 23, 1993.

FUTURE WORK

Future work in the "Development of an Advanced Continuous Mild Gasification Process for the Production of Co-Products" would be to:

- (1) Continue investigations of the temperature/retention time/plastic coal phase in the CMGU.
- (2) Continue work on the current CMGU condenser system to further improve the quality of the collected products.

- (3) Investigate the potential uses of CMGU char (a) as a media for the collection of coal liquid mists from the flare stack, (b) as an activated carbon feed stock, and (c) as a filler material for electrodes.
- (4) Install a 1000 lb./hr. briquetting and coking system for the continuous production of "coke" for blast furnace and foundry cupola testing. This additional continuous coking facility will provide for a totally integrated system for continuously converting coal into char; then continuously briquetting and converting the char briquettes into high quality coke for both blast furnace and foundry coke applications.

In October 1992, CTC was joined by Norfolk Southern Corporation, Elkem Metals Company and Koppers Industries in a feasibility study to determine the commercial attractiveness of a 500 tons/day CTC/CLC® commercial plant to take advantage of the coke shortage projected for the latter half of this decade and beyond. This study indicated excellent returns on investment for such a project. CTC is actively and diligently pursuing potential partners to participate in the building of this commercial plant and future plants.

REFERENCES

1. Pound, G. S., *Coke and Gas*, 21, pp. 396-401, 1959.
2. United Nations Ind. Dev. Org., Vienna, "Carbonization and Hydrocarbonization of Coal," United Nations, New York, 1973.
3. Lowry, H. H., ed., "Chemistry of Coal Utilization," Supplementary Vol., pp. 403-404, 1963.
4. Ibid, pp. 440-442.
5. Woody, G. V., *Industrial and Engineering Chemistry*, 33, No. 7, pp. 842-846, 1941.
6. McQuade, J. D., "The Hayes Process Low Temperature Carbonization Plant at Moundsville, W. Va.," *Combustion*, pp. 28-31, November, 1929.
7. Brownlee, D., "Combined Low Temperature Carbonization and Combustion for Power Stations," *Combustion*, pp. 43-47, December, 1929.
8. Laucks, I. F., "The Screw as a Carbonizing Machine," *Industrial and Engineering Chemistry*, 19, No. 1, pp. 8-11, 1927.
9. Wright, R. E., et al, "Development of an Advanced Continuous Mild Gasification Process for the Production of Co-Products," *Proceedings of the Eleventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, Vol. 6, pp. 263-274, 1991.
10. Wright, R. E., et al, "Development of an Advanced Continuous Mild Gasification Process for the Production of Co-Products," *Proceedings of the Twelfth Annual Gasification and Gas Stream Cleanup Systems Contractor's Review Meeting*, Vol. 2, pp. 550-561, 1992.

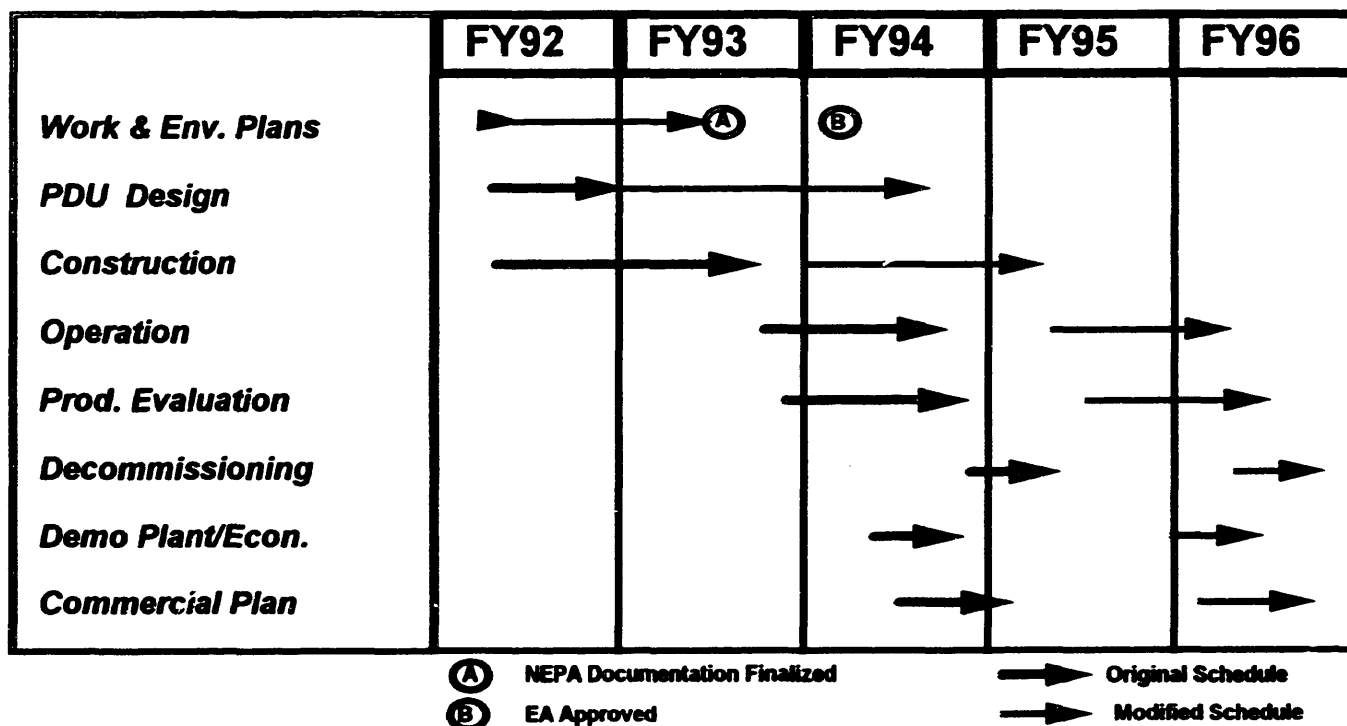
LF-3.2 Value-Added Co-Products From K-M/IGT Facility

CONTRACT INFORMATION

Cooperative Agreement Number	DE-FC21-91MC27391
Contractor	Kerr-McGee Coal Corporation 123 Robert S. Kerr Avenue Oklahoma City, Oklahoma 73102 (405) 270-3778
Contractor Project Manager	John A. L. Campbell (K-M Coal)
Principal Investigators	Ronald H. Carty (IGT) Harold Foster (SIUC)
METC Project Manager	J. Keith Westhusing
Period of Performance	November 21, 1991 to November 20, 1994

SCHEDULE AND MILESTONES

TASK SCHEDULE (Tentative)



OBJECTIVES

The overall objective of this project is to develop the IGT MILDGAS technology for near-term commercialization. The specific objectives of the program are to:

- design, construct, and operate a 24-tons/day adiabatic process development unit (PDU) to obtain process performance data suitable for further design scaleup
- obtain batches of coal-derived co-products for industrial evaluation
- prepare a detailed design of a demonstration unit
- develop technical and economic plans for commercialization of the MILDGAS process.

BACKGROUND INFORMATION

The MILDGAS process is a continuous coal carbonization process operating in a closed system for producing liquid and solid (char) co-products at mild operating conditions up to 50 psig and 1300°F. Because of its mild operating conditions and process simplicity, the technology could be commercialized within the next 5 to 10 years. Systems analysis studies by Bajura and Ghate¹, and Klara and Hand,² all support this prospect. It is capable of processing all eastern caking and western noncaking coals. It is flexible to offer options in the product slate by varying the process conditions and by blending different feed coals. The liquids can be processed as feedstocks for chemicals (e.g., BTX, phenol, cresols, xyenols, naphthalene, and indene), pitch for use as a binder for electrodes in the aluminum industry, and fuels. Depending on the feed coal characteristics and the

operating conditions, the char can be used as an improved, reduced sulfur and moisture, and higher heating value fuel for power generation, or briquetted to make form coke for steel-making blast furnaces or for foundry cupola operations. The briquetting process offers options for blending various chars and additives (like alloying agents) to tailor the properties of the form coke. In addition, the binder for the form coke may be either pitch or a caking coal. The mild gasification and briquetting processes are done entirely within closed vessels which offer significant advantages over conventional coking practices for control of fugitive emissions.

The process splits the coal feed into coarse (+60 mesh) and fine (-60 mesh) fractions. The coarse fraction of the feed coal is fed into the fluidized bed section of the reactor and the fines fraction of the feed is fed to the entrained section. The fluidization gas distributor is designed to promote rapid mixing and dispersal of the incoming coal throughout the bed of char. Under a previous DOE funded program, IGT built and operated a 100-lb/h coal capacity isothermal process research unit (PRU) for the design of the MILDGAS reactor. The program was conducted with the participation of an industrial advisory committee consisting of steel, coal, and tar-processing companies. In the PRU testing, it was determined that the relationship of coal feed rate to inventory of char in the fluidized bed is critical in controlling agglomeration with caking coals.

Two Illinois No. 6 coals, a West Virginia coal, and a subbituminous coal from Rochelle, Wyoming were tested in the PRU. The results of the successful PRU tests, conducted at temperatures in the range of 1035° to 1390°F, with Illinois No. 6 and West Virginia coals show yields of 54% to 76% char, 13% to 28% oils/tars, and 7% to 19% fuel gas. A single test at 1062°F of Wyoming subbituminous coal yielded 65% char, 17% oils/tars, 13% fuel gas, and 5% water.

The criteria for co-product selection were identified from a market survey³ and the advice of the advisory committee. Since char is the major co-product, estimated to comprise about 54% to 76% of the total co-product stream, its beneficial utilization is critical to commercialization of MILDGAS technology.

Many of the existing coking plants in the United States are reaching the limits of useful age. The supplies of metallurgical coke and high-quality coal tar pitch have been declining in the U.S. because of the closing of coke oven operations due to aging and environmental concerns. A portion of the demand for these products is being met by imports. Therefore, environmentally acceptable methods to produce supplementary supplies of coke and tar are urgently needed. The form coke production from the MILDGAS char is continuous with superior environmental control that is difficult and costly to achieve in present coke oven batteries.

Char upgrading studies completed during the PRU program show that the MILDGAS char can be used to produce a form coke with sufficient strength and an acceptable reactivity for metallurgical use. The form coke co-product from the MILDGAS char has two sub-markets. The larger of the two markets for form coke is in blast furnaces for the production of iron. A smaller market for foundry coke is in cupolas for remelting and alloying iron for steel castings.

It is expected from the PRU data that the MILDGAS pitch would require post-treatment to increase aromaticity and remove heteroatoms in order to be acceptable for electrode binders. IGT is currently working on a project funded by DOE and the Illinois Clean Coal Institute for a post treatment to upgrade the MILDGAS liquids. The initial results of this project are very encouraging.

About 67% of the MILDGAS oils/tars are recoverable as soft pitch. For flat and low-slope roofing, coal-tar pitches are superior to asphalt in most characteristics, including water resistance and a "self-healing" property.⁴ A possibility also exists that soft pitch could compete with petroleum-based bitumen for road binders. Blends of coal- and petroleum-based binders have been shown to have improved adhesive properties, water resistance, and skid resistance of highway surfaces.

Yields of BTX and phenols from the MILDGAS PRU were greater than those from coke ovens. These chemical feedstocks are widely used as starting materials to make plastics, synthetic fibers, and building materials.

The MILDGAS liquids, or some fraction thereof, also have the potential for being converted into transportation fuels. The middle to heavy distillates can be used as a diesel blending stock; and, with some upgrading, some of the MILDGAS liquids can be used in gas turbines.

PROJECT DESCRIPTION

The project team currently working on the present PDU development program are Kerr-McGee Coal Corporation (K-M Coal), the Institute of Gas Technology (IGT), Bechtel Corporation (Bechtel), and Southern Illinois University at Carbondale (SIUC).

The 1 ton/hr PDU facility that is to be constructed is comprised of a 2.5-ft ID adiabatic gasifier for the production of gases, coal liquids, and char; a three-stage condensation train to condense and store the liquid products; and coal feeding and char handling equipment. The facility will also incorporate support equipment for environmentally acceptable disposal of process waste.

Coal liquids from the PDU will be evaluated as feedstock for high-value chemicals and fuels by Reilly Industries, Inc. Reilly will also conduct separate modification operations such as thermal treatment with or without a Lewis Acid Catalyst, fractional distillation, and hydrotreating to produce specification-grade products.

The major portion of the char produced will be briquetted by others to make the form coke for blast furnaces and cupolas. The form coke for blast furnaces will be evaluated by several steel companies, including LTV and Armco. The form coke for use in a foundry cupola will be evaluated by General Motors Research Laboratories. In addition, the form coke will also be tested for foundry use at Pellet Technology Corporation's 60-inch cupola. The char from the PDU will also be evaluated at SIUC for relative reactivity and for suitability as a boiler fuel in a fluidized-bed combustor.

