

LIQUEFACTION OF WATER PRETREATED COALS

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Keywords: Pretreatment, Water, Coal, Liquefaction, Pyrolysis

INTRODUCTION

Water pretreatment of coal has been studied previously as a means to increase the yields of liquid products from extraction (1-5), pyrolysis (3-6), or liquefaction (7,8) of coal. However, the mechanisms of this process and the applications to coals of a wide range of ranks are still a subject of considerable debate. The benefit of water pretreatment on increasing yields from direct liquefaction of coal has not been clearly demonstrated, although effects on the composition and molecular weight distribution have been observed (7,8). The goals of this study are to gain an understanding of the chemistry of water or steam coal pretreatments and to assess the importance of such pretreatments on subsequent coal liquefaction.

EXPERIMENTAL

Sample Selection - The selection of coal samples was made from the Argonne Premium Sample Bank. Since pretreatment is potentially most useful for lower rank coals which are subject to retrograde reactions, the coals used were the Zap Lignite, the Wyodak subbituminous and the Illinois No. 6 bituminous. Selected experiments were also done with the Pittsburgh Seam bituminous coal from the same sample bank.

Steam/Water Pretreatment Experiments - A new reactor system was designed to carry out high pressure (up to 6000 psig), high temperature (up to ~ 400°C) steam or water pretreatment of coal in a closed bomb (20 ml) reactor. After 1-3 g coal is fed into the bomb and the reactor head is screwed on to get a gas tight seal, the system is purged with N₂ or evacuated, the high temperature, high pressure valve on the reactor base is closed, and the water is injected directly into the coal through the capillary tube with a ~ 0.1-1.0 ml/min rate. Deaerated and deionized water is used throughout the reaction.

Simultaneously with the water injection, the reactor is immersed into the fluidized sand bath held at the required temperature. The pressure is measured in the water feed capillary tubing directly after the pump. The amount of water pumped in and the temperature determines whether steam and/or water pretreatment is done. The results described in the current paper are for pretreatment with subcritical water at 350°C, 4000 psig and pretreatment times from 10 to 1000 minutes.

After the reaction, the bomb is quickly quenched with water, flooded with up to 300-600 psig N₂ and depressurized with a 0.8 liter previously evacuated sampling tank. The yields of product gases, e.g., H₂, CO₂, CO, CH₄, C₂H₆, C₂H₄, C₂H₂, and H₂S are determined by GC. After opening

the reactor, the pretreated coal is taken out of the reactor by washing it with deionized water and filtering under an N_2 atmosphere. N_2 is passed through the coal sample for about an hour to obtain a sample with approximately the same moisture content as the starting coal sample. In addition to the reactor, an N_2 purged glove box was also constructed to facilitate all the product work up in an oxygen-free environment.

Product Analyses - The residues from the water pretreatment experiments with the four coals were subjected to analysis by programmed pyrolysis (TG-FTIR), solvent extraction, FT-IR, SEM/x-ray analysis and liquefaction experiments in a donor solvent. The liquefaction experiments were done with 0.5 g of coal residue and 3 g of solvent (dihydrophenanthrene) in a 20 ml agitated bomb reactor for 30 min. at 400°C.

RESULTS

Experiments with a Range of Coals - Selected results for the characterization of the residues by TG-FTIR, solvent extraction with pyridine, and liquefaction experiments in a donor solvent are summarized in Figs. 1-3. The results for pyrolysis tar yields (Figs. 1a, 2a, 3a) show a sharp increase at short pretreatment times with a gradual decrease at longer times when compared to the raw coal. The oxygenated gases, CO, CO_2 and H_2O (data not shown) decline with increasing pretreatment time, except for an initial increase in CO. Conversely, the amount of CH_4 from pyrolysis has the opposite trend.

The set of data on pyridine extractables is less complete but indicates that, for the three coals, the yield increases at relatively short pretreatment times (by as much as a factor of two) and gradually declines at longer pretreatment times (see Figs. 1e, 2e, 3e), thus following the same general trend as the tar yield. The larger set of data for the Illinois coal is quite clear with regard to this trend. In the case of the Illinois coal, pretreatment for 20 minutes resulted in a more than doubling of the % DAF pyridine extractables (81 vs. 36%). The results were generally lower when an ampoule of Illinois coal was used which was not freshly opened (compare open circles and solid circles in Figure 3). The results to date indicate that of the four coals examined (Zap, Wyodak, Illinois, Pittsburgh), the Illinois coal is the most sensitive to coal freshness. For the Pittsburgh coal, the pyridine extractables increase slowly with increasing pretreatment time.

The liquefaction results for the two low rank coals (Zap, Wyodak) indicated significant reductions at short pretreatment times, particularly for the Zap lignite, in the yields of toluene and pyridine solubles (see Figs. 1f and 2f). The liquefaction yields for the low rank coals improved at longer pretreatment times but were generally not as high as for the untreated coal. Conversely, improved or similar yields of oils and toluene solubles are observed for selected pretreatment experiments with Illinois coal. However, these results could not be reproduced consistently with Illinois coal. It appeared that the results were sensitive to the "freshness" of the coal. For ampoules which were just opened, the yields of soluble products from the pretreated coals were lower than for samples which had been opened days or weeks earlier and stored in a nitrogen purged glove box. A likely explanation is that the solvent is forming adducts with the water pretreated samples. This conclusion is supported by the observation of negative oil yields, since the oil yields are determined by difference. The very fresh Illinois samples appear to be the most reactive toward solvent adduction. The differences between the fresh and "aged" Illinois samples is also evident by comparing the yields of pyrolysis gases and pyridine extractables in Fig. 3. This same phenomenon may explain why the liquefaction yields for the pretreated Zap and Wyodak coals go through a minimum at short pretreatment times, and are generally less than for the raw coals.

This hypothesis was tested by doing mild oxidation experiments on raw and pretreated Illinois and Zap coals, as discussed below.

Mild Oxidation Experiments - The samples generated in the mild oxidation studies were subjected to characterization by liquefaction in donor solvent (30 min., 400°C in dihydrophenanthrene). The results for toluene solubles and oils for the mild oxidation experiments and reference experiments are summarized in Table 1. This table only includes data for freshly opened ampoules in the case of Illinois coal. Experiment #80 indicates that mild oxidation of a

TABLE I - SUMMARY OF LIQUEFACTION EXPERIMENTS ON ILLINOIS AND ZAP COALS

Coal Type	Run No.	Treatment	Liquefaction Yields DAF %	
			Toluene Solubles	Oils
Ill. #6		---	42 to 48	14 to 17
		pretr.	11 to 40	(-12) to 40
	80	pretr. + H ₂ O ₂ ^(b)	64	19
	84	H ₂ O ₂ ^(a) + pretr.	48	7
	88	H ₂ O ₂ ^(b) + pretr.	62	19
	91	Fe ⁶⁺ ^(c)	49	7
	85	H ₂ O ₂ ^(b)	53	12
	93	H ₂ O ₂ ^(b) + H ₂ S*	90	34
Zap		---	26 to 36	12 to 14
		pretr.	18 to 21	12 to 15
	82	pret. + H ₂ O ₂ ^(b)	30	14

Notes: 150 ML solution, 5 gr. coal: (a) 0.003 M (b) 0.5 M (c) 1 M

All water pretreatments were done at 350°C, 4000 psig for either 20 minutes (#80, #82) or 60 minutes (#84, #88) pretreatment time.

* Liquefaction was done in the presence of 80 psig H₂S.

water pretreated Illinois coal gives an increased yield of toluene solubles and oils from liquefaction of the residue and that the values are generally higher than from liquefaction of the raw coal. Similar results are observed for mild oxidation of a water pretreatment residue from Zap lignite (see experiment #82 in Table 1). These results are consistent with the hypothesis that ortho dihydroxy functionalities created by water pretreatment are responsible for the retrogressive solvent incorporation reactions which artificially reduce the liquefaction yields. This conclusion is based on the assumption that the mild oxidation will remove the dihydroxy functionalities. Additional experiments were done with Illinois coal (#84, #88) where the coal was oxidized prior to water pretreatment. This would serve to remove dihydroxy functionalities which are already

present in the coal and the phenolic groups that are precursors to the dihydroxy functionalities that are formed during water pretreatment. In this case, the toluene solubles and oil yields are also higher than for the coal that was only subjected to water pretreatment. It was also found that mild oxidation by itself (#85) or mild oxidation followed by liquefaction in the presence of H_2S (to restore catalytic activity of pyrite) also gave results that were equal or superior to the raw coal.

FT-IR Analyses of Water Pretreated Coals - Residues from water pretreatment of all four coals were subjected to analysis by quantitative FT-IR functional group analysis. The samples were chosen from a range of pretreatment times (20, 180, 300, 1080, 1200 minutes) at $350^\circ C$, 4000 psig. The quantitative results for aromatic hydrogen (H_{ar}), aliphatic hydrogen (H_{al}), hydroxyl hydrogen (H_{OH}) and ether oxygen (O_{ether}) are given in Fig. 4. For all of the coals, except Pittsburgh, pretreatment led to a monotonic decline in the oxygen content. This is consistent with previous work on water pretreatment (6-9) and with the idea that the process is similar to an accelerated aging of the coal.

A lot of attention has been paid to the effect of water or steam pretreatment on hydroxyl groups. For all four coals, the concentration of hydroxyl OH declined with increasing pretreatment time, except for a small initial increase with Zap. This is in agreement with the results of Khan et al. (9) but not with Brandes et al. (6). Brandes et al. (6) concluded that steam pretreatment significantly increased the number of hydroxyl groups. This conclusion was primarily based on the fact that mild O-alkylation of steam pretreated coal with labeled methyl iodide introduced twice the enrichment of ^{13}C when compared to the raw coal. Some IR data was also used to support this conclusion, using a diffuse reflectance technique which measures surface concentrations. It is possible that the loosening of the structure resulting from steam pretreatment makes the coal more reactive toward the O-alkylation procedure, and that the actual number of hydroxyl groups does not increase significantly. It is also possible that the concentration of OH groups increases on the surface of the water pretreated coals but not in the bulk. Of course, any comparison with previous work must consider the fact that the results in Fig. 4 are for samples produced in subcritical water and over a wide range of pretreatment times. Most of the previous studies (3-6,9) were done in subcritical steam at lower pressures (~1000 psig) and for relatively short times. Some additional work on resolving the -OH region of the spectrum indicated that the concentration of ortho dihydroxy functions does initially increase for all of the coals following water pretreatment.

The trends for hydrogen functional groups appeared to vary with coal type. For the two low rank coals (Zap, Wyodak), pretreatment increased the fraction of aromatic hydrogen, while for the two higher rank coals (Illinois, Pittsburgh), this fraction was decreased. The contrast between the behavior of the Zap and Illinois coals is especially striking in this regard. For the two low rank coals, the amount of aliphatic hydrogen (H_{al}) goes through a maximum with increasing pretreatment time, while for the two higher rank coals, H_{al} declines steadily.

DISCUSSION

The increase in pyridine extractables and tar yields is consistent with literature observations (4,6,9). The tar yields and pyridine solubles yields show a maximum with increasing pretreatment time (except for the Pittsburgh coal) which indicates the onset of retrograde reactions as pretreatment proceeds (10). Conversely, the yields of toluene solubles (TS) from liquefaction are

at a minimum where pyrolysis tar yields are at maximum, which is contrary to previous studies on liquefaction (11) and expectations. However, the individual experimental data around the minimum toluene solubles values were very dispersed, especially for the Illinois No. 6 coal.

Table 1 shows the liquefaction results of experiments with Illinois No. 6 coal in somewhat more detail. Since the oil fraction is measured by weight difference, the only explanation for negative values is that there was solvent incorporation into the toluene insoluble part of the coal matrix and that this depends on how fresh the coal was. In the case of the Illinois coal, an exposure of this particular coal to even very low oxygen concentrations prior to pretreatment apparently causes a very significant change in the pretreatment and subsequent liquefaction behavior. There are reports in the literature of the sensitivity of Illinois No. 6 coal to rapid oxidation at ambient temperatures (12,13). The problem of measuring the incorporated solvent calls for a proper separation of the solvent and solvent derivatives which is very difficult to do on a quantitative basis given the complex nature of the coal liquid.

A second approach, which we have taken, is to hypothesize a reaction scheme for that particular behavior which is in harmony with the experimental data and then to test it. Our hypothesis is that it is the phenoxy radical which reacts with water to form dihydroxy products, as illustrated in Fig. 5, and that the recombination of the dihydroxy and solvent radicals leads to solvent incorporation into the coal matrix, as illustrated in Fig. 6. However, dihydroxy compounds are not stable at such high temperatures and must therefore appear only as intermediate products leading to the "recovery" of the toluene solubles yields after prolonged pretreatment. An example of two decomposition routes for ortho dihydroxy benzenes is shown in Fig. 7.

Phenols are the most widespread components of coals and literature data show a decrease of total phenolic OH in the coal as well as increase of low molecular weight dihydroxy benzenes during water pretreatments (7,14). Our own FT-IR results support this picture as does the initial increase in pyrolytic CO formation (see below). Since phenoxy radicals are relatively stable due to resonance stabilization, they represent a high steady state concentration at elevated temperatures. As the number of condensed aromatic rings adjacent to the phenoxy radical increases, the stability increases and the reactivity decreases. This might be an explanation as to why the Pittsburgh coal behaves differently during water pretreatment than the lower rank coals.

Dihydroxy benzenes are prone to retrograde reactions (15) or decomposition. One type of decomposition may lead to CO evolution from the residue as shown in Fig. 7. Our experimental data show an initial increase in the pyrolytic CO evolution with a maximum in time corresponding to the minimum in the toluene solubles yield and the maximum in the tar yield (see Figs. 1-3). This is in contrast to a general decline in pyrolytic CO₂ and H₂O with increased pretreatment time and a corresponding reduction in organic oxygen content for the water pretreatment residues. There is a small amount of CO formation during pretreatment, but it is an intermediate product only.

McMillen and coworkers (15) found that, under liquefaction conditions, dihydroxy compounds readily couple with themselves or with the solvent (in their case, tetrahydroquinoline) and also form high molecular weight products, the amount of which increases in the presence of coal. The self coupling produces a diaryl cyclic ether molecule. This is consistent with our FT-IR data, (see Fig. 4) which show the ether group concentration reaching a maximum or declining slowly after relatively short hydrothermal treatment times, while the concentration of hydroxyl decreases steadily.

Our suggestion is that one of the principal reactions to cause solvent incorporation into the coal matrix under liquefaction conditions is the reaction of surface ortho dihydroxy functionalities with the solvent. A short hydrothermal treatment will enhance solvent incorporation due to the increased surface concentration of dihydroxies. Prolonged pretreatment will destroy these functionalities, as shown by Ross et al. (12), thus reducing solvent additions but introducing strong crosslinks and resulting in a decrease in liquefaction yields. A parallel process of depolymerization of the coal during hydrothermal treatment is compensating for this new crosslink formation, the final result being a slight increase or no increase of liquefaction yields relative to the untreated coal at long pretreatment times. The proposed mechanism is summarized in Fig. 8.

Since higher yields of toluene solubles and oils were obtained from samples of Illinois coal that were not freshly opened, or were treated with solutions of H_2O_2 our suggestion is that a mild oxidation substantially decreased solvent incorporation by removal of ortho dihydroxy functionalities or their precursors. This result suggests a possible way to avoid the detrimental effect of solvent incorporation and thus significantly increase liquefaction yields from water pretreated coals. Future work will involve additional experiments and literature work to test the hypothesis. The results will also be considered in light of the recent model compound studies of Siskin and Katritsky (16).

CONCLUSIONS

The conclusions can be summarized as follows:

1. The analysis of pyrolysis and pyridine extractables data from water pretreated Zap lignite and Wyodak subbituminous coal (reduction in CO_2 yield, maximum in tar yield, maximum in extractables, increase in CH_4 yield) shows a strong similarity of water pretreatment to an accelerated geological aging process. The results for the Illinois and Pittsburgh bituminous coals were similar, though less dramatic, except for the extractables yields.
2. The geological aging analogy is also consistent with results that were obtained in the literature on steam or water pretreatment, since it explains why the treatment is effective in increasing pyrolysis yields for low rank coals and is ineffective or reduces pyrolysis yields for high rank coals. However, there are certain trends, such as the fact that the CO yield appears to follow the tar yield (goes through a maximum along with the tar) which do not agree completely with this analogy.
3. The FT-IR data indicate a general reduction of oxygen groups during water pretreatment, including hydroxyl groups, although there is an initial increase in dihydroxy functionalities.
4. The results from liquefaction experiments on samples produced to date indicate only modest benefits in the best cases. The worst results are obtained at short pretreatment times where solvent incorporation into the coal is apparently reducing the observed yields of soluble products. For Illinois coal, the best results are obtained from "aged" samples, which appear to be less prone to the solvent adduction reactions.

5. The data are consistent with a mechanism in which water pretreatment increases the concentration of ortho dihydroxy species in the coal at short pretreatment times. Support is provided by FT-IR results and an initial increase in pyrolytic CO formation from the residue. These functions are believed to be responsible for the solvent incorporation reactions. They can be removed by increasing the pretreatment time or mild oxidation of the coal using H₂O₂ after water pretreatment.

ACKNOWLEDGEMENTS

The support of this work by the U.S. DOE Pittsburgh Energy Technology Center under Contract No. DE-AC22-89PC89878 is gratefully acknowledged.

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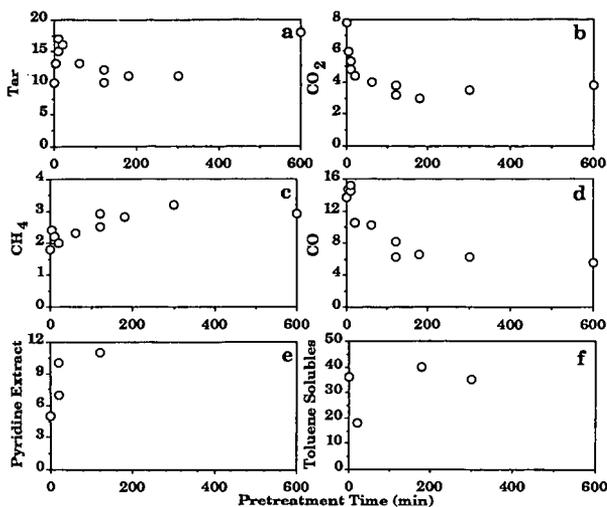


Figure 1. Results from Analysis of Zap Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. (a-d) Data on Pyrolysis Gas Yields from TG-FTIR Analysis; (e) Data for Extractables Yield Using Pyridine at Room Temperature; (f) Data for Toluene Solubles Yield from Donor Solvent Liquefaction. All Results are Given on a DAF Basis.

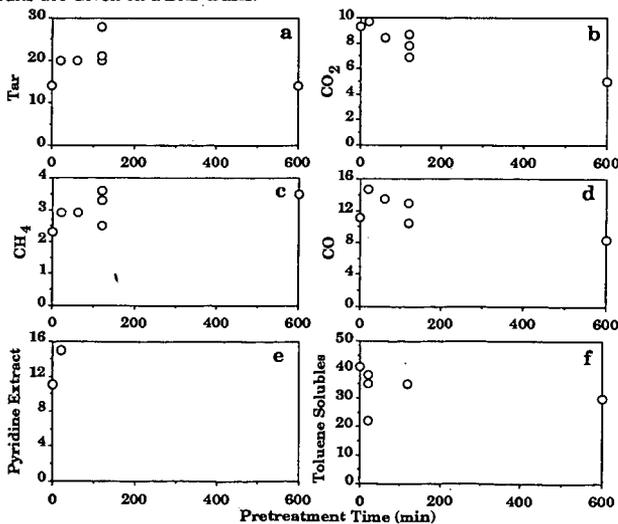


Figure 2. Results from Analysis of Wyodak Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. (a-d) Data on Pyrolysis Gas Yields from TG-FTIR Analysis; (e) Data for Extractables Yield Using Pyridine at Room Temperature; (f) Data for Toluene Solubles Yield from Donor Solvent Liquefaction. All Results are Given on a DAF Basis.

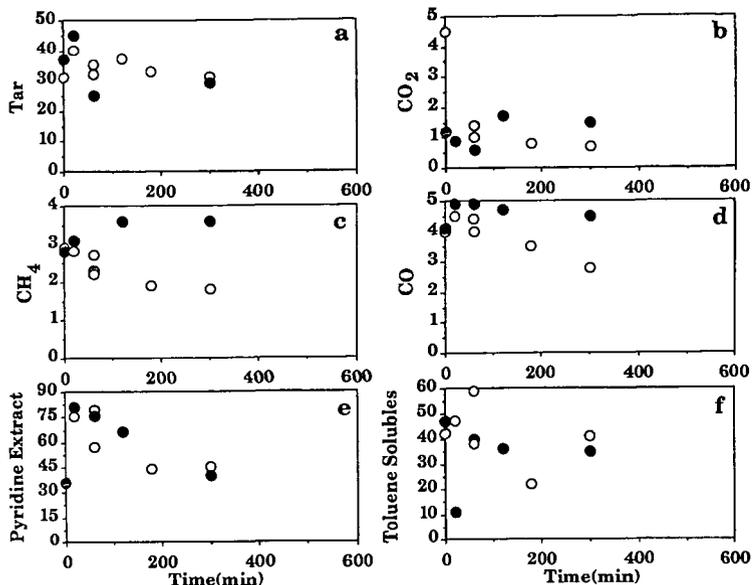


Figure 3. Results from Analysis of Illinois Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. (a-d) Data on Pyrolysis Gas Yields from TG-FTIR Analysis; (e) Data for Extractables Yield Using Pyridine at Room Temperature; (f) Data for Toluene Solubles Yield from Donor Solvent Liquefaction. All Results are Given on a DAF Basis. Solid Circles are for Freshly Opened Samples. Open Circles are for Samples which had been Previously Open.

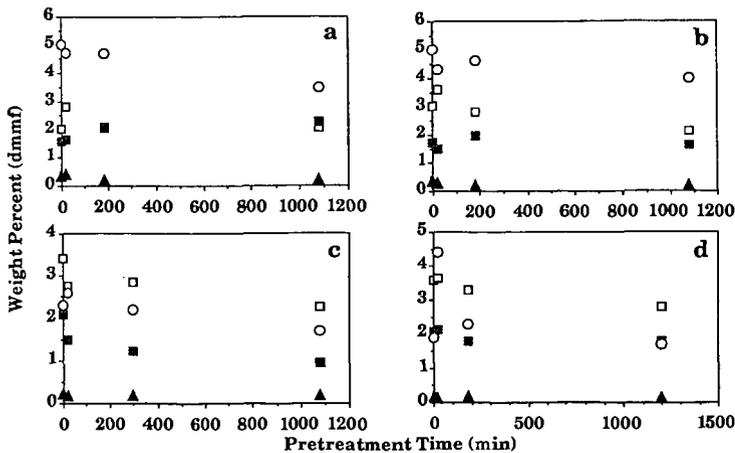


Figure 4. Results from FT-IR Analysis of Residues from Four Coals Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. a) Zap; b) Wyodak; c) Illinois; d) Pittsburgh. □ - H_{al}; ■ - H_{ar}; ▲ - H_{OH}; ○ - O_{ether}.

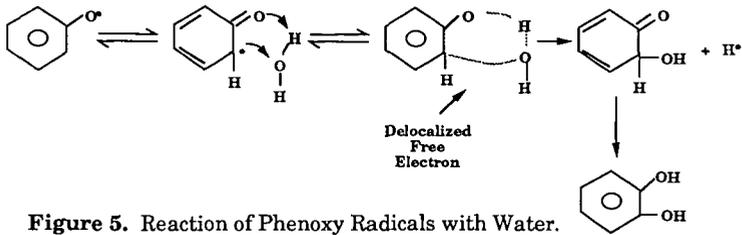


Figure 5. Reaction of Phenoxy Radicals with Water.

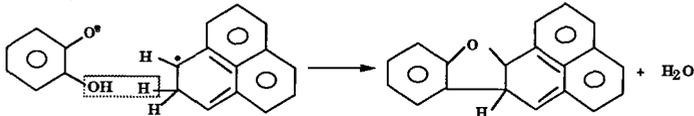


Figure 6. Recombination-Condensation with the Solvent Radical.

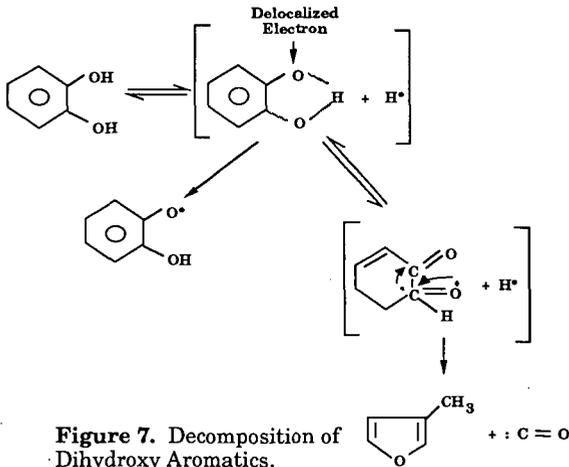


Figure 7. Decomposition of Dihydroxy Aromatics.

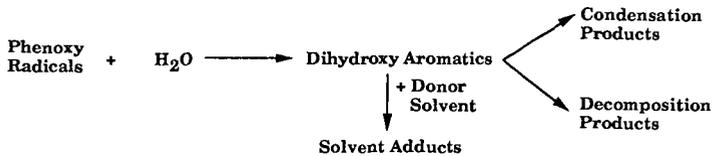


Figure 8. Proposed Mechanism for Water Pretreatment as it Impacts Liquefaction Yields.

OPTIMIZATION OF REACTOR CONFIGURATION IN COAL LIQUEFACTION

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Key Words: Liquefaction
CSTR - Continuous Stirred Tank Reactor
Fixed Bed Reactor

Introduction

The Department of Energy is sponsoring several Advanced Liquefaction Programs which taken together have the potential to reduce product costs from direct liquefaction to a level of \$25 per barrel. HRI has been selected to study the optimization of reactor configurations with a goal of developing a feasible cost-effective processing scheme that will result in an increased overall yield of higher quality distillates. HRI will evaluate combined ebullated-bed and fixed-bed processing, three ebullated-bed stages and interstage feed concentration following the primary reactor. Since the high pressure temperature reactors and associated equipment can comprise 15 to 20% of the capital costs of a grass roots plant, significant savings can result from improved reactor configurations and a decrease in required reactor volume. Further cost reductions will result from expected improvements in product selectivity (gaseous vs liquid) lower hydrogen consumption and better product quality by reduction of heteroatom content and increases in hydrogen content.

The configurations to be studied are :

- Incorporation of a fixed-bed, plug flow reactor after partial conversion and micronization of coal in an upstream CSTR (Continuous Stirred Tank) reactor.
- Comparison of three CSTR reactors with a two-stage system.
- Reconcentration of unreacted solids and residues between stages for improved kinetics in two stage CSTR systems.

An assessment of the preferred temperatures and volumes for multiple stages will also be conducted.

Background

The HRI CTSL⁽¹⁾ Process uses a relatively low temperature first-stage (750-775°F) and a higher second-stage temperature (815-825°F)⁽¹⁾. The first stage, with more favorable hydrogenation conditions, regenerates the hydrogen-donor capacity of the recycle solvent, while accomplishing a significant degree of coal liquefaction (conversion) and production of distillable liquids. The second stage completes the conversion of the coal and produces additional distillable liquids. This process offers a large improvement over earlier processes. With Illinois No. 6 coal over 95% liquefaction of MAF coal has been attained, with a yield of distillate oils (C₄750°F) of 78 W% of MAF coal. The CTSL Process employs an ebullated bed of catalyst, which maintains an expanded condition for catalyst and permits passage of large solid particles and avoids problems in dealing with highly viscous liquefied material especially in the first stages of the coal liquefaction reactions.

A principal debit of the ebullated bed reflects the fact that it is a relatively well mixed system with the reactive phase composition (and reaction potential) throughout the reactor corresponding to the product stream composition, in effect a CSTR (Continuous Stirred Tank Reactor) configuration. Such a mode has a kinetic disadvantage relative to that of a plug flow (fixed bed or packed bed) mode where the reaction potential declines progressively throughout the reactor only reaching that of product stream composition at the outlet of the reactor. This disadvantage of ebullated bed reactors is mitigated to a degree by staging, but even the two stage system requires greater reactor volumes especially when targeting very high conversion levels, in excess of 90%.

The first order (for coal concentration) modelling, using CSTR (Continuous Stirred Tank Reactor) reaction equations, has evolved from analysis of coal conversion results from CTSL and various modes of coal liquefaction experience at the HRI R&D center. Application of such a model requires identification of several species of coal types of different reactivity, more or less corresponding to various maceral types identified by petrographic analyses, although the correlating proportions have been developed from the actual two-stage CTSL, or single stage H-Coal, liquefaction results. Classification into three species (one unreactive) has proven adequate to rationalize CTSL experimental results giving coal conversion between 30% and 97% of MAF coal.

Hydrogen-transfer reactions from donor-solvent constituents in the liquid phase are a factor in coal conversion; however, in the correlation of CTSL results where the donor-solvent is generated in situ including this parameter has not been necessary, even though donor quality changes with catalyst deactivation. The overriding factor is that only small changes in conversion have occurred as the catalyst age in CTSL Bench Experiments.