The product testing to be conducted in the proposed program will yield a realistic assessment of the quality and economic value of both the coal liquids and solids produced. This input is required to update the market potential of the co-products and determine the slate of products and the economics of the demonstration and commercial plants for the MILDGAS process.

Mild Gasification

The mild gasification system employs the IGT MILDGAS reactor concept specifically configured for processing both caking and noncaking coals. This configuration, illustrated in Figure 2, makes provision for separate feed of coal fines to the upper entrained-bed section. The coarser feed fraction enters the lower bubbling-bed section. The lower portion of the bubbling bed section has a turbulent mixing section to handle the caking coals.

The preheated coarse coal is introduced into this turbulent mixing zone, where it is rapidly mixed with devolatilized char and hot fluidizing gas. The rapid mixing and dispersion with the fluidized bed char in this zone prevents agglomeration of the incoming caking coal. The upper portion of the fluidized bed retains the char in dense-phase. The preheated coal fines are introduced into the bottom of the upper high-velocity entrained-flow zone. These fines require little time for heat penetration and pyrolyze rapidly in suspension flow. The preheated coal fines are heated to pyrolysis temperature by the hot gases leaving the fluidized bed.

The heat required for raising the coarse coal feed from preheat to pyrolysis temperature is provided from combustion of a fraction of the recycle product gas from the liquids recovery section.

Char Processing

The char from the gasifier will be used to make briquettes that will be calcined to produce form coke. This form coke briquetting will be conducted offsite of the PDU by a outside group selected for their expertise and suitable briquetting and calcining facilities. The char will also be blended with lime or limestone and briquetted to form a transportable smokeless solid fuel. The char may also be treated with steam to make activated carbon. The unprocessed char product may be tested in combustion systems to produce steam for power generation.

In the expected processing to produce a calcined form coke, dried and ground caking coal will be added to the hot char to act as a binder for the briquette. The char product from the mild gasification will be ground and blended with the coal. The blend will then be heated and masticated to form a matrix of the char in plasticized coal

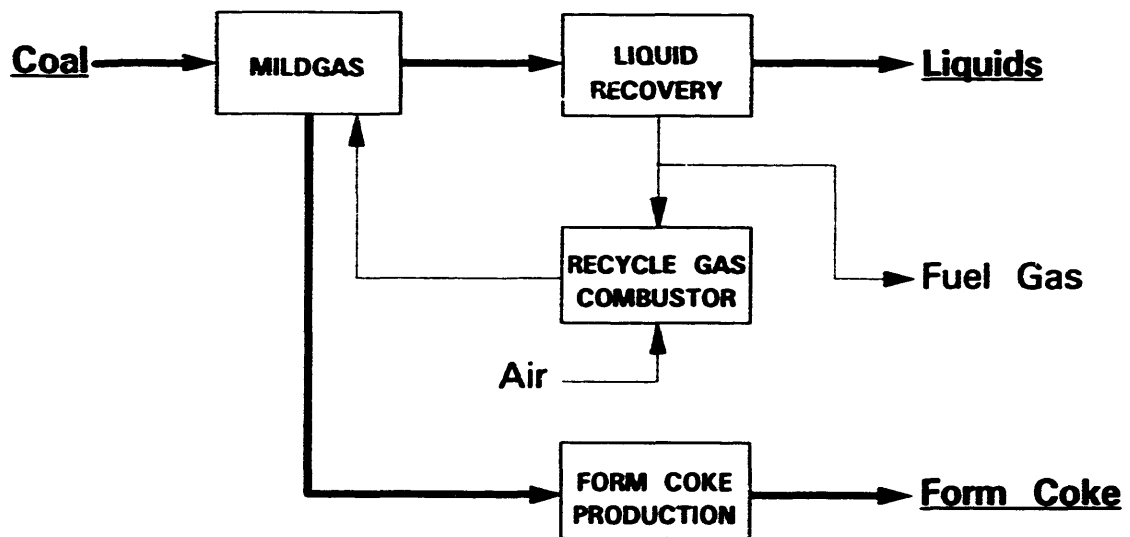


Figure 1. Simplified PDU Process Flow Diagram

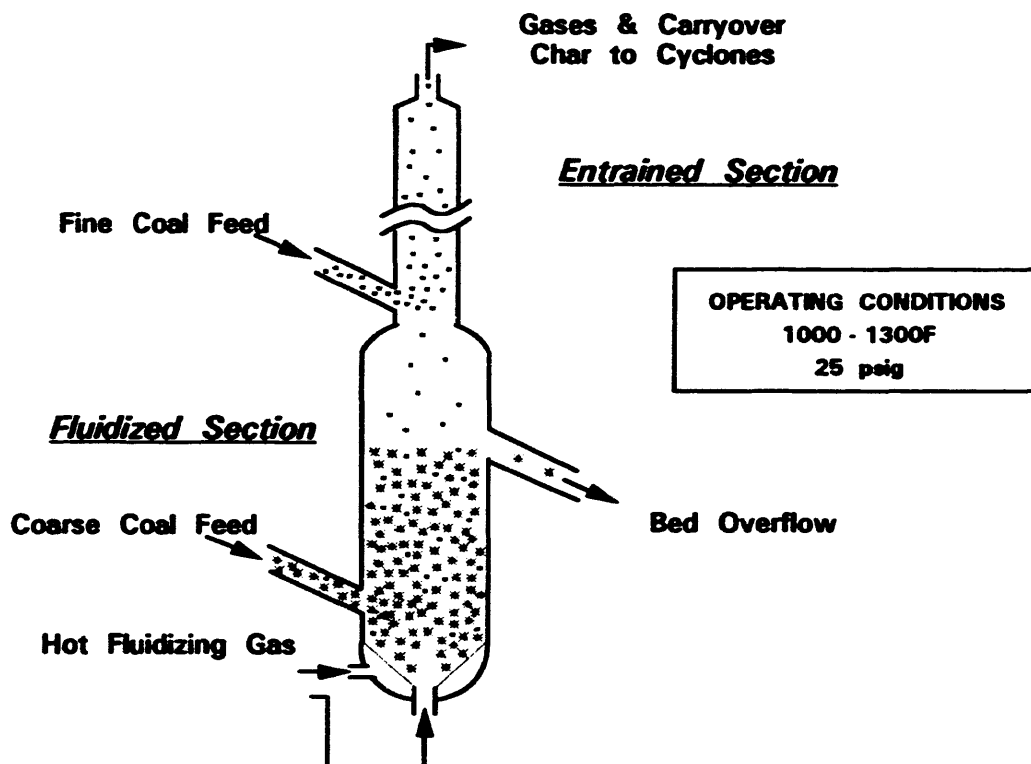


Figure 2. MILDGAS Reactor

binder. The hot plastic mass, is then briquetted. The briquettes are next calcined to remove all volatiles and harden the binding matrix to yield form coke that meets the specification of coke for use in blast furnaces and foundry cupolas.

An alternative is to use the tar/pitch from the mild gasification as the binder. This would lower the temperature for mixing and briquetting the char and binder. The green briquettes would still be calcined at an elevated temperature to cure and harden the pitch/char matrix.

Liquids Upgrading

The product liquids will be recovered in three fractions by successive reduction in condensation temperature. The high-temperature tar condensate will be filtered on-line to remove entrained char fines. It is planned to ship these liquid products offsite to coal tar processors for large-scale product evaluation testing. This evaluation will be supplemented by analytical characterization of representative liquid samples.

PDU Test Program

The objectives of this task are: to conduct mild gasification tests in the PDU with various types of coals; analyze the parametric test results; obtain samples of co-products for upgrading and industrial testing and evaluation; and produce form coke briquettes from MILDGAS char produced in the PDU.

When the PDU system is fully operational, tests will be conducted with three selected coals (a bituminous coal from Illinois, a bituminous coal from West Virginia, and a western subbituminous coal) at the ranges of operating conditions selected from the PRU tests. Specifically, the parameters to be studied in the Phase 1 testing are:

- Coal type (Illinois bituminous, West Virginia bituminous, subbituminous)
- Temperature (1000°, 1300°F)

A series of parametric tests with the three coals are anticipated in Phase 1, including replicates to be selected after evaluation of initial test data. In Phase 2, sustained-operation tests will be conducted with the three candidate coals, and at two temperatures to be selected based on the results of Phase 1 testing. The tests in Phase 2 will produce larger quantities of co-products for industrial evaluation.

Co-Product Upgrading and Evaluation

One of the primary goals of this project is to investigate the necessary upgrading of the co-products to marketable forms and to evaluate the co-products in sufficiently large quantities so that the results can be reliably used for evaluating the potential economics of demonstration- or commercial-scale plants.

The char produced in the PDU will be upgraded by conversion to a calcined briquetted form coke, and to a non-calcined briquetted smokeless fuel. The form coke can be produced employing either coal or coal-derived pitch as a binder for the briquetting operation. Conversion of the char to activated carbon by steam activation will also be investigated.

Evaluation of upgraded char as form coke briquettes will be performed by Pellet Technology Corporation. PTC will evaluate the performance of the form coke in comparison to conventional foundry coke. General Motors Corporation will provide additional evaluation of the form coke for foundry use.

In addition to evaluation of form coke, mild gasification char will also be tested by SIUC for properties relating to its possible use as utility fuel, using a thermogravimetric analyzer (TGA) and a 4-inch-ID bench-scale circulating fluidized-bed.

The segregated liquid product fractions will be submitted to commercial tar processors for evaluation and upgrading through their customary processing operations.

The surplus gas produced in the mild gasification will be analyzed to verify its composition but will not be processed in any way for upgrading.

STATUS

During the past project year, the NEPA Application for construction and operation of the PDU facility at the SIUC site was finalized and all questions required to prepare the Environmental Assessment were answered. The Environmental Assessment has now been approved by DOE Headquarters and sent to the Illinois EPA for comments. In addition, the documentation required for obtaining the Authority to Construct from the State of Illinois has been prepared and will shortly be submitted to the Illinois Environmental Protection Agency. As part of the NEPA documentation, the design of the major units for the PDU was made and bids were obtained from qualified bidders. These bids have now lapsed and new bids must be obtained. As seen in our tentative program schedule, delays due to obtaining the NEPA approval will necessitate extending the program.

FUTURE WORK

During the coming project year, bids for the various sections of the PDU will be assessed and

the cost for the fabrication of the PDU, site preparation, and construction of the remainder of the plant will be estimated. The total estimate for the construction of the PDU will be finalized. Once this plan is approved by DOE and the State of Illinois and the Authority to Construct is obtained, contracts for the plant sections will be issued and construction started.

REFERENCES

1. Bajura, R. A., and M. R. Ghate, "Mild Gasification Offers Coal a Three-Fuel Future," *Modern Power Systems*, October 1986, p. 31-33.
2. Klara, J. M. and Hand, T. J., "Mild Gasification: A New Coal Option," paper presented at Alternate Energy '89, Tucson, Arizona, April 16-18, 1989.
3. Knight, R.A., Gissy, J.L., Onischak, M., Babu, S.P., Carty, R. H. Duthie, R. G., Wootten, H.M., "Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products," Final Report for the Period September 1987-July 1991, Submitted to US DOE Morgantown Energy Technology Center, Morgantown, WV, Contract No. DE-AC-87MC24266, September 1991.
4. Weideman, J. P., "Roofing-Grade Coal Tar Pitches," Koppers company, Inc. Bulletin, Sept 1985.

OF



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2.5

32



2.2



1.1



2.0



1.8



1.25



1.4



1.6

Plenary Session

Summary-Natural Gas Fuel Cells and Natural Gas Turbines

William T. Langan
Morgantown Energy Technology Center

ABSTRACT

Two major programs are being conducted to demonstrate cost-effective, energy efficient, and low environment emission systems for power generation and industrial applications utilizing natural gas as a fuel source. These are the Fuel Cell Program and the Advanced Turbine Systems Program.

Fuel Cell Program

The goal of the fuel cell program is to increase energy and economic efficiency of power generation through the development and commercialization of cost-effective, efficient, and environmentally benign fuel cell systems which will operate on fossil fuels in multiple end-use sectors. The program objectives are to develop and demonstrate cost-effective fuel cell power generation which can be successfully commercialized in the 1990's. Fuel cells produce electricity through the electrochemical oxidation of a fuel. The first market entry units are fueled by natural gas. System studies have shown that fuel cell power plants can be designed with overall system efficiencies in the 50 to 60 percent range. Fuel cell power plants, because of their high efficiency, will help reduce CO₂ emissions that have been linked to "global climatic change." Fuel cells emit very low amounts of NO_x and SO_x in the atmosphere and are extremely quiet. Because of these attributes, they are attractive for future electric utility applications.

The Department of Energy Office of Fossil Energy is participating with the private sector in sponsoring the development of molten carbonate fuel cells and advanced concepts including solid oxide fuel cell technologies for application in the utility and industrial sectors. Phosphoric acid fuel cell development was sponsored by the Office of Fossil Energy in past years and is now being commercialized by the private sector. The fuel cell program has demonstration projects up to 2 megawatts to aid in the market information of the fuel cell technology.

Advanced Turbine Systems Program

The Advanced Turbine Systems Program will develop more efficient gas turbines systems for both utility and industrial electric power generation (including cogeneration). The program will develop base-load power systems for commercial offering in the year 2000. The target fuel for the program is natural gas, however the program will investigate the systems adaptability for coal and biomass firing. The total program costs for the 8-year program are

Jerry Ham
Metairie Site Office

ABSTRACT

The mission of the Environmental/Regulatory Impact Program is to reduce inefficient regulations that impede market operations; promote regulations based on improved scientific information affecting all areas of the gas system; and ensure low cost environmental technology to industry.

Public and regulatory bodies continue to press for more stringent environmental regulations in all energy sectors. Regulations are rapidly becoming more restrictive not only in the levels of pollutants allowed, but also in the number of pollutants regulated. Some environmental statutes require protection of human health and the environment without consideration of potential economic or energy impacts.

There is concern within the exploration and production sectors that increasingly stringent environmental regulations will significantly hinder gas production due to higher compliance costs, without any measurable environmental benefits. This concern will diminish recovery of gas reserves.

In light of this, DOE has taken a proactive role in educating State and Federal government decisionmakers on the cumulative impacts that environmental regulations may have on U.S. gas reserves and production. The agency also attempts to provide industry with the tools to comply with environmental requirements in order to maintain and increase economic gas production, reduce the cost of compliance with current and future requirements, and supply a sound scientific basis for regulation and mitigation measures. The DOE is building a capability to analyze costs and energy impacts of proposed environmental laws and regulations on the gas industry.

The Environmental Sub-program has projects in progress, or planned in the areas of:

- o Gulf of Mexico Discharges
- o Environmental Data Analysis
- o Risk Assessment of Exploration and Production Operations
- o Technology Development to Improve Environmental Performance
- o Environmental Outreach and Technology Transfer

estimated to be \$700 million, consisting of Government cost sharing of approximately \$450 million and \$250 million cost shared by industrial participants.

The Department of Energy's Offices of Fossil Energy and Energy Efficiency and Renewable Energy are jointly responsible for the program. Management of the program is coordinated with the Environmental Protection Agency, the Electric Power Research Institute, the Gas Research Institute, gas turbine manufacturers, the Department of Defense, and others.

The basic program strategy is to fund teams lead by U.S. turbine manufacturers to develop advanced turbine systems from concept and component development to full-scale prototype demonstrations. Major contracts will be competitively awarded, with new competitions at the completion of key development stages. This strategy will allow revaluation of concepts and competitive reduction of the number of systems being developed. Only one utility-scale system and one industrial-scale system will be demonstrated with Federal Government support. In parallel with the major contracts, generic research and development will address key technical issues, and technology will be transferred between this and other programs.

Session LF -- Liquid Fuels Technology

Session LF-4

Gas to Liquids

Overview of PETC's Gas-to-Liquids Program

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and

**Rameshwar D. Srivastava
Burns and Roe Services Corporation**

SUMMARY

The overall goal of the Gas-to-Liquids Program at the U.S. Department of Energy's Pittsburgh Energy Technology Center (PETC) is to develop technologies for the production of hydrocarbon fuels and value-added chemicals from light alkane gases. This research effort has been initiated to develop new or significant innovative improvements over state-of-the-art technologies for the conversion of these gases to marketable fuels and chemicals.

The program is accomplished through staged development from laboratory scale through proof-of-concept scale. Maximum industrial involvement is sought in this program.

CURRENT PROGRAM

PETC's current Gas-to-Liquids Program comprises the development of four primary advanced conversion technologies: partial oxidation; oxidative coupling; pyrolysis; and derivatization, disproportionation, and isomerization.

PARTIAL OXIDATION

Partial oxidation of methane refers to the selective oxidation of methane to methanol or

the conversion of methane to synthesis gas. In both technologies, it is extremely important to control the extent of the oxidation reaction.

Amax Research and Development Center is developing vanadium-phosphate (VPO) catalysts for the partial oxidation of methane to methanol. The vanadium-phosphate catalysts, which have commercial applications in the oxidation of butane to maleic anhydride, are being tailored for application to methane conversion. Amax has developed methods for the synthesis of VPO catalyst precursor and its activation. Currently, the selectivity to methanol is minimal; however, it is hoped that the methanol yield can be increased through the addition of promoters.

A cooperative research and development agreement (CRADA) between Amoco Chemical Company and DOE's Argonne National Laboratory is focusing on the development of oxygen-specific, dense-phase ceramic membranes for the conversion of methane to synthesis gas or methanol. These oxygen-specific membranes permit the passage of oxygen through the membrane while totally excluding nitrogen.

Ceramic powders in the La-Sr-Co-Fe-O system are produced by a solid-state reaction of the constituent carbonate and nitrates. A plastic extrusion technique is used to fabricate the membrane tubes. The extruded tubes are heated and sintered before they are installed in methane conversion reactors, where high methane

conversion efficiencies are expected. If successful, such membranes will permit control of oxygen in the reactor to prevent overoxidation. This will substantially improve the economics of both synthesis gas production technologies and direct conversion technologies for methanol.

Sandia National Laboratory continues to conduct and evaluate the use of biomimetic methods that use the computer-aided molecular design (CAMD) techniques. Through the proper design of the catalyst, it is felt that methane can be selectively converted to methanol at rates that would be of commercial interest.

OXIDATIVE COUPLING

In oxidative coupling, methane and oxygen are catalytically converted to ethylene and/or other intermediates that may be converted further to petrochemicals or other "end use" fuels via existing commercial technologies. Despite numerous investigations, commercially acceptable yields have not yet been achieved.

Worcester Polytechnic Institute (WPI) is developing inorganic membrane reactors for oxidative coupling of methane for the production of C₂ hydrocarbons. Membrane reactors provide optimal quantities of oxygen to provide high selectivities and high yields of C₂ hydrocarbons. Significant work has been performed in developing and testing perovskites, which are selective to oxygen permeation inside the pore structure of alpha-alumina membranes. A membrane reactor was built and the reactor circuit was completed. Selective catalysts are being synthesized and tested.

PYROLYSIS

In pyrolysis, methane is converted directly to olefins, aromatics, or other higher

hydrocarbons by decomposition of methane under controlled thermal and catalytic conditions. SRI International is developing fullerene-based catalysts for the conversion of methane to higher hydrocarbons. Fullerenes ("Buckyballs"), which are new allotropes of carbon, are closed shells of sixty or more atoms. Fullerenes can stabilize methyl radicals, shuttle H-atoms, and act as electrophiles. These properties facilitate catalysis and selective control of the conversion of methane to more selective hydrocarbons at low reaction temperatures.

Altamira Instruments, Inc. is developing a process based on methane pyrolysis followed by rapid quenching of products in a novel reactor. The products are rapidly quenched so that reactions of intermediates to undesirable products can be prevented. This pyrolysis process can produce valuable aromatics. In addition, both free-radical initiators and catalysts will be studied for their possible role in assisting the pyrolysis step.

DERIVATIZATION, DISPROPORTIONATION, AND ISOMERIZATION

The derivatization approach for the conversion of methane to fuels and chemicals is characterized by a two-step process. The first deals with the conversion of methane to a reactive intermediate that can be processed further in a second stage to yield the desired product. Disproportionation and isomerization reactions first convert the light hydrocarbon gases to valuable precursors that can be further processed to liquid fuels.

Oxyhydrochlorination research aims to develop a process for the conversion of light alkane gases to methyl chloride. The methyl chloride can be converted to gasoline-range hydrocarbons. The process was originally developed at PETC. Building upon this work, Dow

Coming Corporation is developing efficient methods for converting methane directly to methyl chloride for subsequent use in the production of silicon polymers. An absorption and stripping system has been developed and considerable work has been performed in the development of copper oxyhydrochlorination catalysts. The oxyhydrochlorination route is more advanced than any other direct conversion technology. This direct route is economically attractive since it will replace methanol (produced from methane via synthesis gas), which is used for the commercial production of methyl chloride.

Using low-cost, recyclable, alkaline earth metal oxides, researchers at the Massachusetts Institute of Technology (MIT) are developing a process that converts methane to solid metal carbides that can be stored, transported, and hydrolyzed to acetylenes. These acetylenes can be converted readily to premium liquid fuels and petrochemicals. A new laboratory-scale plasma reactor has been constructed and tests will be made to convert methane to calcium and magnesium carbides.

The Institute of Gas Technology has begun research on the conversion of methane to carbon disulfide, which can then be converted to hydrocarbons. The first step is unique because it produces hydrogen for use in the second step which reduces the carbon disulfide to gasoline-range hydrocarbons. The University of Delaware has recently initiated work on the use of superacid catalysts for the conversion of light hydrocarbon gases.

FUTURE PLANS

In FY 94, no new projects are expected to be added to the current program. Continued assessment of the potential of the current technologies will determine the economics of these processes for methane gas conversion. For those projects for which commercial targets have not yet been established, Burns and Roe Services Corporation will perform in-depth analyses to determine the commercial targets.

**LF-4.2 Direct Conversion of Methane to Methanol in a
Non-Isothermal Catalytic Membrane Reactor**

CONTRACT INFORMATION

CONTRACT INFORMATION

Contract Number	DE-FG21-90MC27115
Contractor	Department of Chemical Engineering University of Colorado at Boulder Boulder, CO 80309-0424
Contractor Project Manager	Richard D. Noble
Principal Investigators	John L. Falconer Richard D. Noble
METC Project Manager	Venkat K. Venkataraman
Period of Performance	July 19, 1990 to October 1, 1993
Schedule and Milestones	

FY94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J
Modify the reactor system.											
Verify the roles of the catalyst and the membrane.											
Optimize CH ₃ OH yield.											
Annual Report.											

Abstract

The direct partial oxidation of CH₄ to CH₃OH has been studied in a non-permselective, non-isothermal catalytic membrane reactor system. A cooling tube introduced coaxially inside a tubular membrane reactor quenches the product stream rapidly so that further oxidation of CH₃OH is inhibited. Selectivity for CH₃OH formation is significantly higher with quenching than in the

experiments without quenching. For CH₄ conversion of 4% to 7%, CH₃OH selectivity is 40% to 50% with quenching and 25% to 35% without quenching.

OBJECTIVES

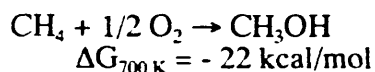
The abundance of natural gas and the steadily

growing world consumption of CH₃OH have increased the need for better ways to convert CH₄ to CH₃OH. Currently, the commercial process for CH₃OH production from CH₄ involves the high-temperature, highly-endothermic steam reforming of CH₄, followed by low temperature CH₃OH synthesis. The direct partial oxidation of CH₄, unlike steam reforming, is highly exothermic, and does not require energy input. A one-step conversion would simplify the utilization of the vast natural gas reserves, many of which are located in remote areas.

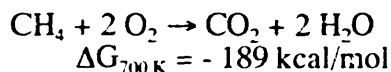
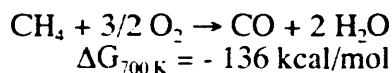
The objectives of this study are to demonstrate the effectiveness of a membrane reactor for the partial oxidation of CH₄ and to better understand the mechanisms inside the membrane reactor. The specific goals are to demonstrate that we can improve CH₃OH yield and to determine the optimal conditions for reactor operation.

BACKGROUND INFORMATION

Thermodynamically, the partial oxidation reaction of CH₄



is feasible, but the reactions



are more favored (1). This means that CH₃OH, an intermediate product, would not be present if the process went to completion. Thus, most published studies of partial oxidation of CH₄ by O₂ report significant selectivity for CH₃OH only at very low CH₄ conversions.

Both homogeneous and heterogeneous oxidation processes have been studied. Helton (2) found that with 6.5% O₂ in the feed gas, selectivities to CH₃OH were 30% to 35% with 99% O₂ consumption at 5 MPa and 675 K. Foulds et al. (3, 4) and Foral (5) reported that, for an O₂ concentration of 8%, the selectivities to CH₃OH were 30% and lower. Recently, Chun and Anthony (6, 7) reported CH₃OH selectivities between 30%

to 40% at an O₂ concentration of 4.35%. All of these studies reported that CH₃OH selectivities decreased with increased temperature and O₂ concentration. For example, when the O₂ concentration in the feed gas increased to 9.5%, Helton (2) observed that selectivities to CH₃OH decreased to 25% or 30%. Foulds et al. (4) observed the selectivity to CH₃OH decreased from 38% at an O₂ concentration of 5% to 28% at an O₂ concentration of 7.5%.