These CTSL correlations are being tested in the current program and will be modified to fit the integrated reaction performance prior to projecting performance of the new reactor configurations.

Using first order kinetic modelling the various reactor configurations can be compared relative to two-stage CSTR performance. *Figure 1* compares reactor volumes to achieve certain coal conversions with Illinois #6 coal. For example as shown, a system following first-order kinetics at 95% conversion would require 130% greater reactor volume as a two-stage than as a plug-flow fixed bed system, all other kinetic factors being equal.

Fixed Bed Reactor

The application of fixed-bed reactors for direct coal conversions was extensively tested in the Synthoil[®] process as a first stage. Problems occurred with plugging, coking and rapid catalytic deactivation. HRI is testing fixed-bed hydrocracking in a second or third stage application where the unconverted coal and ash concentration averages from 10-20% and the particle size is generally less than 325 mesh (44 microns) compared to a typical feed concentration of 35 to 50% and a size of 50 mesh (300 microns). HRI's application as a finishing reactor at low temperature using trilobe catalyst for low pressure drop along with the lower concentration and smaller size should reduce plugging problems and will provide data for modelling.

A simple first-order model with identical rate constants and at a conversions of 95% in two-stages indicates that the CSTR Fixed-Bed would require only 55% of the reactor volume as the CSTR-CSTR configuration.

In modelling the CSTR-Fixed Bed and CSTR-CSTR systems on Black Thunder sub-bituminous, the plug flow option with an isothermal second stage could raise coal conversion by about 3.4% and lower the bottoms plus gas yield by 3.9% of dry coal, with 0.3 W% low hydrogen consumption. The indicated yield of distillates would be 4% higher than in the conventional arrangement, and this yield per unit of hydrogen consumption would be 9% higher.

Three Stage CSTR Systems

The addition of a third ebullated bed in series to the CTSL configuration would assuredly result in closer approach to plug flow-fixed bed potential and involves virtually no processing uncertainties.

The ebullated bed configuration in series differs from previous three stage concepts in control of stage temperatures to obtain an optimum interrelation of hydrogenation and cracking functions. A large part of previous efforts included a high temperature-short contact time pre-reaction of the coal slurry to maximize the degree of coal conversion. Apparently, such a pattern did not promote hydrogenation functions to the degree that would assure the best selectivity to light liquid products, which can be obtained from coupled multistage catalytic system.

It is recognized that three stage testing does not represent a radical innovation, since from the inception of the ebullated bed development it was recognized that the "stirred-tank" effect of the ebullated system has a kinetic disadvantage which could be mitigated in part by staged systems, two, three or more reactors.

However, the effort involves the three ebullated bed configuration largely as a reference for other essential innovations of this program, the use of a fixed bed as the third stage, or the incorporation of a practical method of reconcentration of heavy reactants before entering further staging.

A simple first order kinetic model, with equal temperatures in the stages, indicates that a three-stage system would require 25% less total reactor volume than the two-stage system at a conversion level of 95%.

The three-stage concept can be improved further through interstage product separation and reactant concentration and/or incorporation of a fixed-bed upgrading stage.

Product Stream Concentration

The concentration of primary reactants declines progressively in a plug-flow system and is lower stage-by-stage in a close-coupled, multistage CSTR system. More effective use of reaction space for the conversion of liquid and solid phase reactants can be promoted if their concentrations in the liquid phase could be maintained at higher levels and the hydrogen partial pressure increased. For example, in a three-stage CSTR system with simple first-order kinetics, attaining 95% conversion, the primary reactant concentration being fed to the third stage is about 15% of that in the feed to the first stage. Nominally, if the third stage feed concentration were raised to that of the original feed the proportion of reaction in the third stage could be correspondingly increased. Calculations based on the simple first-order model indicate that a three-stage system of CSTR reactors with reconcentration of the second stage product going to the third stage to obtain the same content of the reacting components as in the first stage feed would require only 43% as much total reactor volume to attain 95% conversion as would be needed in a conventional two-stage system with no interstage feed concentrations. Use of an interstage vapor/liquid separator offers the opportunity to increase the reactant (650 F° slurry) concentration, increasing subsequent stage hydrogen partial pressure (through fresh hydrogen addition), and decreasing the production of by-product light hydrocarbon gases (C_1-C_3) produced from further cracking of the 650 F liquid products.

Experimental

The feedstocks for this program are being obtained from interstage and product samples from HRI's CTSL Bench-Scale and PDU programs on Wyoming Black Thunder sub-bituminous and Illinois #6 bituminous coals.

The principal experimental systems that are being used are:

- A fixed bed microreactor with continuous liquid (slurry) and gaseous feeds.
- A 300 cc fixed bed reactor. This system represents a closer prototype to large scale equipment.
- A rapidly agitated microautoclave, 20 cc in volume, with very rapid heating and cooling. This apparatus used as a batch operation with and without catalysts is in a kinetic regime similar to a fixed bed plug flow reactor. Earlier experimental work has demonstrated kinetic effects of a pattern similar to those of prototype bench unit CTSL operations.
- A Robinson-Mahoney agitated reactor, containing a rotating catalyst basket, with a 1000 cc reaction volume. This system as a continuous flow operation corresponds to a catalytic CSTR configuration of the CTSL system with somewhat greater flexibility and simplicity of operation.

Plans

The program covers two years of activity, starting in October 1991 through September 1993. Experimental work is currently underway. Successful results from this program may be scaled to larger development units in a succeeding optional two year program.

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FIGURE 1

REACTOR CONFIGURATION AND REACTOR VOLUME

First Order Kinetics

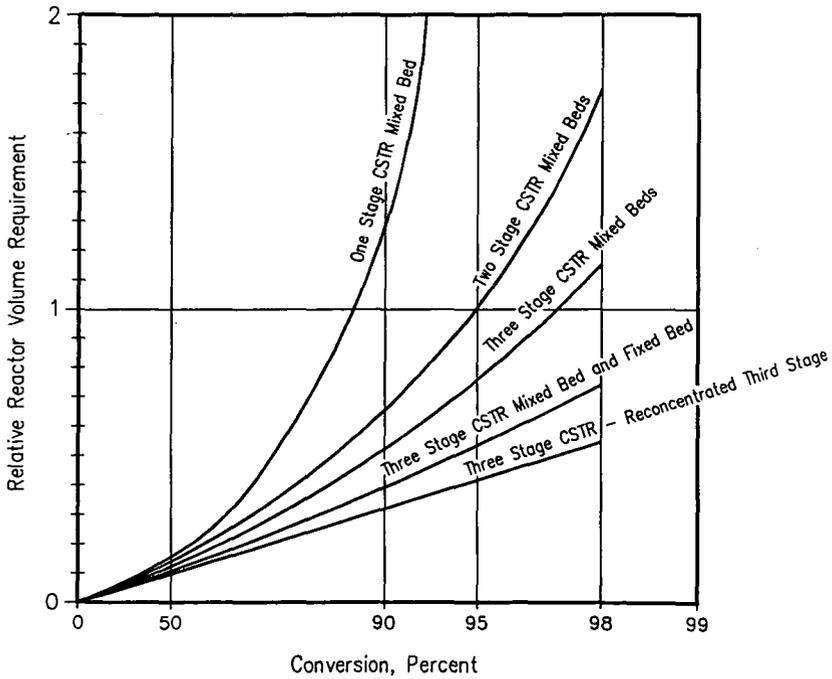


Figure 1. DT coal hydrogenation process, simplified flowsheet.
R, reactor. HS, IS, CS, hot-, intermediate-, cold separator.
VF, vacuum flash unit

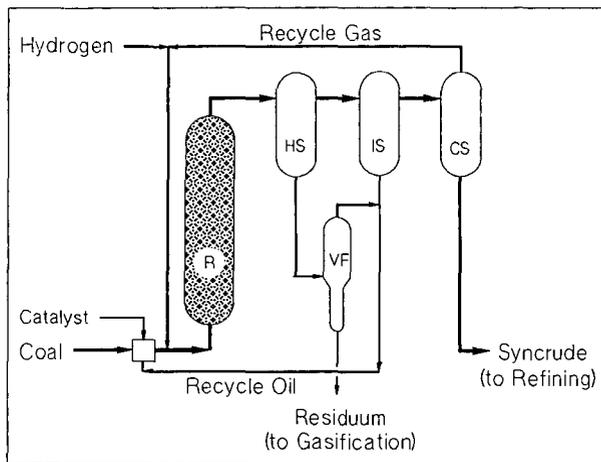


Figure 2. ASTM D-2887 boiling analyses of product and recycle oil from IGOR⁺ coal hydrogenation (dotted lines) and DT coal hydrogenation (solid lines).

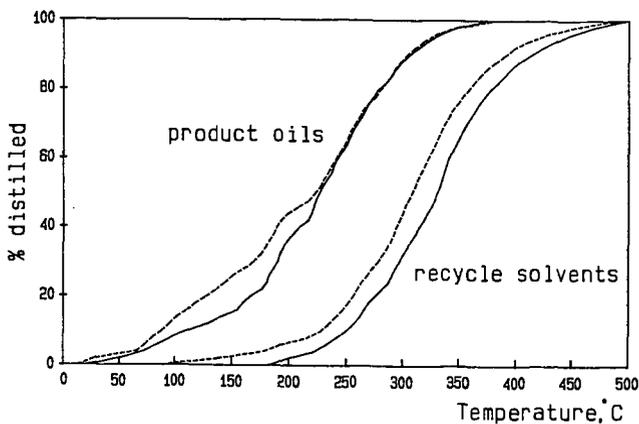


Figure 3. IGOR process, simplified flowsheet.

FB, fixed-bed catalyst. Other symbols, see Fig. 1.

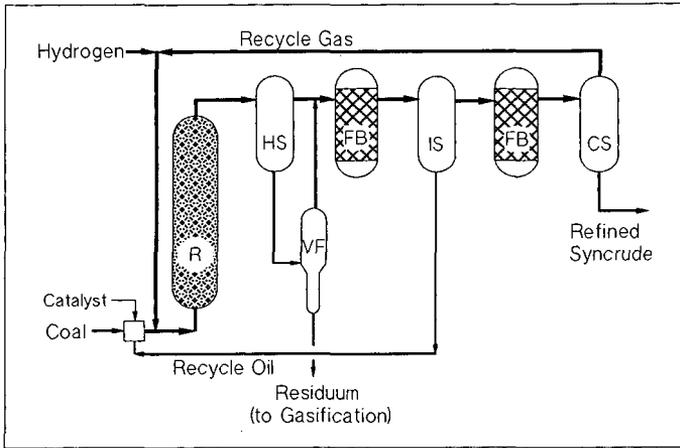
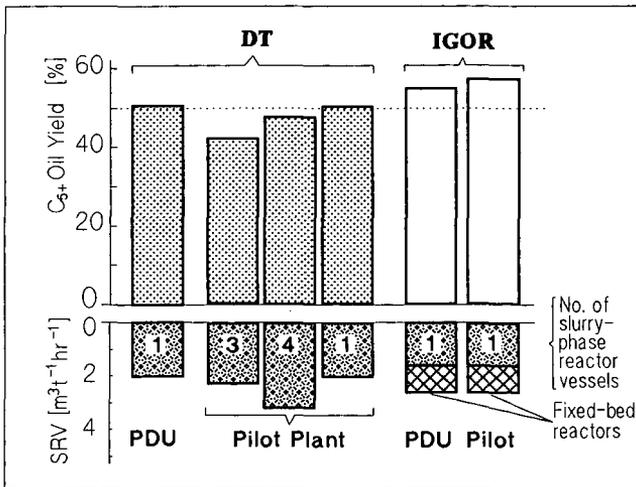


Figure 4. DT and IGOR process scale-up history.

SRV, specific reactor volume, d.a.f. coal basis.



IGOR - TAKING THE SHORT CUT IN COAL HYDROGENATION

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ABSTRACT

The primary liquids obtained from conventional coal hydroconversion processes all require extensive downstream hydrotreating. With a hydrotreating reactor appropriately integrated into a coal hydrogenation scheme, reformer/hydrocracker feed quality specifications can directly be attained, with only one process unit. A further modified arrangement even leads to significantly increased hydrocarbon oil yields from coal. The developing of the novel process, integrated gross oil refining (IGOR), is described. Results and experiences from PDU and from pilot plant operation are discussed.

INTRODUCTION

Several coal hydrogenation processes have been developed to technical maturity since coal-to-oil technologies were given a chance again. A good number of novel features have been successfully incorporated, but the competing schemes can all still be seen as mere modifications of the conventional high-pressure hydrogenation process: Apart from the processing steps they have all in common (slurry preparation, solvent recycle, indirect pre-heating, asphaltenes & solids separation, etc.), there is another joint feature. The primary coal-derived distillates ("syncrudes") are unacceptably high in oxygen and nitrogen contents and require extensive further refining prior to hydrocracking, reforming, or use as a marketable fuel whatsoever. (e.g.¹) Particularly in view of the black sediments that form even during short-term storage, and which are severely poisonous to upgrading catalysts, these syncrudes should only be taken with some reservations as the clean distillates they seem to be.

A further aspect which requires attention is, that the raw syncrudes have biological implications and are perceived as a potential health hazard at least in the working field. In syncrudes, primarily polynuclear aromatics, aromatic nitrogen bases, benzene, and phenols as well are of relevance to health considerations. It has therefore been recommended that the available coal hydrogenation processes be operated or modified such as to yield lower boiling and preferably saturated coal oils.² Developing an entirely different hydrogenation scheme might be another option, yet some way of integration of refining and saturation should already help to improve the technical, environmental, and probably also the economical preconditions for a future coal hydrogenation industry.

EXPERIMENTS AND RESULTS

A 0.2 t/d PDU and a 200 t/d pilot plant have been operated within the development work presented in this paper. All runs referred to in the following were carried out under 30 MPa total pressure, with a German HVBA feed coal and red mud as the catalyst in coal conversion. Commercial Ni-Mo-alumina catalysts were used in the fixed-bed reactors.

As for PDU operation, normally one week runs with the conditions maintained unchanged made a good basis for reliable data. With any mode of integrated refining, the runs were typically extended to last one month or more, primarily in order to make possible catalyst deactivation visible. For the same reason, these runs were repeated after several months.

DT Process Operation.

In order to explain the procedures and equipment used, we will firstly refer to the - earlier - DT process configuration (*Figure 1*), as this process provided the basis for the further developments.

A coal slurry is prepared from dried, ground coal, some powdered once-through catalyst, and a distillate-type process recycle oil. After treat gas addition (high-pressure recycle gas plus hydrogen make-up), the slurry is passed through heat exchangers and pre-heated to 420 °C. The upflow tubular reactor is operated as a rule at 475 °C. Still under process pressure, the reaction products are separated with a series of coolers/heat exchangers and stripper volumes: At about 450 °C minerals, unconverted coal, and little- and nonvolatile organic liquids are removed from the vapors and gases and let down from the hot separator. In a vacuum flash unit, some high-boiling overhead oil is recovered from the hot slurry, and a hot liquid underflow that contains around 50 % solids. The overhead oil is used as a recycle oil component, the underflow residuum as a liquid gasifier feed for hydrogen production.