Hunter et al. (8), and Yarlagadda et al. (9), using pressures from 2 to 12.5 MPa and temperatures from 625 to 755 K, observed CH₃OH selectivities over 80% at CH₄ conversion levels up to 10%. Hunter et al. (8) also observed that the addition of sensitizers (e. g., higher hydrocarbons) to the system reduced the reaction temperature and increased the selectivity to CH₃OH. This indicated that natural gas was a better feed than pure methane. However, their results have been difficult to reproduce in other laboratories (10, 11).

PROJECT DESCRIPTION

Selective and continuous removal of CH₃OH from the reaction zone will increase CH₃OH selectivity, but no process has been successfully demonstrated. Another way to increase CH₃OH selectivity is to inhibit further oxidation of CH₃OH. A modified membrane reactor design was used in an attempt to remove CH₃OH from the reaction region before further oxidation. A cooling tube was inserted inside the membrane reactor so that the system operated non-isothermally. A low temperature region was created within the reactor by the cooling tube, and the product stream reaching this region was quenched. Further oxidation of CH₃OH was effectively inhibited and the selectivity to CH₃OH was increased.

High Pressure System

A high pressure membrane reactor system (designed for a pressure of 10 MPa) was built for this study (Figure 1). Brooks mass flow controllers were used to meter the reactant gases into the system. A 1-m long, 6.35-mm OD stainless steel tube was used to mix CH₄ and O₂ before they enter the reactor. A stainless steel reactor was designed to allow leak-free connection of the ceramic and metallic parts. A quartz tube was inserted into the reactor to isolate the hot stainless steel surface from the reactant mixture. The reactor was externally heated by a Mellen cylindrical furnace. The pressure

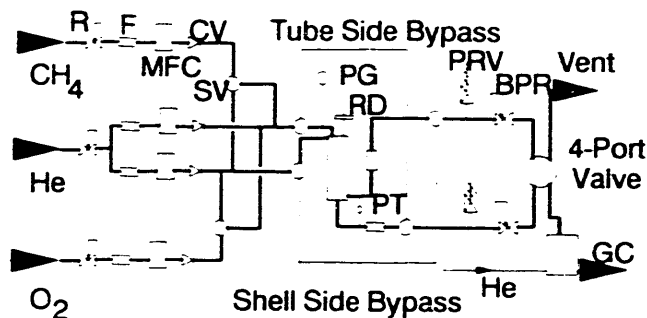


Figure 1. System Diagram

of the system was controlled by TESCO back-pressure regulators installed downstream of the reactor. On-line analysis was done by an HP 5390 gas chromatograph equipped with a thermal conductivity detector.

Catalyst

A 6.35 mm OD stainless steel tube was used as a model plug flow reactor to carry out catalyst studies. A CuO/SiO_2 catalyst, T-1506, from United Catalysts Inc. formed only a trace amount of CH_3OH . Several molybdena based catalysts prepared in this laboratory were used and the best was 1.5% $\text{MoO}_3/\text{SiO}_2$, which yielded 25% selectivity to CH_3OH in the model reactor. A $\text{V}_2\text{O}_5/\text{SiO}_2$ catalyst was a good catalyst for CH_2O formation. Neither $\text{FeO}_3/\text{MoO}_3/\text{SiO}_2$ nor $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts produced CH_3OH under our experimental conditions. Thus, $\text{MoO}_3/\text{SiO}_2$ was used in the membrane reactor.

Quenching Method

A tube with cooling water inside was inserted into the center of the membrane tube (Figure 2) to create a low temperature zone in the reactor. The product stream was collected from the tube side of the membrane. The flow of the gas stream through the membrane was perpendicular to the cold front, and when the gas reached the cool region, its temperature decreased rapidly. Experiments run without quenching indicated that quenching inhibited further gas phase reactions. Without quenching, the temperature of the region inside the reactor was more uniform, but it was probably not isothermal.

Experimental Operation

Ceramic membranes with an average pore diameter of 5 nm and an outer diameter of 10 mm were used. The 15 cm-long membrane tube was glued to two supporting, nonporous α -alumina tubes. The catalyst layer (average thickness was approximately 1 mm) was wrapped on the outside

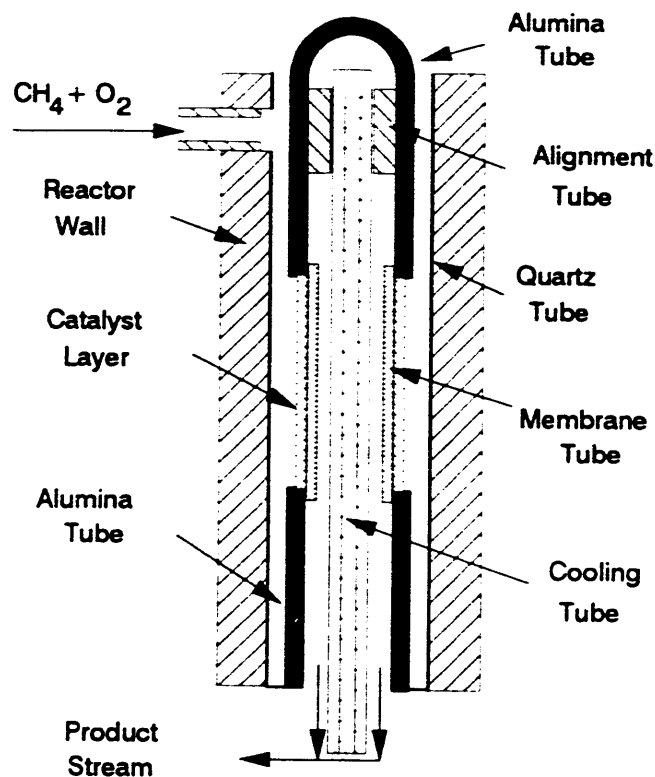


Figure 2. Reactor Diagram

of the membrane by an aluminium foil with small holes. With quenching, the temperatures of outer wall of the reactor were 770 to 830 K. Lower temperatures were used (690 to 710 K) in the absence of quenching because of the smaller radial temperature gradient inside the reactor. Chromel-alumel thermocouples with 304 stainless steel sheaths were inserted to measure the temperatures of the catalyst bed and the exit cooling water. A reactant mixture (8% O_2 in CH_4) was fed into the shell side of the membrane reactor with a flow rate of 0.2 to 0.5 L/min. The residence time in the shell side was about 10 to 20 s, including the time for preheating. The stream permeated radially through the catalyst layer and the membrane and was then quenched. This low temperature stream then left the reactor for GC analysis.

RESULTS AND DISCUSSION

The selectivity to CH_3OH was 40 to 50% with the quenching at a CH_4 conversion level of 4 to 7%.

Without quenching, this selectivity decreased to 25 to 35% at similar CH_4 conversion levels. Methanol selectivity is plotted in Figure 3 as a function of CH_4 conversion at a constant flow rate of 0.5 L/min and a constant pressure of 3.5 MPa. The CH_3OH selectivities decreased with increased CH_4 conversion. With quenching, CH_3OH selectivity was about 50% at 4% CH_4 conversion and about 40% at 7% CH_4 conversion. Without quenching, CH_3OH selectivity varied from 35% at 3% CH_4 conversion to 25% at 7% CH_4 conversion. Quenching significantly improved CH_3OH selectivity in this process.

Although the cooling tube improved CH_3OH selectivity, it also caused the membrane to break, due to the large radial thermal gradient and the different axial thermal expansion between the hot stainless steel reactor wall and the cooler ceramic tubes. To solve this problem, a porous metal tube with 0.5 μm pore size was used instead of ceramic membrane. Results from both ceramic membranes and porous metal tubes are included in Figure 4. Although CH_3OH selectivities were almost the same for both ceramic membranes and porous metal tubes, the methane conversions were slightly higher when ceramic membranes were used.

Figure 5 shows that the combined selectivities of CH_3OH and CO were almost constant at 85 to 90%, with the rest being CO_2 , both with and without quenching. Helton (2) made the same observation. Carbon dioxide was detected at low CH_4 conversions in this study, but CO was detected only when CH_3OH or CH_2O were detected. These results indicated that CO_2 was formed from direct oxidation of CH_4 , but CO may have formed from oxidation of CH_3OH and CH_2O . This is in agreement with the

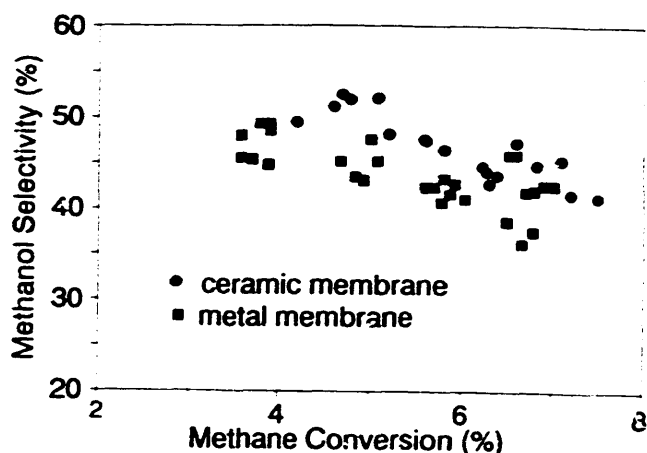


Figure 4. CH_3OH Selectivity vs CH_4 Conversion

observations by Spencer et al. (12, 13). Thus, when quenching was used, the CO selectivity decreased as CH_3OH selectivity increased.

Our selectivities to CH_3OH without quenching were almost the same as those recently published (Table 1). With quenching, CH_3OH selectivities were higher, even though we used pure CH_4 . Higher selectivities to CH_3OH might be expected for natural gas. Formaldehyde selectivities were 1 to 3% at low CH_4 conversion (about 4%), and it was detected only in trace amounts at higher CH_4 conversion. Carbon, hydrogen and oxygen mass balances were all in the range of $100 \pm 5\%$.

Other quenching methods have been reported (2, 15, 16). Dowden and Walker (15) injected liquid water directly into their product stream, and this cooled the stream below 473 K within 30 ms. No comparison data were presented without quenching. Wilms (16) also described a rapid quenching method. At pressures of 4 to 6 MPa and temperatures

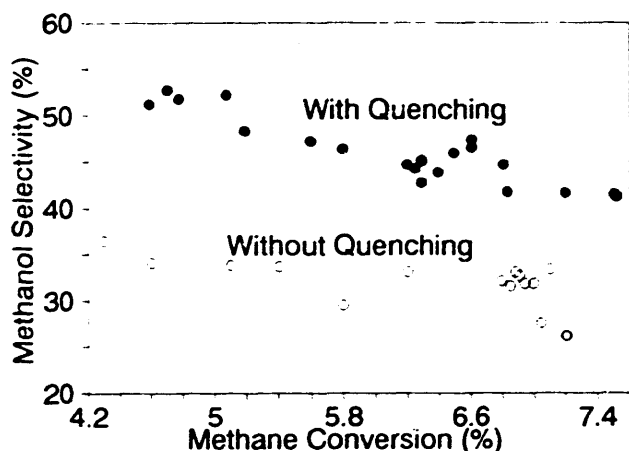


Figure 3. CH_3OH Selectivity vs CH_4 Conversion

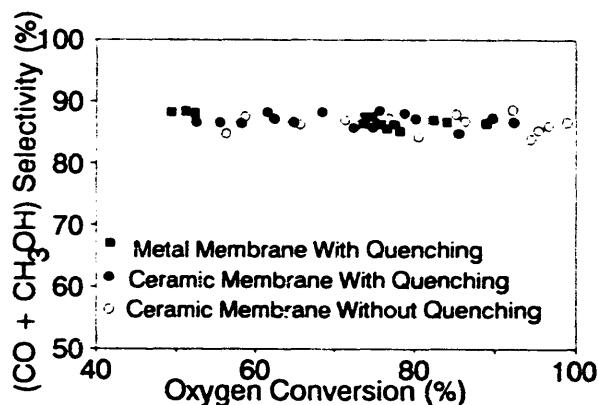


Figure 5. Combined Selectivity vs O_2 Conversion

Table 1. Recently Studies on CH₄ to CH₃OH

T (K)	P (MPa)	Feed	Catalyst	CH ₃ OH Selectivity (mol %)	CH ₄ Conversion (mol %)	Reference
660- 730	5.0	Nat Gas 5 - 6% O ₂	MoO ₃ SiO ₂	25-35	5-7	2
723	5.0	Nat Gas 5% O ₂	Quartz	20-30	2-6	19
650 - 730	3 - 5	CH ₄ 4-8% O ₂	No	30-35	4 - 4.5	3, 4
700	10	Nat Gas 5% O ₂	No	30-35	3 - 5	5
738	6.2	CH ₄ 3.8% O ₂	Sand	34.9	2.9	20
738	6.2	CH ₄ 7% O ₂	Sand	13.2	5.2	20
705 - 770	5.0	CH ₄ 4.35% O ₂	Pyrex	35 - 40	2 - 4	6, 7
770 - 770	5.0	CH ₄ 4.35% O ₂	FeMo, CuMo Ti, V Si, Sn Ti	25 - 30	2 - 4	6, 7

between 743 and 793 K, CH₄ and air were mixed in a small stainless steel reactor. After a residence time of 0.3 to 1.2 min. the mixture was quenched by expansion through a Delaval nozzle. A maximum CH₃OH selectivity of 85% was reached, but the CH₄ conversion was low, only 0.01 to 0.1%. Although these studies concluded quenching was useful, a comparison study by Helton (2) found that quenching had no influence on product selectivities. He cooled the product stream below 535 K at the exit of the reaction zone by cryogenic quench. Selectivities for products were the same as those without quenching.

The quenching method we used has several advantages over previous approaches (2, 15, 16). No extra water is added into the product stream and thus the downstream separation is simplified. The small gas-stream pressure drop makes recycling of unconverted CH₄ easy. A significant difference from previous approaches is that this method quenches the product stream within the reactor instead of after the reactor exit. Quenching improved the process by inhibiting further reactions of CH₃OH. The cooling tube also removed the reaction heat and thus the reaction temperature could be better controlled. In other reactor configurations, reaction heat can raise the reaction temperature, which can accelerate CH₃OH oxidation.

Large discrepancies in CH₃OH selectivities and CH₄ conversions have been reported, with CH₃OH selectivities ranging from less than 10% (17) to over

80% (8, 9, 14). Brown and Parkyns (18), and Burch et al. (11) suggested that CH₃OH selectivity is sensitive to temperature distribution, flow configuration, and detailed reactor design.

FUTURE WORK

The temperature measured for the catalyst layer is about 470 K when the temperature of exiting water from the cooling tube was about 300 K. This temperature is not high enough to catalyze the reaction. The catalyst layer may act as a high surface area material to inhibit free-radical, gas-phase reactions. The membranes, both ceramic and metal membranes, do not effect any separations. Thus the roles of catalyst and membrane in this process will be investigated. Systematic experiments will be performed to better understand the mechanisms inside the reactor, and suitable conditions will be determined to obtain optimal CH₃OH yield.

Low oxygen concentration have been used to stay below the explosion limit. This means the yield of methanol is small. One possibility to increase CH₄ conversion is to use air-like mixture instead of pure O₂. A reactant mixture above the upper explosion limit of methane may be used. Under our experimental conditions, this limit is about 25% methane in air.

REFERENCES

1. Pichai, R. and Klier, K., Partial Oxidation of Methane. *Catal. Rev. Sci. Eng.* **28**, 13 (1986).
2. Helton, T. E., Methanol and Carbon Monoxide Production From Natural Gas. *Ph.D. Dissertation*. Texas A & M University. (1991).
3. Foulds, G. A., Miller, S. A. and Walker, G. S., Gas Phase Partial Oxidation of Methane. *Prep. Symp. - Am. Chem. Soc., Div. of Petro. Chem., Natural Gas Upgrading II.* **37**, 26 (1992).
4. Foulds, G. A., Gray, B. F., Miller, S. A. and Walker, G. S., Homogeneous Gas-Phase Oxidation of Methane Using Oxygen as Oxidant in an Annular Reactor. *Ind. Eng. Chem. Res.*, **32**, 780 (1993).
5. Foral, M. J., The Noncatalytic Partial Oxidation of Natural Gas to Methanol. *Prep. Symp. - Am. Chem. Soc., Div. of Petro. Chem., Natural Gas Upgrading II.* **37**, 34 (1992).

6. Chun, J. W. and Anthony, R. G., Catalytic Oxidation of Methane to Methanol. *Ind. Eng. Chem. Res.*, **32**, 259 (1993).
7. Chun, J. W. and Anthony, R. G., Partial Oxidation of Methane, methanol, and Mixture of Methane and Methanol, Methane and Ethane, and Methane, Carbon Dioxide, and Carbon Monoxide. *Ind. Eng. Chem. Res.*, **32**, 788 (1993).
8. Hunter, N. R., Gesser, H. D., Morton, L. A., Yarlagadda, P. S. and Fung, D. P. C., Methanol Formation at High Pressure by the Catalyzed Oxidation of Natural Gas and by the Sensitized Oxidation of Methane. *Appl. Catal.*, **57**, 45 (1990).
9. Yarlagadda, P. S., Morton, L. A., Hunter, N. R. and Gesser, H. D., Direct Conversion of Methane to Methanol in a Flow Reactor. *Ind. Eng. Chem. Res.*, **27**, 252 (1988).
10. Thomas, D. J., Willi, R. and Baiker, A., Partial Oxidation of Methane: The Role of Surface Reaction. *Ind. Eng. Chem. Res.*, **31**, 2272 (1992).
11. Burch, R., Squire, G. D. and Tsang, S. C., Direct Conversion of Methane into Methanol. *J. Chem. Soc., Faraday Transactions*. **85**, 3561 (1989).
12. Spencer, N. D., Partial Oxidation of Methane to Formaldehyde by Means of Molecular Oxygen. *J. Catal.*, **109**, 187 (1988).
13. Spencer, N. D. and Pereira, C., V_2O_5 - SiO_2 Catalyzed Methane Partial Oxidation with Molecular Oxygen. *J. Catal.*, **116**, 399 (1989).
14. Gesser, H. D., Hunter, N. R. and Prakash, C. B., The Direct Conversion to Methanol by Controlled Oxidation. *Chem. Rev.*, **85**, 235 (1985).
15. Dowden, D. A. and Walker, G. T., *GB Patent 1,244,001* Aug. 25, 1971.
16. Wilms, M., Methode zur kinetischen kontrolle der methanoxidation. *Ph.D. Dissertation*. Technische Hochschule Aachen, (1989).
17. Fukuoka, N., Omata, K. and Fujimoto, K., Effect of Additives on Partial Oxidation of Methane. *Pacificchem'89, Abstract, Conference proceedings*, 135 (1989).
18. Brown, M. J. and Parkyns, N. D., Progress in the Partial Oxidation of Methane to Methanol and Formaldehyde. *Catal. Today*. **8**, 305 (1991).
19. Rytz, D. W. and Baiker, A., Partial Oxidation of Methane to Methanol in a Flow Reactor at Elevated Pressure. *Ind. Eng. Chem. Res.*, **30**, 2287 (1991).
20. Walsh, D. E., Martenak, D. J., Han, S. and Palermo, R. E., Direct Oxidative Methane Conversion at Elevated Pressure and Moderate Temperature. *Ind. Eng. Chem. Res.*, **31**, 1259 (1992).

LF-4.3**Catalytic Conversion of Light Alkanes--
Research and Proof-of-Concept Stages****CONTRACT INFORMATION**

Contract Number DE-FC21-90MC26029

Contractor Sun Company, Inc.
P.O. Box 1135
Marcus Hook, PA 19061
(215) 447-1731

Contractor Project Manager/P.I. Dr. James E. Lyons

Business Coordinator Dr. Allen W. Hancock, II

METC Project Manager Rodney D. Malone

Period of Performance May 1, 1992 to October 30, 1993

Schedule and Milestones

1992
M J J A S O N D

1993
J F M A M J J A S O

RESEARCH STAGE:

Synthesize, Characterize, Test
Catalysts for Alkane Oxidation

Phase I Metalloporphyrins

Phase II Poloxoanions

Phase III Metal Oxides

NO COST EXTENSION:

Complete Research Stage

PROOF-OF-CONCEPT STAGE:

Isobutane Oxidation

Process Development

C₁-C₃ Research

OBJECTIVES

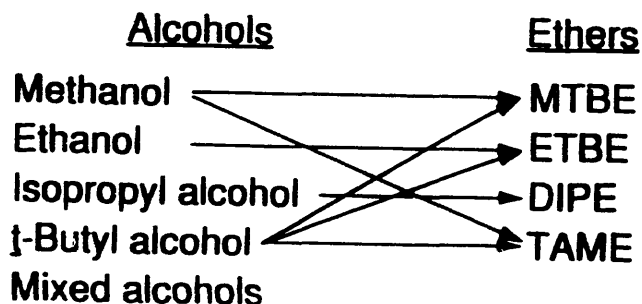
The objective of this program is (1) to find new materials which are able to catalyze the direct reaction of light alkanes (methane, ethane, propane, butanes with molecular oxygen to form alcohols and (2) to develop practical processes for the direct oxidative conversion of natural gas and its C₁-C₄ components producing high performance alcohol-rich liquid oxygenates for use both as alternative transportation fuels and as environmentally superior reformulated gasolines.

BACKGROUND INFORMATION

Natural gas is an abundant resource that can provide an inexpensive feedstock for production of liquid transportation fuel. Light hydrocarbons whether from natural gas or petroleum refining are rejected in large part from the gasoline pool in response to environmental regulations of vapor pressure emissions. The direct reaction of light alkanes with air or oxygen to give an alcohol-rich oxidate would: a) utilize inexpensive feedstocks unacceptable for liquid transportation fuel use, b) produce a material that would have superior gasoline performance properties such as driveability and high octane, c) produce a clean-burning alternative to conventional gasoline for use in areas that fail to meet air quality standards, and d) produce oxygenates to be used in reformulated gasolines that meet Clean Air Act Amendment guidelines for oxygenate content and pollution abatement. The alcohols that might be derived from the C₁-C₄ component of natural gas (methane, ethane, propane, butanes) together with the ethers that can be made from them would represent nearly the entire range of oxygenates that will be used in reformulated gasoline, Figure 1. Their properties, Table 1, are generally excellent for use in gasoline.

There are, however, no commercial catalysts or processes for performing the DIRECT air oxidation of a light alkane to an alcohol efficiently and in good yield and selectivity. Commercial liquid or vapor phase

Figure 1. Oxy Synguels



Alcohol-ether blends

oxidation catalysts give much deeper oxidations and do not produce alcohols as reaction products(1,2). Biological catalysts such as Cytochrome P-450 which hydroxylates C-H bonds in the liver (3) and methane monooxygenase which converts methane to methanol (4) are enzymatic catalyst systems that perform the chemistry of interest, Figure 2. Cytochrome P-450 has an oxidation-active iron center in a porphyrin macrocycle (heme) whereas MMO is a diiron non-heme catalyst. The biological systems have many drawbacks, however. Firstly, they are not robust to industrial processing conditions; secondly, they require the stoichiometric use of costly coreductants; and thirdly they are monooxygenases and use only half of the added oxygen to make product, wasting the rest in water production. Nonetheless, we felt that there was much that could be learned from these systems about how to construct industrial catalysts that might possess some of their desirable features including oxygen activation and alcohol production, while avoiding some of the pitfalls of the biological catalysts. In this paper we show how we have produced families of catalysts using biological design criteria which give unprecedented alkane oxidation activity and have moved from the research stage into proof-of-concept mode for alcohol production.