The oil fraction condensed through appropriate temperature reduction (to around 300 °C) of the hot separator overhead vapors, is obtained as the intermediate separator letdown in just the amount required for coal slurry preparation. By further cooling of the high-pressure vapors and gases, the net syncrude yield condenses, along with process water which separates readily from the organic phase. - The high-pressure gases that leave the cold separator are oil-scrubbed for hydrocarbon gas reduction, and recycled to the hydrogenation unit.

DT Process Modification: Integrated Net Oil Refining.

Much as with practically any proven coal hydrogenation process, the syncrudes recovered from DT coal conversion will require extensive refining. With respect to their eventual utilization as motor fuels and possibly jet fuels, DT syncrudes have favorable boiling ranges (end points lie around 330 °C). But in order to meet the existing specifications for marketable fuels and hydro-conversion feed oils, respectively, the high concentrations of oxygen and nitrogen containing compounds as well as fused-ring aromatics need be radically reduced. Because of the essentially cyclic nature of coal-derived oils, comparatively severe conditions are required in the hydro-refining of such feed.

We found that it is not only viable but even advantageous to integrate a hydrorefining and saturation stage into a coal hydrogenation plant rather than running the units separately.³ With a fixed-bed catalytic reactor arranged downstream the intermediate separator, the product oil vapors are hydrotreated still before they are condensed and let down. Thus, by taking advantage of both the high-pressure, hydrogen-rich gas as well as the sensible heat of the separator overhead stream, appreciable savings in investment and energy costs can be realized.

Extended PDU runs established that the product oil qualities obtained with separate refining are attained with integrated refining as well. The total heteroatoms concentration - nitrogen, oxygen, and sulfur - can be kept well below 10 mg/kg. Oil yields from separate and from integrated refining, respectively, are naturally about the same: With the little reactive German bituminous feed coal, the yields of refined C₄+ oil amount to 54 % w/w on dry, ash-free coal in both cases.

Integrated Gross Oil Refining.

Further coal hydrogenation tests included a modified integrated refining scheme in which the fixed-bed reactor was arranged such as to hydrotreat not only the net product but also the oil continually recycled for coal slurry preparation ("gross oil refining"). The heavy distillate fraction - vacuum flash overhead oil - was injected before the reactor. With a liquid hourly space velocity four times the previous one and with the feed boiling range much higher at that, several hundred mg/kg hetero atoms were left in the net product oil. Net oil yield, however, had surprisingly soared to more than 60 %. Tracer and other investigations have made clear that the yield improvement is brought about thanks to a much extended liquid/solid residence time in the coal conversion reactor.⁴ The "driving force" is enhanced oil stripping which in turn is due to the more readily volatile recycle oil, see the boiling curves plotted in *Figure 2*.

With nitrogen contents between 80 and 100 mg/kg and even higher oxygen levels, the product oil fails to meet minimum feed specifications for further processing over bifunctional catalysts. In other words, the extra oil yield is obtained at the expense of quality, which additional hydrotreatment indispensable.

The process recycle oil, once equilibrated through continual recycling, will - simply speaking - behave as an inert diluent that does not undergo further hydrogenation reactions. Seen from this point of view, the fixed-bed reactor is merely treating the net product oil, though at an unfavorably high space velocity. Therefore, it seemed promising to apportion the catalyst filling into two separate but smaller reactor volumes, with the first one employed for gross-oil- and the second one for net-oil-treatment only (see *Figure 3*).⁵ The results received with this mode of operation fully answered the expectations, as both high oil yield and perfect quality were obtained now at the same time. This process mode was named IGOR⁺. It compares favorably with other processes as can be concluded from *Table 1* - in particular when considering the rather low reactivity of German bituminous coal. A synopsis of PDU results obtained with the various process modes discussed above is shown in *Table 2*.

DISCUSSION

Process operation experiences.

Even if quite obvious, it should be noted that IGOR⁺ product oil, thoroughly different from any syncrude, is water-white, stable in storage, and completely free of "that certain coal-oil smell". Less obvious, most of the process internal oil streams, particularly the recycle solvent inventory, have a merely faint, "clean" odor and separate easily from water. Moreover thanks to IGOR⁺, any biotoxic potential suspected in the previous process liquids has in all probability been removed. The improvement of the environmental conditions, in particular at the PDU with its frequently opened containers and its occasional leaks and spills, is unmistakable.

With the IGOR modes of operation, a new situation was encountered in coal slurry handling: Density and viscosity of the recycle oil had become too low to keep the solids suspended so that settling, pump failures, and other problems emerged. As a countermeasure, the earlier slurry viscosity was re-adjusted to its previous value by simply raising solids concentration from 42 to 51 % (coal-to-oil ratios, 1:1.4 and 1:1, resp.). As the slurry feed rate was not correspondingly reduced, this meant an increase in specific coal feed rate by 20 %. It turned out that, different from the DT process, oil yield suffered only little from the elevated specific coal feed rate. At the same time, apparently due to the reduced liquid feed load to the first fixed-bed reactor, product analyses showed no sign of oil quality reduction. Thus, a slurry solids concentration of more than 50 %, and a specific feed rate of 0.6 kg m.a.f coal per hour and per liter of reactor volume, became features of IGOR "standard" operation conditions.

Coal conversion temperatures in the IGOR process are somewhat lower than in the DT process which results in a reduced gas make and thus, in a comparatively lower hydrogen demand. Some extra hydrogen, on the other hand, is consumed in the methanation of the carbon oxides which takes inevitably place at the highly active refining catalysts. The coals that are typically fed to the process form only little carbon oxides (roughly 1 % on coal under DT process conditions) so this is certainly not too great a drawback. But a great advantage was found as well:

In any conventional coal hydrogenation process, continuous purge water injection is mandatory in order to prevent plugging of high-pressure gas lines with carbon dioxide derived salts, essentially ammonium carbamates. Hence sour water output is much higher than would be brought about from only hydrodeoxygenation and the coal moisture. With integrated refining there are no carbon oxides left, so purge water is no longer necessary. At the same time, refining has completely removed the phenols. Accordingly there is not only much less waste water to be treated but it does also no longer contain phenols that had to be dealt with. Total Organic Carbon had averaged 10,000 mg/kg in the conventional process (DT); with IGOR⁺, TOC values never exceeded 50 mg/kg.

Scale-up Experiences and Results.⁷

In most if not all direct coal liquefaction projects that were continued to pilot scale, the syncrude yields obtained in the PDUs could not be reproduced on a hundred-tons-per-day level [LIT X]. Initially, this was also true for the DT process. A single volume (11 l) made the PDU coal conversion reactor while a tanks-in-series reactor system was used on pilot plant scale, much as with the I.G. technology development. At identical specific coal feed rates, three tubular reactors (5 m³ each) gave significantly less oil yield on coal than had been obtained with the PDU. Even with a much lower specific feed rate - a fourth 5 m³ cylinder added - and with the reaction temperature elevated by 10 K in addition, oil yield still remained slightly below the PDU results. Contrary to all expectations, this changed when the cascade was replaced by a 15-m³ capacity, cheaper-to-fabricate "large-volume reactor". Now the results were exactly the same as those in the 1,400 times smaller unit.

The process was tested on pilot scale directly with the large-volume reactor; as the fixed-bed catalytic reactors, the 5-m³ cylinders were used. The results obtained were even somewhat more favorable than in the small-scale tests. In *Figure 4*, the above development history is illustrated and reviewed.

With the large KOHLEÖL pilot plant at Bottrop, still another benefit of the IGOR process could be demonstrated. It has been possible to bring the coal slurry up to reaction starting temperature exclusively through heat exchange with reaction product streams and preheating of the treat gas. In other words the slurry preheater, always an expensive and delicate component of the plant, was no longer necessary.

CONCLUSION

More recently in the PDU, a different bituminous coal - much more reactive yet higher in minerals at the same time (11 % ash, dry) - was processed under "standard" IGOR⁺ operation conditions. In the product oil, a total hetero atoms content of less than 5 mg/kg was achieved, and the C₄⁺ yield came as high as 66 % on d.a.f.coal.

Thus far in IGOR process testing, with totalized operation periods of up to 330 days, in neither of the two fixed-bed reactors were observed signs of serious catalyst deactivation. Presently, the only limitation foreseen is with feed coals that have too high an oxygen content and thus excessive carbon oxides formation, so that uneconomically much hydrogen might be spent in methanation.

The most apparent advantages of the process over its predecessors can be summarized as follows. IGOR⁺ means:

Reduced

- equipment needs
- recycle oil flow
- hydrocarbon gas formation
- waste water treatment requirements

Eliminated

- purge water injection
- carbon oxides
- phenols
- polynuclear aromatics & aromatic amines
- slurry preheater

Increased

- oil from coal yields
- specific coal feed rate
- coal concentration in the slurry feed

Improved

- product quality
 - naphtha cut ready for reforming,
 - gas oil cut ready for hydrocracking
 - or blending with diesel fuel
- working place environment
- overall plant operation
- process efficiency and economy

Rather than by splitting apart coal-to-oil conversion into discrete stages that can be individually optimized but will also suffer from individual idiosyncrasies, good yields of clean hydrocarbon liquids are also accessible in a more straightforward method using a relatively simple, integrated hydrogenation process.

ACKNOWLEDGMENT

Funding of the KOHLEÖL development program by the Minister für Wirtschaft, Mittelstand und Technologie des Landes Nordrhein-Westfalen is gratefully acknowledged.

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Table 1. Syncrude yields and properties from different coal hydrogenation processes.
[Data partly after Peluso et al.⁶]

PROCESS:	EDS	H-Coal	ITSL	SRC II	DT	IGOR ⁷
Feed coal	Illinois # 6	Indiana # 5	Kentucky # 9	Ruhr Gasflamm, Prosper		
- Carbon	% d.a.f. 77	78	78	79.5	85	
C ₄₊ Oil yield	% on d.a.f. coal 39	50	56	43	55	60
Oil Inspection:						
- Boiling end	ASTM D86, °C 520	520	450	480	330	331
- Hydrogen	% 11.2	10.7	10.7	9.6	10.0	13.7
- Oxygen	mg/kg 15,000	15,000	7,000	35,000	27,000	< 5
- Nitrogen	mg/kg 3,000	3,000	4,000	1,400	9,000	< 2
- Sulfur	mg/kg 800	800	800	2,000	800	< 1

Table 2. Feed and product characterization for DT and IGOR process modes.

PROCESS:		DT	IGOR	IGOR ⁺
Feed Coal		Ruhr Gasflamm, Prosper (HVBA)		
Proximate analysis				
Ash			5.1	
Volatile matter	% dry		36.5	
Elemental analysis				
Carbon	% d.a.f.		84.8	
Hydrogen	"		5.6	
Oxygen	"		7.2	
Nitrogen	"		1.5	
Sulfur	% dry		1.0	
PDU Operation Conditions:				
Specif. d.a.f. coal feed rate	kg ltr ⁻¹ hr ⁻¹	0.5	0.5	0.6
Coal/oil ratio in slurry feed	kg kg ⁻¹	1 : 1.4	1 : 1	1 : 1
Total pressure	MPa	30	30	30
Reaction temperature	°C	475	470	470
Catalyst in coal conversion	(dispersed)	red mud	red mud	red mud
Catalyst in hydrotreating	(fixed bed)	—	Ni—Mo	Ni—Mo
Hydrogen consumption	% on d.a.f. coal	6.7	9.3	9.0
Product Yields:				
C ₄₊ Net product oil	% on d.a.f. coal	55	61	60.5
Flash residuum [a.f. basis]	"	24	20	21
C ₁ —C ₃ Hydrocarbon gases	"	20	18	17
Reaction water & inorg. gases	"	7.5	10	10
C ₅₊ Oil Inspection:				
Density @ 20°C	g cm ⁻³	0.930	0.844	0.833
Boiling analysis, ASTM D86				
I.B.P.	°C	96	87	80
10 %	"	144	127	115
30 %	"	196	183	175
50 %	"	222	226	220
70 %	"	250	252	251
90 %	"	290	289	289
F.B.P.	"	330	331	331
Elements				
Hydrogen	%	10.0	13.0	13.7
Oxygen	mg/kg	9,000	85	< 5
Nitrogen	mg/kg	27,000	160	< 2

HIGH CONVERSION IN COAL LIQUEFACTION WITH LOW HC GAS PRODUCTION

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INTRODUCTION

For the past 30 years or more the projected cost of producing a synthetic crude from coal has been from 50% to 100% (sometimes more) higher than the cost of crude petroleum at the time of comparison. The work in this research program addresses that fact, and represents an attempt to significantly reduce the cost of producing liquids from coal. Inasmuch as hydrogen is an expensive reactant, a principal objective in this research is to avoid large-scale use of hydrogen, to be achieved by minimizing the production of hydrocarbon gases in the conversion process. It is noted that one can exercise much greater control over the chemistry intended to occur in a system if the reactions can be carried out in a fluid phase, liquid or gaseous, compared with reactions in the solid phase. This is particularly true when coal is the solid-phase reactant. An objective in this work, therefore, is to proceed from solid coal to a liquid as inexpensively as possible.

A process for direct conversion of coal to liquids usually begins by slurring the coal in a liquid. Inasmuch as there does not exist a reliable technology for introducing dry solids into a region in which pressures of 1500 psig or higher must exist, slurring the coal in a liquid is used to permit pumping the coal into the pressurized region. The presence of a liquid phase surrounding the coal particles after introduction into the reactor, as well as inside of the pores and channels of the coal, inhibits heat transfer into the particle by any means one may choose to use to heat the coal particles to reaction temperature (generally above 400 °C), resulting in residence times in the hot zone of many minutes, characteristically between 15 minutes and one hour. One loses control over most of the chemistry of the process. Specifically, when the coal and its primary conversion products are exposed to temperatures above 375 °C for such long periods of time, many thermal degradation reactions occur, most of them undesirable. These reactions lead to high yields of hydrocarbon gases, hence high hydrogen consumption. They also lead to asphaltene production, making the downstream processing of the liquids more difficult.

The experiments being conducted in this work were designed to examine the chemistry which may occur when the coal particle

is heated to reaction temperature in times of one or two seconds, and the liquefaction process to form primary liquids is completed in times measured in seconds rather than minutes. It was expected, and is now observed, that conversions greater than 70% by weight of the coal, accompanied by ratios of liquids/HC gases of 10/1 or greater, can be achieved. The question of how coal may be introduced into a system to achieve these results, a question probably in the mind of the reader, is not an objective of this research program. However this question is now being addressed in a proposal now in preparation. The theoretical considerations which underlie that concept indicate a reasonable promise of success experimentally.