Table 1. PROPERTIES OF ETHERS AND ALCOHOLS

<u>PROPERTY</u>	<u>MTBE</u>	<u>ETBE</u>	<u>GTBA</u>	<u>IPA</u>	<u>ETOH</u>	<u>MeOH</u>
Oxygen, wt %	18.2	15.7	21.6	26.6	34	49.9
Sp. Gravity	0.74	0.74	0.791	0.789	0.79	0.796
Boiling Point, °F	131	163	181	180	172	149
RVP (lbs/in ²)	7.8	2.5	1.8	1.8	2.3	4.6
Blending RVP	9	5	12	14	23	75
RON BV	110-122	117-121	~103	113-119	~122	126
MON BV	98-102	100-105	~91	95-101	~96	104
(R+M)/2 BV	103-110	~110	~97	104-110	~100	115

PROJECT DESCRIPTION

Consideration of the proposed mechanism for the oxidation activity of Cytochrome P-450 and Methane Monooxygenase, Figure 2, suggested to us that a catalyst which was able to reductively bind oxygen, not between an iron(III) center and a proton as do the biological systems, but between two iron(III) centers, Figure 3, might give the desired dioxygenase activity for alkane hydroxylation (5-10). We decided to use metals in synthetic porphyrins or related macrocycles to simulate P-450 activity and metals in polyoxoanions and zeolitic frameworks to look for MMO-like activity. Substituting all of the C-H bonds with C-F or C-X bonds in porphyrin-like macrocyclic metal complexes ("Teflon Porphyrins") would produce a catalyst thermally and oxidatively stable enough to withstand industrial processing conditions. Polycxoanionic and zeolitic structures should provide stable frameworks for oxidation active metal centers as well. Finally, if catalytic processes similar to the hypothetical pathway shown in Figure 3 could be achieved, highly electron deficient metal complexes would be required in order to generate the extraordinarily high M(III)/M(II) reduction potentials needed to return M(III) to the catalytically active M(II) and to complete the catalytic cycle. Thus,

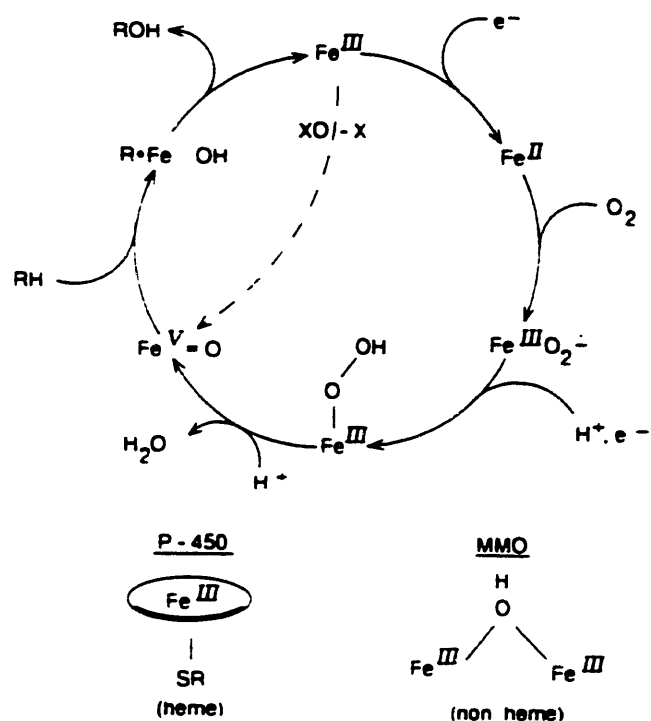


Figure 2. Biological/Blomimetic Alkane Oxidation

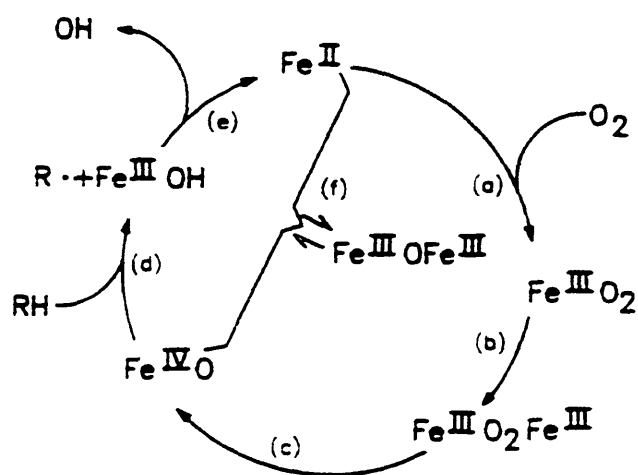


Figure 3. Hypothetical Synthetic Dioxygenase

early work in our laboratories (5-14) showed that selective oxidation of light alkanes could be accomplished by oxidation active metal centers in electron deficient porphyrin-like macrocycles, polyoxoanions and zeolites. Catalysts containing iron centers were among the most active of our early systems.

During the period of performance summarized in this report, we completed the research phase designed to synthesize, characterize and test catalysts of the type referred to above and found high activity and selectivity to alcohols and related oxygenates. For this reason we have entered the proof-of-concept stage of this work aimed at generating practical catalytic conversion methods. Because the ease of activation of C-H bonds over our catalysts follows the order: isobutane > propane > ethane > methane, we will demonstrate proof-of-concept of a process from field butanes to tert-butyl alcohol first. During this time there will be continued research activity on the alkanes C₁-C₃ so that on completion of the isobutane work we will be prepared to enter the proof-of-concept stage for a propane to isopropyl alcohol (IPA) process. Development of processes to convert methane and natural gas to methanol will follow successful completion of these studies.

RESULTS

Oxidation-Active Metal Centers in Electron Deficient Macrocycles. Work in our laboratories has demonstrated direct correlations between the degree of oxidation activity of the corresponding metalloporphyrin complex. The best catalysts in these series were iron complexes, although complexes of Co, Ru, Mn, and Cr were also active. We further found a correlation between the degree of halogenation and the Fe(III)/Fe(II) reduction potential in a series of iron haloporphyrins. Finally, as shown in Figure 4, there is a direct relationship between the Fe(III)/Fe(II) reduction potential and the catalytic activity for the air-oxidation of both isobutane and propane in benzene as solvent. Rates and selectivities (~90%) were so encouraging that we studied oxidations of neat isobutane in a well controlled automated 500ml autoclave, Table 2.

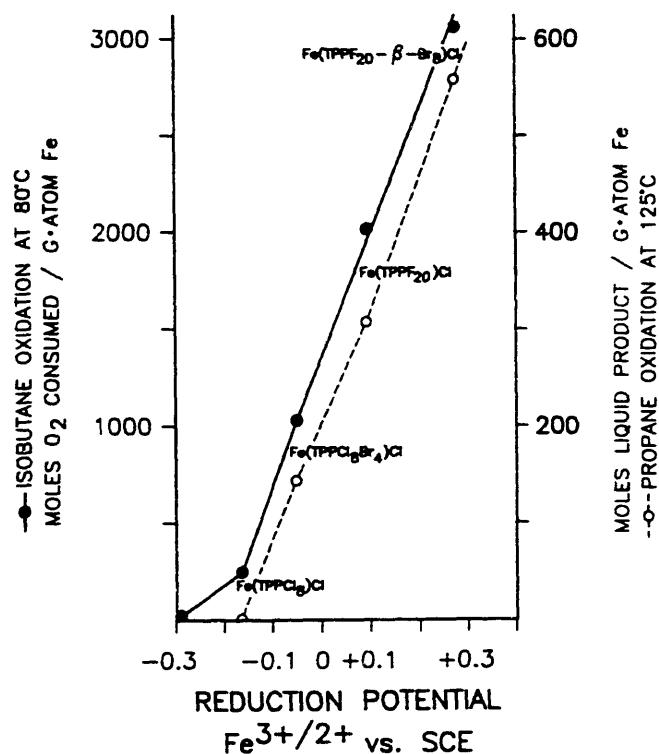


Figure 4. Catalyst Activity vs. Redox Potential

Table 2. IRON HALOPORPHYRIN-CATALYZED ISOBUTANE OXIDATIONS^a

CATALYST	T, °C	T, HRS	CHARGE TO REACTOR		CONVERSION	SELECT.	
			i-C ₄ H ₁₀	O ₂	i-C ₄ H ₁₀ , %	TBA, % ^b	ION ^c
Fe(TPPF ₂₀ β-Br ₈)Cl	80	3	1870	53	17	87	10,660
	80	3	1862	100	28	83	17,150
	80	3	1865	47	14	91	8,420
	25	71.5	1862	53	22	92	13,560
Fe(TPPF ₂₀)OH	24	143	1871	53	18	95	12,150

a). ISOBUTANE OXIDIZED BY AN OXYGEN-CONTAINING GAS (75 ATM, DILUENT = N₂), LIQ. PHASE (180 ml), 3 HOURS. O₂ ADDED AS USED.

b) (MOLES TBA/MOLES LIQUID PRODUCT) × 100.

c) MODELS (TBA + ACETONE) PRODUCED/MOLE CATALYST USED.

Unprecedented rates of alkane oxidation were observed for the perhaloporphyrinato iron complex, Fe(TPPF₂₀β-Br₈)Cl. The X-Ray crystal structure of this catalyst was determined for the first time, Figure 5, (15),(16) and was virtually identical to the structure proposed by our earlier molecular design techniques.

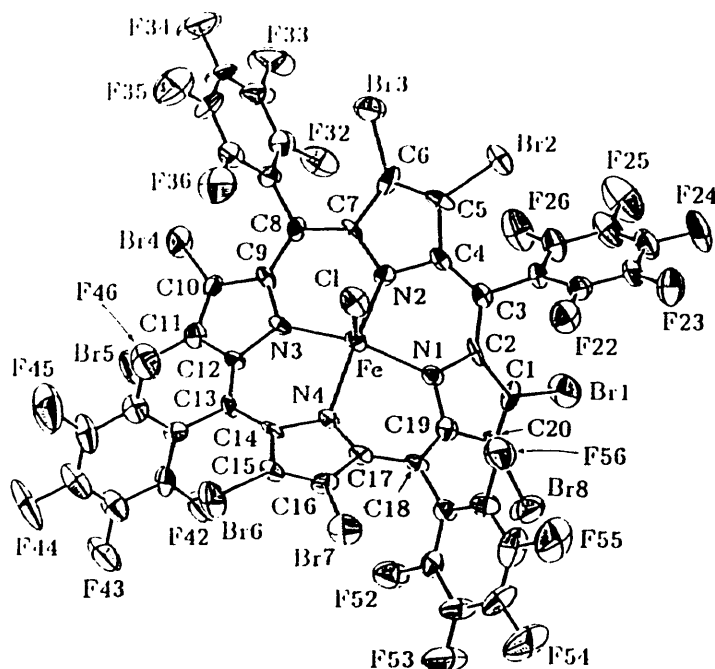


Figure 5. X-Ray Structure of Fe(TPPF₂₀β-Br₈)Cl

We also made the perhaloporphyrin complex, Fe(TPPF₂₀β-Cl₈)Cl, and found that it had similarly high activity. Thus, replacing the 28 hydrogens of tetraphenylporphyrinatoiron complexes with halogens had created a relatively robust highly active electron deficient metaloporphyrin catalyst which was **more than an order of magnitude more active** than any known alkane oxidation catalyst to date. We were so encouraged by these results that we moved into the proof-of-concept phase for this research. We will use metaloporphyrins or related macrocyclic complexes for future process research in the areas of oxidation of isobutane to TBA and propane to IPA.

Oxidation-Active Metal Centers in Polyoxoanions. Oxidation-active metals such as Mn, Cr, Ru, Fe, Co and others have been placed in the framework of heteropoly acids and polyoxoanions such as those having the Keggin structure (17). These complexes and their syntheses have been described in previous reports to this group (17,18). Structures having one metal center as well as two and three adjacent metal centers were prepared. When two or more oxidation-active metal centers were introduced they could be the same or different. The Keggin catalysts were thermally stable. They could accept

Table 3.
Isobutane Oxidations Catalyzed by Polyoxometallates^a

Catalyst μ Moles	Time Hrs.	Products, mMoles			iC_4 Conv. %	TBA Sel. %	TO Moles PROD/ Mole CAT
		TBA	TBH	Acetone			
$(Bu_4N)_6[PW_9Cr_3O_{37}]-6$	6	6	11	2	2	32	3,200
$H_6[PW_9Cr_3O_{37}]-5$	6	2	2	2	1	22	1,500
$(Bu_4N)_6[PW_9Fe_3O_{37}]-6$	6	2	5	1	1	22	1,300
$H_6[PW_9Fe_3O_{37}]-2$	3	11	4	1	2	64	3,300
$(Bu_4N)_6[PW_9Fe_2NiO_{37}]-6$	6	6	8	2	2	37	2,700
$H_6[PW_9Fe_2NiO_{38}]-5$	6	8	12	2	2.5	32	5,000
$(Bu_4N)_6[PW_9Fe_2NiO_{38}]-6^b$	6	9	10	9	3	33	4,700

^a Isobutane, 1.0 mole, was added to the catalyst and sodium azide, 0.10 g in 37.7 g of acetonitrile and 1500 psig of air was added to the reactor. The reaction mixture was heated for the designated time, cooled, and analyzed by GC.

^b No sodium azide added to this run.

adjacent iron centers and could, therefore, serve as MMO models. Liquid phase oxidations of methane, ethane, propane and isobutane were carried out. Isobutane oxidations such as those shown in Table 3, suffered from low selectivity since *tert*-butyl hydroperoxide, TBHP, was always a major oxidation product. Propane oxidations occurred at a rapid rate only at temperatures of 150°C or above and selectivity was also modest. In addition, hydrolytic stability and solubility limited the homogeneous catalytic application of these catalysts. Attempts to adjust M(III)/M(II) reduction potential met with some success but these catalysts never exhibited the superb low temperature oxidation activity of the metalloporphyrins nor did reactions give the high selectivities of the electron-deficient macrocyclic complexes. The decision, therefore was made to go forward in proof-of-concept mode with the electron-deficient macrocyclic complexes rather than with polyoxoanionic complexes.

Ethane and methane were also oxidized in

benzene solution in the presence of a variety of framework substituted Keggin polyoxoanions and heteropolyacids. Methane yields and selectivities were extremely low and rates were very slow. The heterogeneous catalysts discussed in the next section were far superior for methane oxidation. Although interesting selectivities were obtained for ethanol from ethane, some of our heterogeneous zeolite catalysts were superior for ethane oxidation as well. Thus, it seems that although the Keggin catalysts were able to promote all of the reactions of interest (19-23) the electron deficient porphyrins were superior for isobutane and propane oxidations, and the zeolite or related heterogeneous catalysts were better for methane and ethane. Future work on Keggin polyoxoanions will therefore be restricted to their use as precursors of heterogeneous catalysts.