EXPERIMENTAL

Two reactor systems have been designed and constructed, namely a batch micro-reactor and a continuous-flow tubular reactor.

A sketch of the micro-reactor is shown in Figure 1. The reactor has an internal volume of 107 cc, and is constructed of stainless steel. It is designed to accommodate pressures up to 3000 psig at temperatures up to 600 °C. The coal sample is supported on a stainless steel gauze, attached to two electrodes to provide for electrical heating. A thermocouple is mounted immediately above the wire gauze, not touching the gauze but such that it will be embedded in the coal sample. A second thermocouple is placed to read temperatures in the gas space between the coal sample and the wall of the reactor. Cooling coils are located in the walls of the reactor, but they have not been required for experiments at the short times of these experiments. A special temperature controller was constructed which provides for rapid heat-up to the required temperature, while avoiding temperature over-shoot of more than a few degrees.

In a typical experiment, coal is crushed to pass through a 200 mesh Tyler Series screen (coal particles -74 microns). The soluble acid catalyst (see Table I) is impregnated into the pores of the dry coal, and the solvent evaporated. Two hundred grams of coal are placed on the wire gauze, exercising care to ensure that the coal particles completely surround the tip of the thermocouple. The reactor is closed, and pressurized with hydrogen to a calculated pressure such that the pressure at operating temperature will be about 1500 psig. At the completion of the experiment at a predetermined time, the reactor system is quenched. The gases are passed to a gas sampler, then to a wet-test meter. Gas samples are analyzed by gas chromatograph (GC). From the GC analysis and wet-test meter measurements, quantities of individual hydrocarbon gases are calculated. The liquids collected from the vessel are combined with liquids removed from the solids by extraction, and weighed. The solids are weighed.

The continuous flow reactor consists of a straight stainless steel tube, 5/16 inch inside diameter, heated by a series of electrical heating jackets, each operated from a temperature controller. The length of the reactor is increased by adding tube sections. Coal is prepared as described above, and fed to the reactor from a lock hopper utilizing a star feeder. Hot hydrogen gas is injected into the reactor with the coal. Residence times in the reactor are established by changes in gas flow rates, coupled with changes in coal feed rates by the star feeder, and by changes in reactor tube length. The products from the reactor pass through a solids separation vessel, maintained at the temperature of the reactor, then through two cooled vessels for liquids removal. The gases pass to a gas sampler, then to a wet-test meter. Determinations of product quantities and analyses are as described above.

RESULTS AND DISCUSSION

Representative experimental data from the microreactor are presented in Table I. The coal sample consisted of 200 mg of a Wyodak sub-bituminous coal. The experiment was conducted as described above. After 20 seconds, the system was quenched, and products removed and analyzed as described above. Fifty percent by weight of the coal was converted to liquids and gases in this experiment, with a ratio of liquids/HC gases of 10.6/1.0. The extracted char was then used as the solid feed for a second pass of 20 seconds duration. An additional 58% of the char (representing 29% of the original coal), was converted in this second pass, resulting in a total conversion of 79% by weight of the coal. In the second pass the ratio of liquids/HC gases was extremely high, namely about 23/1. When the results of the two passes are combined, the overall ratio liquids/HC gases is 15/1. Duplicate experiments revealed very good reproducibility of the data.

The data of Table I reveal important information relative to the potential for conversion of coal to high liquid yields with low yields of hydrocarbon gases. In the microreactor the coal sample sits on the heating mantle, with the thermocouple buried inside of the coal sample. The thermocouple indicated achieving reaction temperature in the coal sample in about 2-3 seconds. A second thermocouple located midway between the coal sample and the wall of the reactor indicated a maximum temperature at that location in the gas phase of 80 °C. During the experiment of 20 seconds (per pass) as the coal structure is depolymerized and molecules formed, made possible in large yields by the catalyst, much of the liquid-size molecules with sufficient vapor pressure at 500 °C distill from the residual coal mass to be almost instantly quenched in the surrounding gas phase, which is at a temperature well below that required for extensive cracking of these molecules, thus leading to very low gas yields. Under

these conditions, in the first pass those easily-released units in the coal, which upon release yield HC gases, together with any HC gases formed by thermal cracking, constitute not more than about 8% by weight of the total products evolving from the residual coal in that pass (approximately 4% of the weight of the original coal). The additional gases formed following the first pass constitute an extremely small portion of the products evolving during the second pass (about an additional 1% of the weight of the original coal). Thus the results in Table I reveal a liquid yield of about 74% by weight of the coal, while limiting hydrocarbon gases to about 5% by weight of the coal.

A sample of the data obtained from experiments conducted in the continuous-flow tubular reactor are presented in Table II. The coal utilized in this experiment was also a Wyodak sub-bituminous coal. Gas-flow rates in this experiment indicated a solids (and products) residence time in the reactor of about 17 seconds. In the first pass of the solids through the reactor, about 56% of the coal, by weight, was converted to liquids and gases, with a ratio of liquids/HC gases of 8.3/1.0. Following removal of the liquids from the solids by extraction, these solids were fed to the tubular reactor for a second pass, under reactor conditions identical to the first pass. In the second pass, 37% of those solids (representing about 16% by weight of the original coal fed in the first pass) was converted, for a total combined conversion in the two passes of 72%. The ratio of liquids/HC gases in the second pass was about 14/1, and the overall ratio liquids/HC gases for the two passes was 9.5/1.0.

The mechanics of the liquids and solids in the continuous-flow system utilized in these experiments are different from those which obtain in the microreactor, leading to lower ratios of liquids to HC gases. However one can visualize a continuous-flow system which may give yields and product ratios approaching those observed in the microreactor system. It may be difficult to operate such a system configuration at a bench scale.

The liquid products obtained from reactions of the Wyodak coal in the microreactor in the presence of MoS_2 or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ catalyst were subjected to GC and FTIR analysis.

Gas chromatography on a 12-ft x 1/8-in column packed with 8% OV-17 on 100-120 mesh Chromosorb HP indicated that essentially all of the product components are distillable between ca 100-300 °C. The chromatogram consisted of well-resolved peaks corresponding to low-molecular weight cleavage products. The chemical compound types present were clarified by FTIR analysis of product films, using a Perkin-Elmer, 1600 Series FTIR Spectrometer. Figure 2 provides an example of FTIR spectra for the liquid products.

The spectrum indicates the presence of several types of functional groups and characteristic aromatic ring substitution patterns in components of the liquid product, as follows: phenolic (and possibly alcoholic and carboxylic acid) groups, (O-H stretching bands between $3200-3650\text{ cm}^{-1}$; non-associated OH groups, sharp band near 3640 cm^{-1} ; associated OH groups, broad band between $3250-3450\text{ cm}^{-1}$); CH_3 , CH_2 and CH groups in alkyl substituents (or paraffins) and CH_2 and CH groups in naphthenic rings (at least three C-H stretching bands in the $2830-2980\text{ cm}^{-1}$ region); carbonyl groups in esters and possibly carboxylic acids ($\text{C}=\text{O}$ stretching bands near 1731 and 1767 cm^{-1} , due to aromatic and saturated esters, correspondingly); aromatic rings (breathing band near 1602 cm^{-1}); CH_3 , CH_2 and CH groups (C-H bending maxima between $1340-1470\text{ cm}^{-1}$); phenolic and aryl etheric groups (C-O stretching bands in the $1150-1310\text{ cm}^{-1}$ region); penta-substituted aromatic rings, viz., a single non-substituted aromatic hydrogen (weak C-H out-of-plane bending band at 885 cm^{-1} ; low concentration); tetra- and penta-substituted aromatic rings, viz., 1 or 2 adjacent non-substituted aromatic hydrogens (C-H out-of-plane bending band near 861 cm^{-1}); tri- and tetra-substituted aromatic rings, viz., 2 or 3 adjacent non-substituted aromatic rings (C-H out-of-plane bending band at 811 cm^{-1}); ortho-disubstituted aromatic rings, viz., 4 adjacent non-substituted aromatic hydrogens (C-H out-of-plane medium-intensity bending band near 767 cm^{-1} and a strong bending band at 745 cm^{-1} , indicating relatively high concentration of this ring-substitution type); and monosubstituted aromatic rings, viz., 5 adjacent aromatic hydrogens (very weak band at 697 cm^{-1} ; very low concentration of this ring-substitution type).

The molecular weight distribution of product components and more precise structural information are presently being sought by GC/MS.

TABLE I

Experimental Data from the Microreactor

Coal feed: Wyodak sub-bituminous, -200 mesh

Reactor temperature: 500 °C

Reactor pressure: 1500 psig

Time at reactor temperature: 20 seconds per pass

Catalyst: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, impregnated from acetone solution

<u>Run No.</u>	<u>Pass</u>	<u>Pass % Conv. Liquids + HC gases</u>	<u>Cum. Conv. Liquids + HC gases</u>	<u>Pass ratio Liq/HC gases</u>	<u>Cumulative ratio Liq./HC gases</u>
23-1	1st	50.0	50.0	10.6	10.6
23-2	2nd	58.0	79.0	22.6	15.0

TABLE II

Experimental Data from the Continuous Reactor

Coal feed: Wyodak sub-bituminous, -65, +100 mesh

Reactor temperature: 450 °C

Reactor pressure: 1500 psig

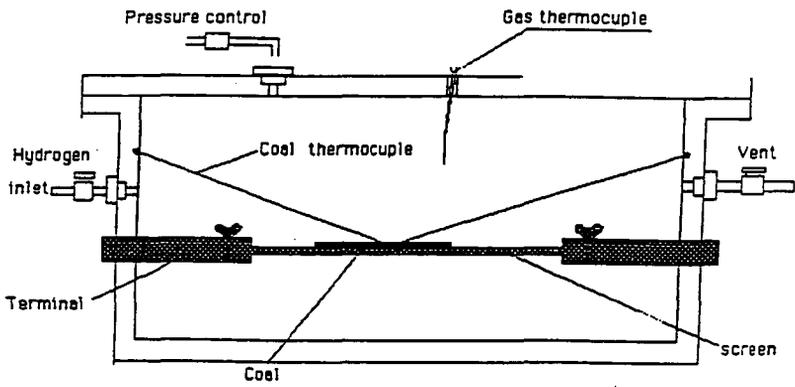
Gas flow velocity: 0.8 feet/sec

Catalyst: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, impregnated from acetone solution

Material balance: 93%, based upon dmmf coal

<u>Pass</u>	<u>Pass % Conversion Liq. + HC gases</u>	<u>Cumulative % Con. Liquids + gases</u>	<u>Pass ratio Liq/HC gases</u>	<u>Cumulative ratio Liq./HC gases</u>
1st	55.6 %	55.6 %	8.3	8.3
2nd	37.2 %	72.7 %	13.7	9.5

FIGURE 1
The Micro-reactor



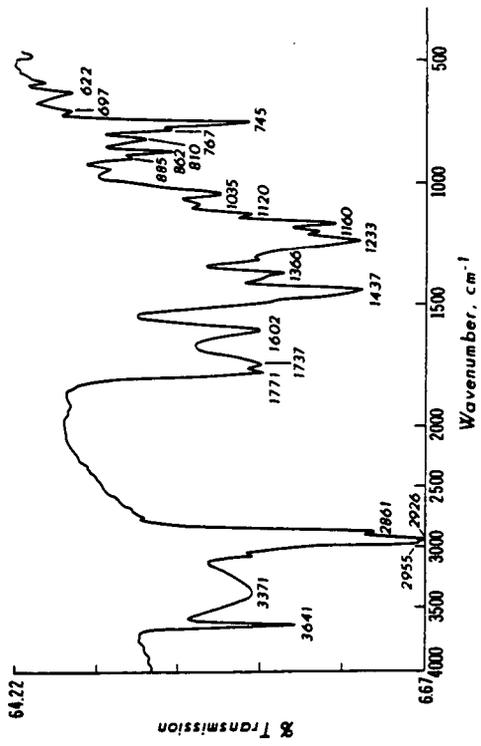


Fig. 2. FTIR Spectrum of Liquids from the Short Residence Time Procedure.

BIOLIQUEFACTION OF COAL SYNTHESIS GAS

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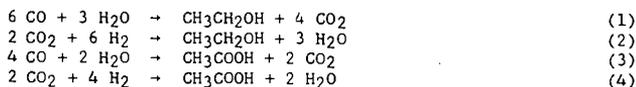
INTRODUCTION

Synthesis gas, a mixture of primarily CO, H₂ and CO₂, is a major building block in the production of fuels and chemicals. The gas may be produced from several sources, including coal, oil shale, tar sands, heavy residues, biomass or natural gas. Most synthesis gas is produced today by catalytic reforming of natural gas, although the partial oxidation of heavy liquids is also practiced (Graboski, 1984). Only a small percentage of the synthesis gas currently produced is by gasification of solid fuel. However, because of the large reserves of coal in the United States (300 year supply at the current consumption rate (Specks and Klussman, 1982)), synthesis gas production from coal will become an important technology in the future.

Coal gasification, which is a combination of pyrolysis and combustion reactions (Simbeck *et al.* 1982), produces a gas consisting of more than 50 percent H₂ and CO, the balance being a mixture of CO₂, CH₄, H₂S, COS and nitrogen compounds. The actual composition depends upon process conditions and the coal that is employed. The raw gas has a low to medium Btu content, with a heating value of 160-450 Btu/SCF, depending on whether air or oxygen is used during gasification (Coffin, 1984). Following quenching and purification, the synthesis gas contains 25-35 percent H₂, 40-65 percent CO, 1-20 percent CO₂, 0-7 percent CH₄ and other compounds in small quantities.

Catalytic processes may be used to convert syngas into a variety of fuels and chemicals, such as, methane, methanol, formaldehyde, acetic acid, etc. (Courty and Chaumette, 1987). Microorganisms may also be used to convert synthesis gas components into fuels and chemicals. Biological processes, although generally slower than chemical reactions, have several advantages over catalytic processes, such as higher specificity, higher yields, lower energy costs and generally greater resistance to poisoning. Furthermore, the irreversible character of biological reactions allows complete conversion and avoids thermodynamic equilibrium relationships.

Clostridium ljungdahlii, Strain PETC, was originally isolated from animal waste in the University of Arkansas laboratories, and is the only known organism capable of producing ethanol from CO, CO₂, and H₂ in synthesis gas (Barik *et al.* 1988). The overall stoichiometry for the formation of ethanol and acetate from CO and H₂/CO₂ has been established as (Vega *et al.* 1989a):



However, under optimal growth conditions, the organism produces acetate in favor of ethanol, with acetate:ethanol product ratios as high as 20:1 (Vega *et al.* 1989a). Research has concentrated on improving the product ratio in favor of ethanol using techniques found to be successful in boosting solvent production by other clostridial species. Improvements in solvent formation over acid production by clostridia have been obtained by utilizing nutrient limitation (Bahl *et al.*, 1986), reducing agent addition (Rao *et al.* 1987; Rao and Mutharasan, 1988), pH shift (Holt *et al.*, 1984; Huang *et al.*, 1986), hydrogen addition (Su *et al.*, 1981) and alternate medium constituents.