Oxidation-Active Metal Centers in Zeolites.

We have had a measure of success in the selective oxidation of methane and ethane in the vapor phase

over heterogeneous zeolitic catalyst systems. In our early work (17,18,24,25) we showed that iron sodalite having large amounts of iron in the framework could give rather high selectivity to methanol (~70%) from methane at 7% conversion under the proper reaction conditions. The reactor configuration was very important. In a CSTR selectivities seldom exceeded 20%; in a fully packed tubular reactor 30% selectivity could be observed and in a top-loaded tubular reactor up to 50% selectivity could be obtained. In order to obtain higher selectivities it was necessary to employ more elaborate reactor systems often using reactive distillation to remove methanol from the catalyst bed as formed. We were also able to oxidize ethane to a mixture of methanol and ethanol in fair selectivity. More recently we have found that framework substituted aluminophosphates catalyzed methane oxidation at lower temperatures than did iron sodalite but reaction selectivity did not improve. Tables 4 and 5 compare the oxidation activity of Fe[SOD] and MnAPO catalysts in a top-loaded tubular reactor.

We currently interpret the results of our experiments over iron sodalite (26-28) and metal framework-substituted aluminophosphates as proceeding in two stages: a) catalytic activation by metal-O species to form surface methyl radicals followed by b) desorption of the methyl radicals into the vapor space where they become involved in gas phase autoxidation processes. Kinetic modelling backed by laboratory experiment (24) showed that methanol yields from gas phase free radical processes exhibit a maximum that falls short of values that we believe to be economically attractive. For this reason we are now in the process of synthesizing and characterizing a new generation of catalysts that are designed to keep the cleaved methane molecule in the coordination sphere so that it can form methanol directly on the surface. Highly hydrophobic surfaces are under construction which are designed to expel the formed methanol from the surface before over-oxidation.

ISOBUTANE CONVERSION TO tert-BUTYL ALCOHOL PROOF-OF-CONCEPT

Butanes were historically added to gasoline for their octane and ignitic properties. Vapor pressure restrictions now result in much lower usage of these materials in gasoline. Several manufacturing processes now exist for converting field butane to oxygenates such as TBA and MTBE (29), Figure 6. The first of these routes involves a) isomerization of butanes to isobutane, b) dehydrogenation of isobutane to isobutylene, and c) etherification of isobutane to MTBE. This process has a very expensive isobutane dehydrogenation step which raises process costs. Another route involves a) isomerization of butanes, b) oxidation of isobutane to tert-butyl hydroperoxide, TBHP, c) epoxidation of propylene with TBHP to PO and TBA, d) dehydration of TBA to isobutylene, and e) etherification of isobutylene to MTBE. This route has two more steps and requires production of propylene oxide, PO, for economic viability. Since the size of the MTBE market dwarfs that of PO, only a segment of the MTBE produced can be made this way.

Direct oxidation of isobutane to TBA using an electron deficient porphyrin complex provides a patented route (30-38) that would avoid the costly dehydrogenation step. Sun's perhaloporphyrin catalysts are by far the most active known catalysts for this transformation and preliminary economic analysis has been performed which indicates the relationship between catalyst activity, life and cost needed for a superior process. We envision a simple, direct oxidation process requiring only a reactor system and a still to produce TBA from isobutane, Figure 7. Process development efforts have lowered catalyst costs and proprietary additives have enhanced catalyst life. Work continues to increase catalyst activity. One way to enhance activity is to introduce electron withdrawing groups into the porphyrin macrocycle that are more powerful than halogens. Nitro groups on the periphery of ironporphyrin complexes give the greatest increase in Fe(III)/(II) reduction potential of any group that we have

Table 4. Methane Oxidations Over MnAPO-5 and Fe_x[Fe]SOD^a

CATALYST	GAS FLOW Mls/Min	T°C ^b	PRODUCTS, M MOLES / Hr.				O ₂ CONV.%	CH ₄ CONV.%	CH ₃ OH Sel.%
			CH ₃ OH	CH ₂ O	CO	CO ₂			
MnAPO-5	55	375	2.20	0.04	2.24	0.99	86	4.7	40
MnAPO-5	98	375	4.60	0.13	4.94	1.36	93	5.2	42
MnAPO-5	377	375	15.20	1.14	22.00	5.05	99	5.4	35
Fe _x [Fe]SOD	50	410	2.22	na	2.84	0.66	91	5.4	≤ 39
Fe _x [Fe]SOD	92	410	4.02	na	5.32	0.96	93	5.3	≤ 39
Fe _x [Fe]SOD	378	410	20.96	na	19.74	3.14	90	5.5	≤ 48
MnAPO-5	55	365	1.59	0.08	1.47	0.41	58	3.1	45
Fe _x [Fe]SOD	50	390	0.70	na	1.33	0.32	49	2.3	≤ 33

^a 3/1 Methane/Air continuously passed over 1.5 cc Catalyst
Top-loaded into a 5 mL heated quartz-lined reactor at 800 psig.

^b Applied external temperature (to reactor skin)

Table 5. Ethane Oxidations Over MnAPO-5 and Fe_x[Fe]SOD^a

Catalyst	Gas Flow		Carbon Selectivity %				Ethane Conv. %	Alcohol Sel.%	Liq. Oxyg. Sel.%
	Mis/Min	T°C	CH ₃ OH	C ₂ H ₅ OH	CH ₂ O	CH ₃ CHO			
Fe _x [Fe]SOD	165	290	33.3	16.7	tr	na	0.2	(50.0)	na
MnAPO-5	92	290	26.8	18.8	6.7	4.0	2.9	45.6	56.3
Fe _x [Fe]SOD	161	300	26.8	15.7	9.0	4.8	3.7	42.5	56.3
MnAPO-5	190	300	36.8	21.9	11.3	5.2	3.5	58.7	75.2
Fe _x [Fe]SOD	386	315	20.6	6.8	15.9	4.3	3.7	27.4	47.6
MnAPO-5	400	300	32.6	16.3	10.9	4.5	4.0	48.9	64.3

^a P = 400 psig, 3/1 C₂H₆/Air

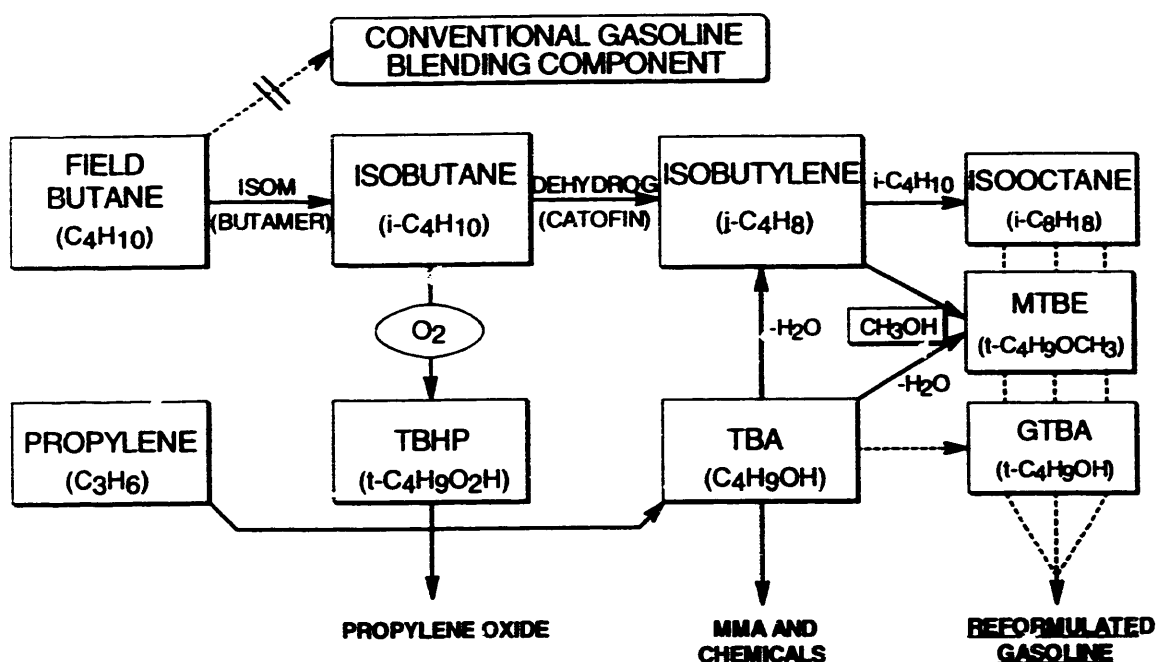


Figure 6. Historical and Current Fuel Applications of Field Butanes

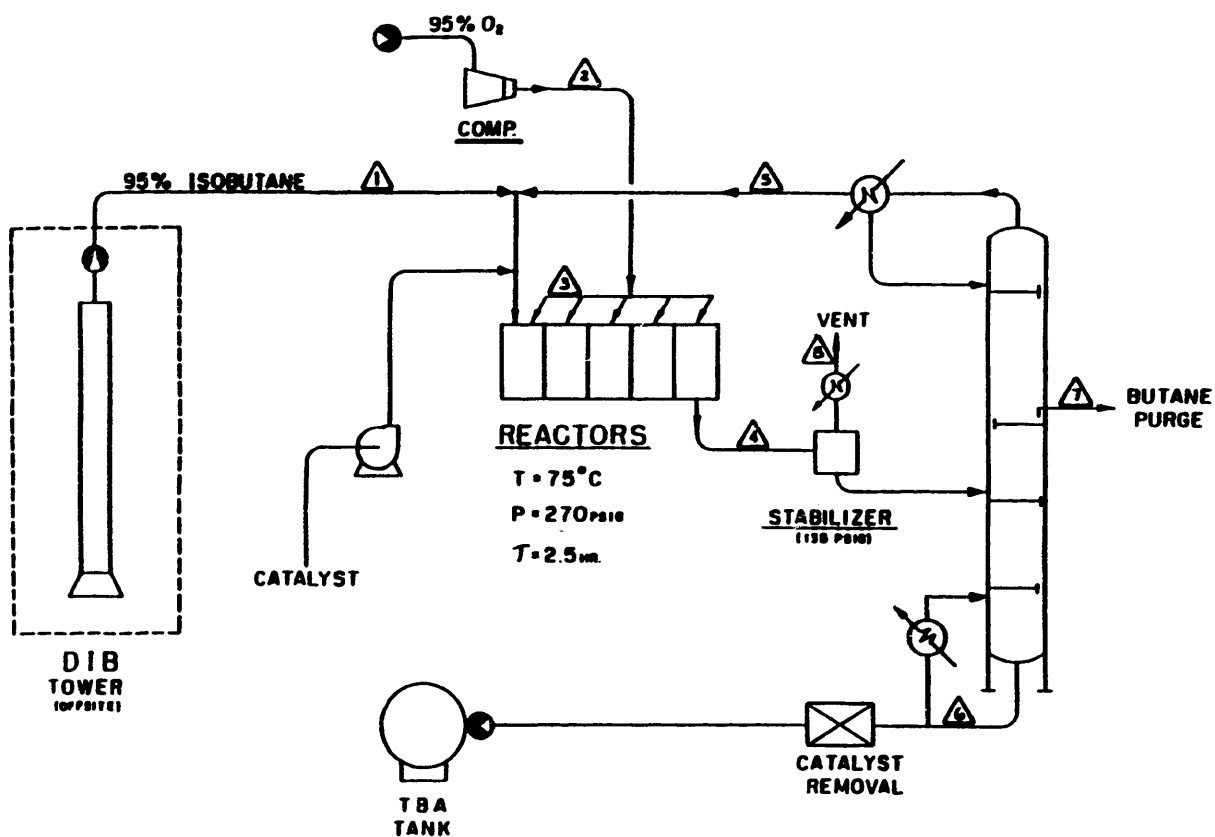


Figure 7. Process Flow Diagram for Isobutane Oxidation to TBA

used. Table 6 shows how a totally inactive iron porphyrin complex can be made highly active for isobutane oxidation by replacing only four C-H bonds with C-NO₂ groups. The degree of activity directly correlates with the number of nitro groups that are substituted onto the porphyrin periphery. Other highly active catalysts are being synthesized using powerful electrophiles other than the nitro group. Lower catalyst costs are being achieved both by superior synthetic techniques and also by preparing effective analogs whose macrocyclic structure has lower molecular weight.