The purpose of this paper is to present results of batch and continuous laboratory studies with *C. ljungdahlii* in converting CO, CO₂ and H₂ in synthesis gas to ethanol. In addition, the effects of the sulfur gases H₂S and COS on growth, substrate uptake and product formation are presented and discussed.

MATERIALS AND METHODS

Organism and Medium. *Clostridium ljungdahlii*; Strain PETC, was originally isolated from chicken waste in the University of Arkansas laboratories, and later identified and characterized by Dr. R. S. Tanner, University of Oklahoma, Department of Botany and Microbiology. The culture was stored in a non-shaking incubator (Precision Scientific, Chicago, IL) at pH 5 and 37°C on a basal medium and synthesis gas (65% CO, 24% H₂ and 11% CO₂), and transferred every two weeks.

Equipment and Procedures. Medium preparation was carried in an atmosphere of 80% N₂ and 20% CO₂, as described by Hungate (1969) and Ljungdahl and Wiegel (1986). The initial pH was adjusted to 4.0-4.5 with HCl. Batch experiments were carried out in serum stoppered bottles with working volumes of 158 mL (Wheaton Scientific, Millville, NJ) or 1218 mL (Bellco Glass, Inc., Vineland, NJ). Continuous experiments were performed in Bioflo fermenters (New Brunswick Scientific, New Brunswick, NJ), modified for anaerobic operation. The medium used in the fermentations for the kinetic analyses contained yeast extract, vitamins, and minerals. The medium in continuous reactor studies and sulfur tolerance studies contained no yeast extract and minimal B-vitamins.

Analytical Procedures. Cell concentrations (in mg/L) were determined by comparing optical density readings at 580 nm in a Bausch and Lomb (Milton Roy Company, Rochester, NY) Spectronic 21 spectrophotometer with a standard calibration curve. Gas compositions were obtained by gas chromatography with a 180 cm Carbosphere, 60/80 mesh, column. Liquid analyses were performed by gas chromatography on previously acidified samples in a 60 cm column packed with Porapak QS at 180°C. 1-Propanol was used as the internal standard during liquid phase analysis after first verifying that 1-propanol was not present as a product.

RESULTS AND DISCUSSION

Development of a Kinetic Model. Figures 1 and 2 show cell concentration and substrate (CO) profiles for the conversion of CO to ethanol and acetate by *C. ljungdahlii* in batch culture. Initial CO partial pressures ranging from 1.0-1.6 atm in synthesis gas were used in order to study the effects of CO on cell growth and substrate uptake. A medium containing 0.01% yeast extract was used in this study.

Figure 1 shows that cell growth was essentially the same at each CO partial pressure up to a batch fermentation time of 100 h. At this time, the cell concentration increased with increasing CO partial pressure. The cell yield on CO, $Y_{X/S}$, was found to be 0.79 g cells/mol CO. The time for complete CO utilization was essentially constant with CO partial pressure (Figure 2). Also, the rate of CO utilization, as obtained from the slopes of the plots, was essentially constant with initial CO partial pressure. Product profiles (data not shown) showed ethanol to acetate molar product ratios of approximately 1:10 regardless of CO partial pressure due to the presence of yeast extract.

A kinetic analysis was performed on the data to determine kinetic parameters for growth and CO uptake utilizing a modified Monod model to include substrate inhibition (Andrews, 1969):

$$\mu = \frac{\mu_m P_{CO}^L}{K_p + P_{CO}^L + (P_{CO}^L)^2/W} \quad (5)$$

and

$$q_{CO} = \frac{q_m P_{CO}^L}{K'_p + P_{CO}^L + (P_{CO}^L)^2/W'} \quad (6)$$

The parameters μ_m , q_m , K_p , K'_p , W , and W' are kinetic parameters to be determined. A similar set of equations may be written for the uptake of H_2 , if desired.

The procedure for finding the kinetic parameters involves first finding the mass transfer coefficient, K_{La} , via material balance on the mass transfer-controlled gas-liquid system. The estimation of K_{La} involves finding the volumetric CO disappearance in the closed system, $-(1/V_L) dN_{CO}/dt$, and plotting it as a function of the partial pressure of CO in the gas phase. If part of the data fall on a straight line, mass transfer limiting conditions may be assumed. This generally occurs at low CO partial pressures or at high cell concentrations. The procedure is demonstrated in Figure 3. As noted in the figure, K_{La}/H equals 8.55 mmol CO/atm·L·h.

Once K_{La}/H is determined, the dissolved CO tension, P_{CO}^L (analogous to the dissolved CO concentration in the liquid phase), is found for situations where mass transfer is not controlling. The parameters in Equations (5) and (6) may then be found by rearranging the equations and performing a quadratic regression as illustrated in Figures 4 and 5 for the specific growth rate and specific uptake rate, respectively. A detailed presentation of this procedure has been shown previously for the bacterium *Peptostreptococcus productus* (Vega et al. 1989b).

Straight lines are obtained in plotting either P_{CO}^L/μ or P_{CO}^L/q as a function of P_{CO}^L (Figures 4 and 5), indicating that substrate inhibition was unimportant at least for $P_{CO}^L \leq 1.1$ atm. Furthermore, the intercepts on the

ordinates in both figures were essentially zero, indicating that K_p and K_p were negligible in comparison to P_{CO} . Thus, Equations (5) and (6) reduce to zero-order equations for *C. ljungdahlii* grown on CO, with $P_{CO} \leq 1.1$ atm.

and

$$\mu = \mu_m = 0.04 \text{ h}^{-1}$$
$$q = q_m = 42.7 \text{ mmol CO/g cell}\cdot\text{h}$$

If the specific uptake rate of CO is converted to a carbon mass basis, a value of 0.22 g C/g cell·h is obtained for q_m , which is comparable to the rate of glucose uptake by *Saccharomyces cerevisiae* with a q_m of 0.27 g C/g cell·h (Vega, 1985). This rate indicates that *C. ljungdahlii* has reaction rates equivalent to other organisms that are used for commercial fermentations.

THE USE OF CELL RECYCLE IN THE CSTR

A cell recycle apparatus was used in conjunction with a standard CSTR as a method to increase the cell concentration inside the reactor. This is particularly important since total product formation with *C. ljungdahlii* has been shown to be proportional to the cell concentration inside the reactor.

Fermentations were carried out in a 1.6 L CSTR with cell recycle. The total liquid volume in the reactor was 1.0 L, consisting of basal medium without yeast extract and one-half B-vitamins. Ammonium phosphate dibasic was used to enhance cell growth. The temperature of the reactor was held constant at 37°C and the agitation rate was 400 rpm. The gas flow rate was 16.5 mL/min and the liquid flow rate was 300 mL/d.

Figures 6 and 7 show cell concentration and product concentration profiles for the CSTR with cell recycle. In these experiments, the CO conversion was rather low. As is shown in Figure 6, the maximum cell concentration reached was 1300 mg/L at 800 h, increasing significantly from the 200 mg/L concentration after 300 h. The product concentrations, shown in Figure 16, changed significantly with time. At a time of 300 h, the ethanol concentration was about 4 g/L and the acetate concentration was nearly 2 g/L. At a later fermentation time of 800 h, the ethanol concentration reached 15 g/L with an acetate concentration of 4 g/L. Other cell recycle studies have shown a 6 g/L ethanol concentration with a corresponding zero acetate concentration.

SULFUR GAS TOLERANCE OF *C. LJUNGDAHLII*

Many bacterial cultures capable of converting CO to products have been found to be quite tolerant of the sulfur gases H₂S and COS (Vega et al., 1990; Smith et al., 1991). *Peptostreptococcus productus*, for example, which converts CO to acetate, is able to successfully convert CO to acetate in the presence of 19.7 percent H₂S or COS after culture acclimation. The methanogen *Methanobacterium formicicum*, on the other hand, is able to tolerate only 6.6 percent H₂S or COS. However, even this latter result is encouraging, since typical coal-derived synthesis gas contains only 1-2 percent sulfur gases, mainly as H₂S.

C. ljungdahlii, grown in the presence of Na₂S in place of cysteine-HCl as the reducing agent for several weeks, was evaluated for its tolerance to H₂S and COS in batch bottle experiments. The 155 mL bottles containing 50 mL of liquid medium devoid of yeast extract and adjusted to pH 4.3, were first gassed with synthesis gas to a pressure of 10.7 psig. The desired amount of H₂S or COS (2.5 mL-20mL) at 1 atm was then added. This batch system was allowed to equilibrate overnight. As a final step 10 mL of *C. ljungdahlii* were added prior to incubation at 34°C.

The effects of H₂S on growth and substrate uptake by *C. ljungdahlii* are shown in Figures 8 and 9, respectively. As is noted in Figure 8, growth was not significantly slowed at H₂S concentrations below 5.2 percent. Upon the addition of 9.9 percent H₂S, however, growth essentially stopped. Similar results are noted with substrate uptake in the presence of H₂S (see Figure 9). The presence of H₂S slowed the rates of substrate uptake only slightly up to an H₂S concentration at 5.2 mole percent. Similar results were obtained with concentrations of COS up to 5.2 percent.

These concentrations are for in excess of maximum sulfur gas concentrations possible in coal synthesis gas. It should also be realized that dramatic effects can be obtained with prolonged sulfur gas acclimation. *P. productus*, for example, was only marginally tolerant of H₂S and COS in initial studies. Concentrations up to 20 percent were tolerated after a period of acclimation to the sulfur gases.

CONCLUSIONS

The anaerobic bacterium *Clostridium ljungdahlii* has been shown to be effective in converting CO, CO₂ and H₂ to ethanol. Rates of carbon uptake by *C. ljungdahlii* comparable to the rate of carbon uptake by the yeast *Saccharomyces cerevisiae* have been obtained. A CSTR cell recycle system has been shown to be effective in permitting the cell concentrations necessary for high concentrations of ethanol. An ethanol concentration of 13 g/L with a corresponding acetate concentration of 4 g/L has been attained. Alternatively, an ethanol concentration of 6 g/L without the presence of acetate has been reported. Finally, *C. ljungdahlii* has been shown to be tolerant of H₂S or COS in concentrations exceeding typical levels in synthesis gas.

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ACKNOWLEDGMENT

The work presented in this paper was made possible through the financial support of the U. S. Department of Energy, Pittsburgh Energy Technology Center, under contract numbers DE-AC22-88PC79813 and DE-AC22-89PC89876.

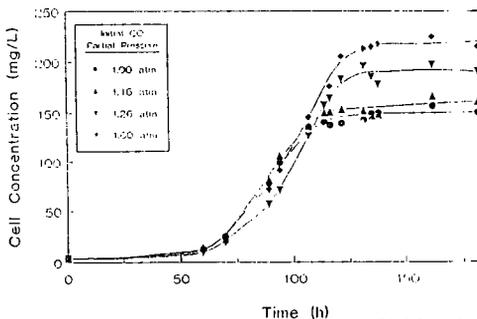


Figure 1. Cell Concentration Profile for the Fermentation of CO by *G. Ljungdahlii*

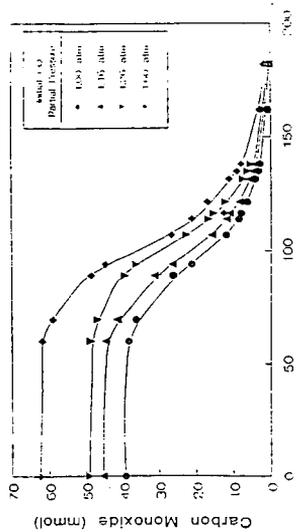


Figure 2. CO Profile for the Fermentation of CO by *S. limosus*.

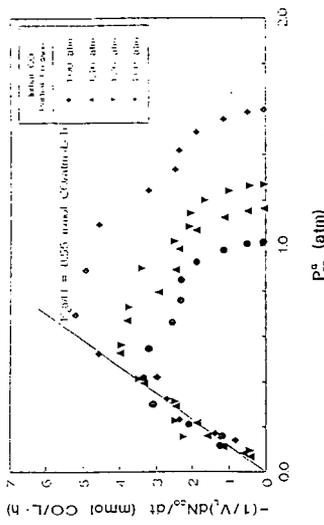


Figure 3. Determination of the Mass Transfer Coefficient for the Fermentation of CO by *S. limosus*.

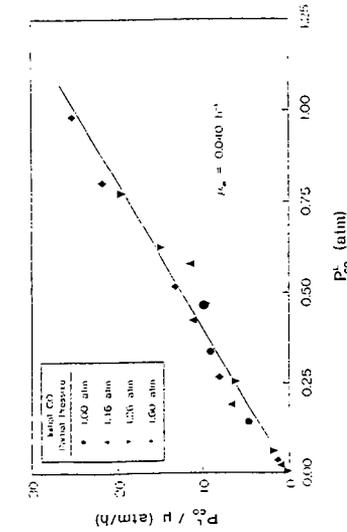


Figure 4. Determination of Monod Model Kinetics for the Rate of Cell Growth by *S. limosus*.

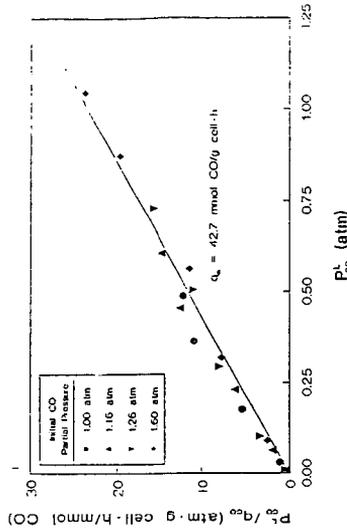


Figure 5. Determination of Monod Model Kinetics for the Rate of CO Uptake by *S. limosus*.