While examining isobutane oxidation reactions, we made several new observations that are relevant to potential new process technology. Firstly, our perhalo and nitroporphyrin catalysts are the most active known catalysts for converting TBHP to TBA (39,40). This reaction, in fact, is one of the fastest homogeneous catalytic reactions observed to date proceeding at well over one hundred cycles per second. Secondly, a related set of complexes catalyzes the transfer of oxygen from TBHP to isobutane to give TBA. These observations make possible new process opportunities for converting field butanes to reformulated gasoline which are being evaluated for their process potential, Figure 8. All of these process approaches alleviate the need for expensive dehydrogenation and none of them are dependent on propylene oxide production, Figure 7.

FUTURE WORK

Work in the future will concentrate on synthesizing, characterizing and testing more highly electron deficient porphyrin macrocycles as hosts for oxidation active transition metal centers including iron, manganese, chromium, ruthenium, cobalt and others. Although iron complexes of currently available complexes are superior to most others for rapid low temperature alkane oxidations, it is possible that as electron withdrawal becomes even greater, other metal centers will become superior. A major effort in the synthesis of binucleating macrocycles has begun.

Ligand systems which coordinate two iron centers may increase the rate of reaction by reductively binding and cleaving the dioxygen molecule within a single complex. Homogeneous catalysts related to our electron deficient porphyrin complexes will no doubt be used not only to demonstrate proof-of-concept for converting isobutane to TBA but also have potential for entering proof-of-concept stage for converting propane to IPA. Bi-metal centers are being supported in hydrophobic surfaces to be used as heterogeneous catalysts for oxidizing methane and natural gas to methanol. At this time we expect that the most desirable method for methane conversion is via one-step direct oxidation in the vapor phase, however other alternatives are being pursued as well.

Laboratory success achieved during the period of performance resulted in proceeding from the research stage into the proof-of-concept stage for this work. The hydrocarbons that are found in natural gas vary in the ease of their catalytic conversion to alcohols. Isobutane is the most readily converted, butane and propane are somewhat more difficult, ethane is next and methane is the most difficult to convert of all. For this reason we have entered the proof-of-concept stage for a process to convert field butanes to an environmentally friendly, high performance transportation fuel. On completion of this activity we will begin proof-of-concept development of a process for converting propane to isopropyl alcohol, followed by a similar program for converting methane or natural gas, into a methanol-rich oxidate. While pursuing the proof-of-concept development of isobutane oxidation we continue to lay the research groundwork for developmental work on conversion of the C₁-C₃ components of natural gas.

REFERENCES

- (1) J. E. Lyons, "Soluble and Supported Metal Catalysts for Hydrocarbon Oxidation in Liquid and Vapor Phase," Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis, J. M. Basset, et al. (Eds.), Kluwer Academic Publishers, 97 (1988).

Table 6. Isobutane Oxidation Activity of Iron Porphyrin Complexes

Complex	T = 60°C		T = 80°C	
	TO ^c	Sel. ^d	TO ^c	Sel. ^d
[Fe(OEP)] ₂ O ^b	0	–	0	–
{Fe[5,15-(NO ₂) ₂ OEP]} ₂ O	360	88	970	89
[Fe(OEP)(NO ₂) ₄] ₂ O	800	88	1680	88

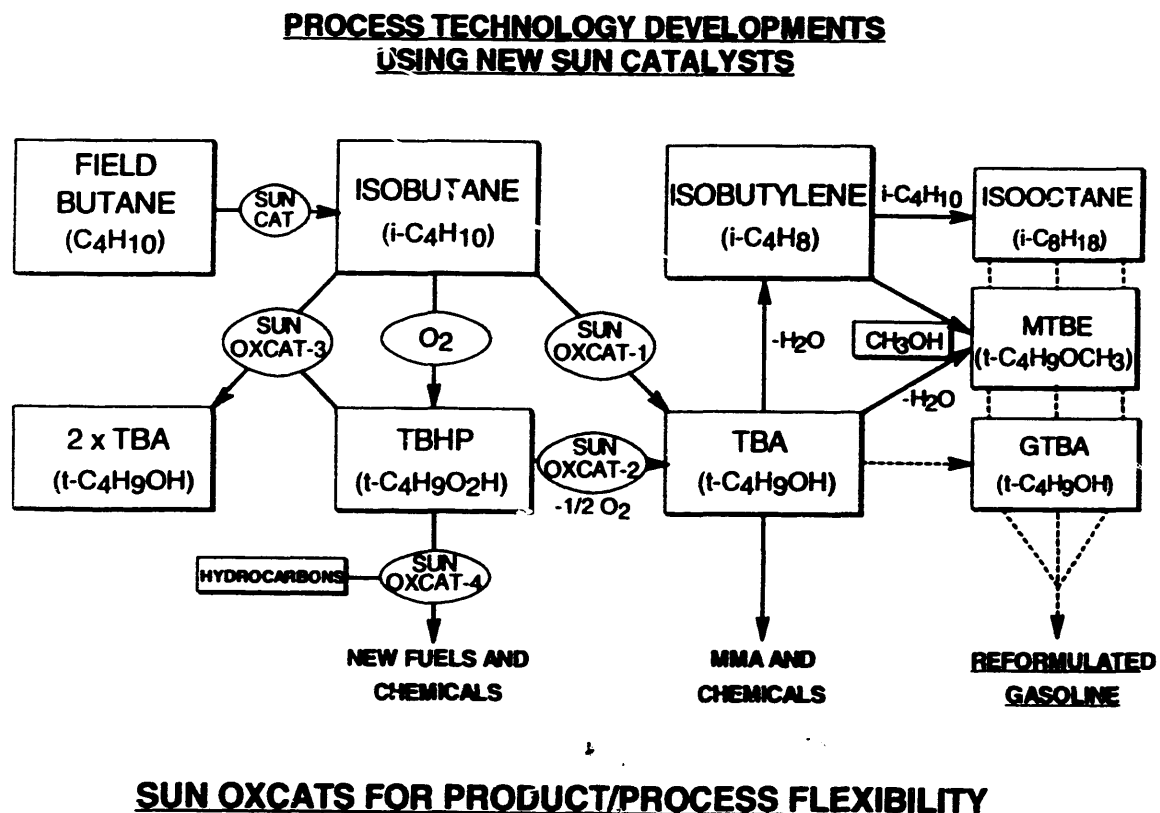
^a Isobutane, 7g, in 30 ml benzene containing 0.013 mmole complex, heated and stirred at reaction temperature for 5 hours under 100 psig of O₂.

^b CEP = Octaethylporphyrinato

^c TO = Turnovers = moles (TBA + acetone)/moles catalyst.

^d Sel. = (moles t-butyl alcohol produced/total moles liquid product x 100.)

Figure 8. Isobutane Oxidation - Proof-of-Concept Stage



- (2) J. E. Lyons, "Catalytic Oxidation in the Liquid Phase," Applied Industrial Catalysis, **3**, Academic Press, New York, pp. 131-214 (1984).
- (3) Cyclochrome P-450: Structure, Mechanism and Biochemistry, P.R. Ortiz de Montellano (Ed.), Plenum Press, New York (1986).
- (4) H. Dalton and J. Green, J. Biol. Chem., **264** (1989) 17698.
- (5) P. E. Ellis, Jr. and J. E. Lyons, J. Chem. Soc. Chem. Commun., (1987) 1187.
- (6) P. E. Ellis, Jr. and J. E. Lyons, J. Chem. Soc. Chem Commun., (1989) 1189.
- (7) P. E. Ellis, Jr. and J. E. Lyons, J. Chem. Soc. Chem. Commun., (1989) 1315.
- (8) P. E. Ellis, Jr. and J. E. Lyons, Catalysis Letters **3**, (1989) 389.
- (9) P. E. Ellis, Jr. and J. E. Lyons, Preprints of the Division of Petroleum Chemistry, ACS, Vol. 35, No. 2, April (1990).
- (10) P. E. Ellis, Jr. and J. E. Lyons, Coordination Chem. Rev., **105** (1990) 181.
- (11) J. E. Lyons and P. E. Ellis, Jr., Catalysis Letters, **8** (1991) 45.
- (12) J. E. Lyons and P. E. Ellis, Jr., Applied Catalysis A General, **84** (1992) L1-L6.
- (13) J. E. Lyons, P. E. Ellis, Jr., R. W. Wagner, P. B. Thompson, H. B. Gray, M. E. Hughes and J. A. Hodge, Preprints Pet. Div., **37** (1992) 307.
- (14) J. E. Lyons, "Catalytic Conversion of Light Alkanes," GRI Contractor Review Meeting, Methane Reaction Science Program, Paris, France, Aug. 25-27 (1991).
- (15) Unpublished Work by H. B. Gray, W. P. Schaefer, et al.
- (16) Related structures have been determined: a) R. E. Marsh, W. P. Schaefer, J. A. Hodge, M. E. Hughes, H. B. Gray, J. E. Lyons and P. E. Ellis, Jr., Acta Cryst. Sec. C, **V 49** (1993) 1339. b) W. P. Schaefer, J. A. Hodge, M. E. Hughes, H. B. Gray, J. E. Lyons, P. E. Ellis, Jr. and R. W. Wagner, Acta Cryst. Sec. C, **V 49** (1993) 1342.
- (17) J. E. Lyons, P. E. Ellis, Jr. and V. A. Durante, Proceedings of the Natural Gas R&D Contractors Review Meeting, DOE/METC - 89/6103 (1989) 164.
- (18) J. E. Lyons, Proc. Nat. Gas R&D Contractors Review Meeting, DOE/METC - 91/6117 (1990) 276.
- (19) J. E. Lyons, P. E. Ellis, Jr., H. K. Myers, Jr., G. Suld and W. A. Langdale, U. S. Patent 4,803,187, Feb. 7 (1989).
- (20) P. E. Ellis, Jr. and J. E. Lyons, U. S. Patent 5,091,354, Feb. 25 (1992).
- (21) J. E. Lyons, P. E. Ellis, Jr., W. A. Langdale and H. K. Myers, Jr., U. S. Patent 4,916,101, Apr. 23 (1990).
- (22) P. E. Ellis, Jr. and J. E. Lyons, U. S. Patent 4,898,989, Feb. 6 (1990).
- (23) J. E. Lyons, P. E. Ellis, Jr., H. K. Myers, Jr., G. Suld and W. A. Langdale, U. S. Patent 4,859,798, Aug. 22 (1989).
- (24) J. E. Lyons, Proc. Nat. Gas R&D Review Meeting, DOE/METC - 92/6125 (1992) 266.
- (25) J. E. Lyons, P. E. Ellis, Jr. and V. A. Durante, Studies in Surface Science and Catalysis, **67**, Elsevier, N.Y. (1991) 99.

- | | | | |
|------|---|------|--|
| (26) | V. A. Durante, D. W. Walker, S. M. Gussow and J. E. Lyons, U. S. Patent 4,918,249. | (34) | P. E. Ellis, Jr., J. E. Lyons and H. K. Myers, Jr., U. S. Patent 5,093,491, Mar. 3 (1992). |
| (27) | V. A. Durante, D. W. Walker, S. M. Gussow, J. E. Lyons and R. C. Hayes, U. S. Patent 5,132,472, July 21 (1992). | (35) | P. E. Ellis, Jr. and J. E. Lyons, U. S. Patent 4,970,348, Nov. 13 (1990). |
| (28) | J. E. Lyons, V. A. Durante and D. W. Walker, U.S. Patent 5,220,080, June 15 (1993). | (36) | P. E. Ellis, Jr., J. E. Lyons and H. K. Myers, Jr., U. S. Patent 4,900,871, Feb. 13 (1990). |
| (29) | P. R. Sarathy and G. S. Suffridge, <u>Hydrocarbon Processing</u> , Feb. (1993) 43. | (37) | P. E. Ellis, Jr., J. E. Lyons and H. K. Myers, Jr., U. S. Patent 4,895,682, Jan. 23 (1990). |
| (30) | P. E. Ellis, Jr. and J. E. Lyons, U. S. Patent 5,254,740, Oct. 19 (1993). | (38) | P. E. Ellis, Jr., J. E. Lyons and H. K. Myers, Jr., U. S. Patent 4,895,680, Jan. 23 (1990). |
| (31) | P. E. Ellis, Jr. and J. E. Lyons, U. S. Patent 5,212,300, May 18 (1993). | (39) | J. E. Lyons, P. E. Ellis, Jr., H. K. Myers, Jr., and R. W. Wagner, <u>J. Catal.</u> , <u>141</u> (1993) 311. |
| (32) | P. E. Ellis, Jr. and J. E. Lyons, U. S. Patent 5,120,882, June 9 (1992). | (40) | J. E. Lyons and P. E. Ellis, Jr., U.S. Patent 5,120,886, June 9 (1992). |
| (33) | P. E. Ellis, Jr. and J. E. Lyons, U. S. Patent 5,118,886, June 2 (1992). | | |