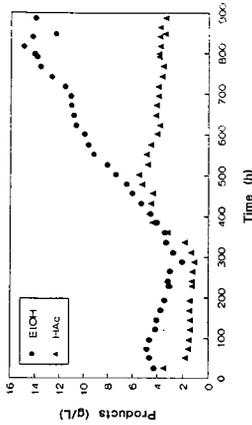


Figure 7. Ethanol and Acetic Acid Concentration Profiles for *E. LimbuhlII* in the CSTB with Cell Recycle

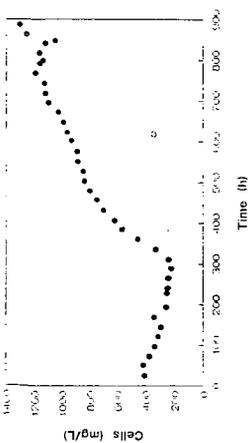


Figure 8. Cell Concentration Profile for *E. LimbuhlII* in the CSTB with Cell Recycle

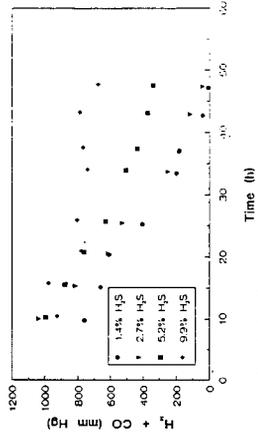


Figure 9. The Effects of H_2S on CO and H_2S in Batch Culture

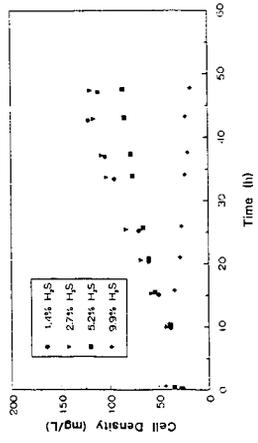


Figure 10. The Effects of H_2S on the Growth of *E. LimbuhlII* in Batch Culture

COPROCESSING OF COAL AND WASTE RUBBER

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Keywords: coal, rubber, coprocessing

ABSTRACT

The disposal of used tires, the main source of waste rubber, is an important environmental problem. We describe a method to transform used rubber tires into useful liquid products by coprocessing them with coal. Carbon black, an important constituent in rubber tires, provides a good hydrocracking catalyst during coprocessing. Due to the presence of carbon black in the rubber tires, the yields of liquids obtained by coal-rubber tires coprocessing are superior to those that could be obtained by coprocessing rubber with coal in the absence of carbon black.

INTRODUCTION

Over 200 million used rubber tires are discarded each year in the United States¹. When not indiscriminately dumped, they are usually either stockpiled or landfilled. Neither of these methods of disposal is likely to be accepted in the future, and major efforts are under way to find more environmentally acceptable solutions for the disposal of used rubber tires. Recently, Gillen² and D. J. Stopek, et al.³ reported successful coal-used rubber tires cofiring tests in power plants in Ohio and Illinois, respectively.

A different possible approach for the use of rubber tires is their coprocessing with coal to obtain liquids⁴. In this approach, we can take advantage of both the high hydrogen content of the organic material in rubber tires and of the good solvent properties of the depolymerized rubber to aid coal liquefaction. Also, the carbon black, a major constituent of rubber tires, can act as a catalyst in the process⁵⁻⁷. The liquids produced in coprocessing coal and tires could be a source of transportation fuels, or could be used in the production of new tires by replacing the petroleum-based aromatic oil. The unreacted coal and the carbon black remaining from tires can then be burned.

EXPERIMENTAL

The materials used in these experiments were: Illinois #6 coal, 20 mesh; tread material from a highway-collected rubber tire; vulcanized tread material; styrene-butadiene rubber; cis-polybutadiene rubber; aromatic oil provided by Dr. E. T. McDonell, Michelin America Small Tire Co. Akron, Ohio; elemental sulfur (Fisher Scientific Co.); and carbon black Mogul L (138 m²/g) provided by Cabot Corp. The elemental analyses of tires and of the coal used in these experiments are given in Table 1. The composition of the tread material as provided by E. T. McDonell is given in Table 2.

Liquefaction Experiments. The liquefaction experiments using shredded rubber tire materials and coal were performed in a laboratory shaker autoclave. In all experiments described, the reaction temperature was 425°C, the reaction time was 60 minutes, and the initial hydrogen pressure (at room temperature) was 1000 psi. The relative amounts of materials are given in Tables 3 and 4. In a typical liquefaction experiment the total amount of materials was 6-7 g.

After liquefaction, the liquid and solid products were separated by methylene chloride extraction followed by filtration. After the removal of methylene chloride by evaporation in a rotary evaporator, the residue was extracted with heptane, the soluble part separated again by filtration, and the heptane removed by evaporation in a rotary evaporator.

The conversion was calculated as the percent of the methylene chloride soluble materials vs. the initial organic materials in the reactants. For convenience of discussion, the heptane-soluble fraction will be defined as "oils" and the heptane-insoluble, methylene chloride-soluble fraction of the products as "asphaltenes." The insoluble solids are: unreacted coal, mineral matter from coal, and carbon black and zinc oxide from rubber tires.

The elemental analyses were performed by Huffmann Laboratories, Golden, CO and by PETC.

RESULTS AND DISCUSSION

Several tests were performed to test the concept of coal-rubber tire coprocessing and to assess the properties of the liquids obtained. The organic material from both highway-collected rubber

tire material and the tread material provided by Michelin are converted completely to liquid, heptane-soluble materials when processed alone under the above described conditions. In both cases the gas formation was under 1%. When shredded rubber tire material and Illinois #6 coal were coprocessed, coal conversions to methylene chloride soluble materials were ~51% and ~56% respectively, when the ratio of organic materials from tread and coal was 0.74 : 1 and 1.4 : 1. For comparison, when Illinois #6 was liquefied under the same experimental conditions in the presence of tetralin⁸ (ratio tetralin : coal, 2 : 1, by weight) the coal conversion was 57 %. The percent of heptane-soluble material obtained from coal was 31 % when the liquefaction was performed in the presence of tetralin⁸, and 37 - 41 %, when the liquefaction was performed in the presence of rubber-tread material⁴. The heptane-soluble oils that constitute the majority (~87 %) of the liquefied material are rich in hydrogen (Table 3).

As can be seen from the data in Table 2, carbon black is an important constituent of rubber tire material. From the information received from Dr. McDonnell¹, the usual surface area of the carbon black used in rubber tires is around 100 m²/g. We have found carbon blacks to be good catalysts in hydrocracking reactions⁵⁻⁷. We hypothesized that the carbon black present in rubber tires could exhibit catalytic activity during coal-rubber tire coprocessing. To check this assumption, coprocessing experiments were performed in the presence and in the absence of carbon black. When coal and a mixture of all the components of the tread material described in Table 2 were coprocessed, the conversions were very similar (~71%) to those obtained with the vulcanized tread material, and the gas production was under 1%. However, when the coal was coprocessed with the same components of tread material except carbon black the conversion decreased to 60% and the gas production increased to 6% (Table 4). Elemental analyses of the heptane soluble liquid products obtained in the experiments described in Table 4 are given in Table 5.

Comparative data for conversion to liquids (71% vs. 60%) when the coprocessing is performed in the presence and in the absence of carbon black indicate its role during coprocessing. The reduction in the quantity of gas formed when coprocessing is performed in the presence of carbon black (1% gases) versus in the absence of carbon black (6% gases) suggests the possibility that the aromatic fragments from coal products or rubber are alkylated with aliphatic fragments formed during rubber depolymerization. We have not yet succeeded in the unequivocal identification of such reactions, but

work with model compounds will soon be started.

Work with model compounds⁵⁻⁶ has shown that carbon blacks are good catalysts at temperatures lower than those described in this paper, and that their catalytic activity at constant concentration is dependent on the surface area. Two logical developments of rubber tire-coal coprocessing studies would be 1. Coprocessing at lower temperatures (350-400°C), and 2. Coprocessing in the presence of high surface carbon blacks. The carbon blacks currently used in the rubber industry have surface areas in the range of 100 m²/g, but carbon blacks with surface areas over 1400 m²/g are commercially available⁶.

Data in Table 2 indicate that a heavy petroleum fraction ("aromatic oil") is used in a rather large concentration (20% by wt. in the tread material) in rubber tires. Since an automobile tire contains about 15 pounds of organic materials (i.e., 3 lb aromatic oil), a production of about 200 million rubber tires per year will require about 600 million pounds (273,000 tons) per year of aromatic oils. Preliminary results (Table 6) indicate that at least a part of this oil could be generated from coprocessing coal with used rubber tires, so that a valuable, hydrogen-rich material can be recycled.

From a process viewpoint, it may be advantageous to recycle a part of the liquid product, so that a feed slurry of coal and shredded rubber tires can be manipulated more easily. Also, our data with model compounds^{5,7} indicate that high pressure is not necessary for reactions in the presence of carbon black. Both lines of research deserve further study.

CONCLUSIONS

Our experimental results show that the coprocessing of used rubber tire and coal can provide an alternative use for waste rubber materials. The liquids formed in this coprocessing are hydrogen rich and are a potential source for the aromatic oil component in new tires. Also, these liquids can be a source of transportation fuels.

ACKNOWLEDGEMENTS

We want to express our gratitude to Dr. E. T. McDonell of Michelin America Small Tire Co., Akron, Ohio, for providing us with samples of vulcanized rubber materials, and the components used in the manufacture of rubber tires, as well as for the information

concerning the composition and disposal problems related to rubber tires. We want to thank A. V. Cugini and his research associates at the Pittsburgh Energy Technology Center for their help with shaker bomb experiments.

The technical discussions with Dr. B. Blaustein, PETC, and his editorial help are gratefully acknowledged.

This research was supported in part by an appointment to the Postgraduate Research Training program under Contract DE-AC05-76OR00033 between U.S. DOE and Oak Ridge Associated Universities (C.M. Smith). C. M. Smith's current address: Corning Incorporated Polymer Research Department, Corning, N.Y. 14831.

DISCLAIMER

Reference in the paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE 1. Elemental analyses: rubber tires and Illinois #6 coal

Sample	Elemental composition Organic components, wt%			Inorganics wt. %
	C	H	S	
Illinois #6 coal	80.4	5.4	2.1	11
Rubber tire*	82.6	11.0	2.9	34**
Tread material*	85.3	11.0	2.9	34**

* Calculated elemental composition of the organic material after correction for the 34% of inorganic material present in tread material.

** The inorganics present as 34% of the tread consist of carbon black (33) and zinc oxide (1).

TABLE 2. Rubber tire (tread material) composition.

Composition	%
styrene-butadiene rubber	35
cis-polybutadiene rubber	8.5
aromatic oil (from petroleum)	20
carbon black	33
zinc oxide	1
sulfur	1

TABLE 3. Elemental analyses of heptane-soluble products obtained from liquefaction of used rubber tires and tread material.

Sample	Heptane-Soluble Products Elemental Analysis, wt.%		
	C	H	S
Used rubber tire	86.5	10.9	0.4
Illinois #6 / used rubber tire (1/1.4 by wt. organics)	84.5	10.5	0.5
tread material (Michelin)	88.9	10.1	0.1
Illinois #6/tread material (1/0.74 by wt. organics)	87.8	9.7	0.5

TABLE 4. Coprocessing of coal and rubber materials in the presence and absence of carbon black.^a

Sample		#Conversion (wt. %)			Liquids Composition	
Rubber	Coal	All	rubber	coal	Oils	Asphaltenes
1. Tread mat.	none	100	100	-	100	0
2. Tread mat.	yes	71	43	28	89	11
3. Tread comp*	yes	73	43	30	84	16
4. Tread.mod**	yes	60	-	-	87	13

^aReaction conditions: 60 min, 425°C. Weight ratio organic materials in rubber/coal 0.74:1.

1 and 2. Vulcanized tread material (Table 2).

3. Tread material compounds (mixed in the proportion described in Table 2).

4. As 3, but without carbon black.

Based on methylene chloride soluble material.

* <1% gas.

** 6% gas.

TABLE 5. Elemental analyses of heptane-soluble fractions (Expt. identified in Table 4).

Exp.#	Elemental Analysis (wt. %)				
	C	H	N	S	O
1	88.9	10.1	0.25	0.13	1.2
2	87.8	9.7	0.36	0.47	1.7
3	87.5	9.5	0.56	0.47	2.0
4	87.5	9.4	0.36	0.57	2.2

TABLE 6. Comparative elemental analyses of petroleum based "aromatic oil" and heptane-soluble coprocessing products.

Sample	Elemental Analysis (wt.%)			
	C	H	N	S
"Aromatic oil"	86.8	10.2	-	2.28
Heptane-soluble (Table 5, Expt. 2)	87.8	9.7	0.36	0.47

LIQUEFACTION OF A SUBBITUMINOUS COAL IN THE PRESENCE OF NOVEL MICROEMULSION-BASED MOLYBDENUM CATALYSTS

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INTRODUCTION

The state of knowledge in catalysis of direct coal liquefaction has been reviewed recently by Derbyshire (1988). An efficient catalyst for coal solubilization and/or upgrading of coal liquids not only improves the yield and distribution of products but relaxes some of the stringent demands placed upon the (process-derived) solvent. An inexpensive, disposable catalyst, which does not have to be recycled or recovered, is of particular interest for improved process economics (and thus commercialization potential). Use of "dispersed" catalysts (i.e., catalysts which are "unsupported" or initially supported by the coal prior to its dissolution) has been of increasing interest in recent years (Utz et al., 1989; Cugini et al., 1991; Hirschon and Wilson, 1991; Miki et al., 1991; Bi et al., 1991), particularly for the dissolution stage of coal liquefaction, but also for liquid upgrading purposes. In most studies, the relatively expensive molybdenum-based catalysts have been found to provide greater rate enhancement (at comparable catalyst loadings) than the inexpensive iron-based catalysts. (Both are probably most active in their (at least partially) sulfided form.) Derbyshire (1988) correctly concludes, however, that "there is usually insufficient information available on catalyst dispersion and composition to provide a sound basis for direct comparison" and that "the available information on catalyst dispersion is totally inadequate."

The objective of our work is to use a novel approach to synthesize direct liquefaction catalysts of known particle size (and thus known dispersion). It is based on the molecular design of metal-loaded reverse micelles (microemulsions). In particular, the synthesis and catalytic testing of nanosize molybdenum sulfide particles is of interest. In this regard, the approach taken here differs from the early work at the Dow Chemical Company (Moll and Quarderer, 1979) in which micrometer-size particles were obtained by emulsifying a solution of AHM in a recycle oil. The emphasis in this paper, which reports the results of our initial efforts, is on the synthesis and use of molybdenum-based catalyst particles but the techniques being developed should also be generally applicable.

EXPERIMENTAL SECTION

Microemulsion Catalyst Synthesis. Molybdenum sulfide particles were synthesized in three different microemulsion systems: (a) 0.1 M sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/decane/water (b) 0.1 M polyoxyethylene nonylphenyl ether (NP-5)/cyclohexane/water, and (c) 0.4 M NP-5/tetralin/benzyl alcohol/water. The use of an anionic (AOT) and a nonionic (NP-5) surfactant was thus explored. The microemulsions were prepared at room temperature by first adding 10% sulfuric acid to the oil/surfactant solution. The acid-solubilized microemulsion was deoxygenated by bubbling nitrogen through it for 20 min. This procedure was followed by adding 10^{-3} , 10^{-3} and 10^{-2} M ammonium tetrathiomolybdate (ATTM) to the AOT/decane, NP-5/cyclohexane and NP-5/tetralin/benzyl alcohol systems, respectively. Additional information on the microemulsion synthesis procedures are given in a companion publication (Boakye et al., 1992). To investigate the effect of particle size on liquefaction kinetics, the water-to-surfactant molar ratio was varied during microemulsion formulation.

For comparative purposes, molybdenum catalysts were also prepared in a conventional manner, by excess-solution impregnation. The catalyst precursor was ammonium heptamolybdate (AHM). It was dissolved in deionized water, at 1 % (wt) Mo loading. Five grams of coal were added to this solution and stirred overnight at 60 °C. The impregnated coal was dried under vacuum for 48 h at room temperature. In selected experiments, the pH of the solution was adjusted to 2.5 using formic acid.

Coal Liquefaction. Conventional liquefaction experiments were conducted following the procedures used previously at Penn State (Derbyshire et al., 1986; Davis et al., 1991). The coal (2.5 g), tetralin (5 g) and carbon disulfide (0.12 g) were charged into a standard (25 cc) tubing bomb reactor and agitated for 30 min in a preheated fluidized sand bath. The reaction conditions were: 350 ± 2 °C, 1000 psig H_2 (cold). In the case of microemulsion-based NP-5/cyclohexane catalysts, the microemulsion was added to 2.5 g of coal; no tetralin was used. Tetralin was added to the AOT/decane system. The NP-5/tetralin/benzyl alcohol catalyst system was also simply added to 2.5 g of coal in the tubing bomb reactor. "Blank" microemulsions, without the molybdenum catalyst, were also tested.

After reaction, the tubing bomb was rinsed with hexane into a weighed ceramic thimble. The reaction products were extracted with hexane in a conventional Soxhlet extractor assembly for 12-18 h, until the solvent falling back into the flask was absolutely colorless. The hexane was removed in a rotary vacuum evaporator and the product left behind (referred to as oils) was weighed. The thimble with the residue (referred to as residue) was dried and weighed. The reaction yields are thus reported as weight percent oils (hexane solubles) plus gases; gas production at the relatively low temperature of 350 °C was not very significant, however.

RESULTS AND DISCUSSION

A Wyodak subbituminous coal was used in this study. Its properties are summarized in Table 1. Figure 1 shows the plot of the average particle size vs. the water-to-surfactant molar ratio (R) for molybdenum sulfide in the 0.4 NP-5/tetralin/benzyl alcohol microemulsion. It is interesting to note that an optimum R value exists for which a minimum particle size of ca. 40 nm was obtained.

Tables 2 and 3 show the yield of oils (plus gas) in liquefaction tests using the AOT/decane and NP-5/cyclohexane microemulsions. At comparable Mo loadings, the yields are lower for the latter system, possibly due to the absence of a hydrogen donor solvent, whose role is crucial for low-rank coals when an efficient catalyst is not available to meet the relatively high hydrogen demand (Derbyshire and Stansberry, 1987).

Table 4 illustrates the use of NP-5/tetralin microemulsions for R values of 1-4. The oil (plus gas) yield is seen to be remarkably high at low Mo loadings. Furthermore, a comparison with the data in Figure 1, as well as those in Table 3, suggests that there is an optimum water-to-surfactant ratio for which the average particle size is at a minimum and the yield of oils at a maximum. (The oils produced are relatively viscous, suggesting that they contain some higher-molecular-weight (hexane-soluble) components.)

Table 5 was compiled in an attempt to place our initial results into proper perspective. For a subbituminous coal, high oil yields were obtained by Weller and Pelipetz (1951), when the catalyst precursor was added to the coal in an acidic medium. This could be due either to the favorable interaction with the coal or to a more effective sulfidation of the catalyst. It should be noted, however, that our attempt to maximize the dispersion of the catalyst at pH=2.5 by favoring the electrostatic interaction between the positively charged coal surface and molybdate anions (Solar et al., 1990) was not successful.

Hirschon and Wilson (1991) have recently reported relatively high yields (~84%) of toluene-solubles (corresponding roughly to the sum of asphaltenes, oils and gases) for an Illinois No. 6 bituminous coal (425 °C, 500 psi H₂, 20 min) using an organometallic Mo complex, with 0.6 mmol Mo/g coal, i.e., 5.8% Mo. The use of an organometallic Fe complex resulted in yields of ~40% (in the absence of a hydrogen donor solvent), with ~3.4% Fe. Also using "dispersed-phase" Mo catalysts (1000 ppm of ATTM, MoS₃, AHM), Utz et al. (1989) obtained yields of ≤60% heptane-solubles for a bituminous coal (425 °C, 1000 psi H₂, 1 h). Similar results were reported more recently for "dispersed-phase" Fe catalysts by Cugini et al. (1991).

Under appropriately selected conditions, the microemulsion-based catalysts are seen to be able to produce comparable yields of oils at much lower Mo loadings.

CONCLUSIONS

Our initial results on the kinetics of coal liquefaction in the presence of microemulsion-mediated molybdenum sulfide particles are very encouraging. Yields of oils which are equal or superior to those obtained using conventional catalyst preparation techniques are achieved at molybdenum loadings that are lower by one order of magnitude. At a more fundamental level, the variation in the water-to-surfactant molar ratio, during the formulation of the microemulsion system, offers the possibility to vary catalyst particle size and surface area over a wide range. This in turn allows the testing of correlations between liquefaction kinetics and catalyst dispersion.

ACKNOWLEDGMENTS

This study is being supported by the Department of Energy on Contract No. DE-AC22-90PC90054. The coal used was obtained from the Penn State/DOE Coal Sample and Data Bank.

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Table 1
 Characteristics of Low-Rank Coal Used in the Liquefaction Experiments

Penn State Sample Bank Number	PSOC 1401
Seam	Lower Wyodak
State	Wyoming
ASTM Rank	Subbituminous B
Mean Maximum Vitrinite Reflectance, %	0.42
Ultimate Analysis, % daf	
Carbon	72.23
Hydrogen	4.59
Nitrogen	1.06
Sulfur (total)	0.29
Oxygen (by difference)	21.83
Proximate Analysis	
Moisture	16.33
Volatile Matter	37.74
Fixed Carbon	41.14
Ash	4.79
Petrographic Composition (% vol, mf)	
Vitrinite	85.0
Liptinite	2.0
Inertinite	13.0

Table 2
 Preliminary Results of Liquefaction Tests with the
 AOT/Decane Microemulsion Catalyst

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue
4	Coal/Mo ME	1.2 ppm	33.8	66.2
8	Coal/Mo ME	2.6 ppm	47.9	52.1

Table 3
Results of Liquefaction Tests with the 0.1 M NP-5/Cyclohexane
Microemulsion (ME) Molybdenum Sulfide Catalyst

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue ^a
17	Coal/Mo ME (R=0.5)	1.9 ppm	14.1	85.9
18	Coal/Mo ME (R=1)	2.0 ppm	19.9	80.1
19	Coal/Mo ME (R=2)	2.0 ppm	20.5	79.5
20	Coal/Mo ME (R=3)	1.9 ppm	14.4	85.6
21	Coal/ME ^b	0.0 ppm	4.6	95.4

^a Includes preasphaltenes and asphaltenes

^b Surfactant plus cyclohexane alone

Table 4
Results of Liquefaction Tests Using 0.4 M NP-5/Tetralin/Benzyl Alcohol
Microemulsion (ME) Molybdenum Sulfide Catalyst ^a

Run #	Sample	Mo Loading	Yield of Oils (+Gas), %	% Residue ^b
23	Coal/Mo ME (R=1)	58 ppm	78.4	21.6
24	Coal/Mo ME (R=2)	118 ppm	83.2	16.8
26	Coal/Mo ME (R=3)	185 ppm	9.1	90.9
27	Coal/Mo ME (R=4)	243 ppm	9.9	90.1
29	Coal/ME (R=1)	0.0 ppm	7.3	92.7
30	Coal/ME (R=2)	0.0 ppm	5.2	94.8
31	Coal/ME (R=3)	0.0 ppm	2.9	97.1
32	Coal/ME (R=4)	0.0 ppm	6.2	93.8

^a Coal/tetralin = 1/2.5-2.6

^b Includes preasphaltenes and asphaltenes

Table 5
Compilation of Results of Liquefaction Tests on Subbituminous Coals
Using Conventional Catalysts

Author(s)	Coal	Conditions	Catalyst	Yield of Oils (+Gas), %
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	None	10.4
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	AHM ^a (1% Mo)	41.1
Weller and Pelipetz (1951)	Subbit. B	450 °C, 1 h 1000 psi H ₂	AHM ^b (1% Mo)	76.5
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	425 °C, 10 min 1000 psi H ₂	None	37.8
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	425 °C, 10 min 1000 psi H ₂	SAM ^c (1% Mo)	24.9
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	None	32.0
Epstein (1987) (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	SAM (1% Mo)	44.0
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	None	11.2
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	SAM (1% Mo)	14.0
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	350 °C, 1 h 1000 psi H ₂	STM (1% Mo)	14.7
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	None	16.9
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	SAM (1% Mo)	21.7
Burgess and Schobert (see Burgess et al., 1991)	Subbit. B	Two-stage ^d	STM (1% Mo)	30.7
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	AHM/CS ₂ (1% Mo)	70.2
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	AHM/CS ₂ (1% Mo) ^g	71.1
This study	Subbit. B	350 °C, 30 min 1000 psi H ₂	None	29.1

^a AHM = ammonium heptamolybdate

^b AHM acidified with H₂SO₄

^c SAM = sulfided ammonium molybdate

^d 350 °C, 1 h; 425 °C, 10 min

^e STM = sulfided tetrahydroquinolinium molybdate

^f ATTM = ammonium tetrathiomolybdate

^g pH adjusted to 2.5 during catalyst impregnation

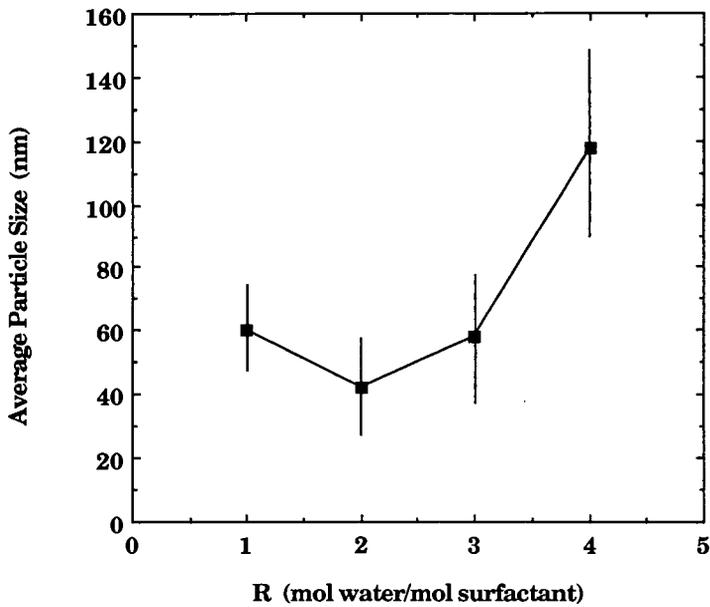


Figure 1. Effect of water-to-surfactant molar ratio (R) on the average particle diameter for the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion.

NEW SYNTHETIC METHODS FOR THE PRODUCTION OF ULTRA-FINE COAL LIQUEFACTION CATALYSTS.

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ABSTRACT

Nanometer-sized catalysts have several advantages over conventional micrometer-sized catalysts including higher surface area, better diffusion properties and longer catalytic lifetimes. We have developed methods to produce large quantities of very small iron-oxides using reverse micelle and rapid thermal decomposition of solutes (RTDS) technologies. The synthesis and characterization of these iron-based nanometer-sized catalysts will be presented. The catalytic activity of the iron particles toward model compounds and coals will also be discussed.

INTRODUCTION

There is currently extensive interest in new technologies for coal liquefaction that are economical and environmentally sound. One such new method of interest is the use of highly dispersed, ultra-fine, coal liquefaction catalysts. Of particular interest are catalysts containing iron as the major foundation and catalytic agent because of the low costs involved. A variety of iron containing catalysts and catalyst precursors have been used to liquefy coal and researchers have also shown the utility of highly dispersed iron compounds for the liquefaction of coal.²⁻¹⁰

We describe results from two different catalyst preparation technologies; rapid thermal decomposition of solutes (RTDS) and a modified reverse micelle synthesis. Both of these methods allow selective, gram-scale production of nanometer-sized iron-containing materials. These nanoscale particles have been tested for catalyst selectivity using a model compound.

EXPERIMENTAL

Particle Synthesis

In a typical small scale preparation of iron-oxide from reverse micelles, 12 ml of a 1 M aqueous solution of $\text{FeNH}_4(\text{SO}_4)_2$, 2 g sodium dodecyl sulfate, 150 ml of a 0.12 M isooctane solution of bis(2-ethylhexyl)sulfosuccinate sodium salt (AOT) were mixed together with vigorous stirring. Ammonia or another base was then added to the gold colored homogeneous reverse micellar solution to precipitate the iron-oxide. The iron-oxide product was washed with isooctane, water and acetone. Approximately 1.5 g of clean, dry, iron-bearing product was collected in a typical bench-scale run using this procedure. The RTDS process involves the rapid thermal decomposition of soluble precursors under controlled conditions at elevated pressures. Grams of the desired materials can be produced in minutes with this technique.

Catalyst Testing

The model coal compound naphthyl bibenzylmethane was synthesized using the method developed by Dr. Paul Dowd.¹¹ The synthetic procedure involved the Friedel-Crafts acylation of bibenzyl with 1-naphthoyl chloride in carbon disulfide followed by purification of the naphthyl bibenzyl ketone by column chromatography. The ketone was reduced using the Huang-Minlon modification of the Wolf-Kishner reduction. The purity of the model compound, after column chromatography, was greater than 98% as determined by gas chromatography (GC).

In our typical catalyst testing procedure, adapted from the method of Farcasiu and Smith,¹¹ 25 mg of naphthyl bibenzylmethane, 100 mg of 9,10-dihydrophenanthrene, 3 mg of sulfur, and 3 mg of catalyst were sealed in a pyrex tube under vacuum. The pyrex tube was heated inside a stainless steel bomb in a fluidized sand bath at 400°C for one hour and

then cooled quickly. The contents of the tube were dissolved in a known volume of methylene chloride containing a known amount of tert-butylbenzene as a GC calibration standard. The methylene chloride solution was filtered through silica gel to remove the suspended iron catalyst and analyzed by GC/FID or GC/MS on a 15 m DB-17 column. The GC analysis was conducted with on-column injection at 40°C with a 10°C/minute ramp to 100°C followed by a 5°C/minute ramp to 280°C. The temperature was held at 280°C for 38 minutes.

RESULTS and DISCUSSION

Table I shows sizes and morphologies determined by transmission electron microscopy (TEM) and X-ray diffraction (XRD) of selected iron containing catalysts produced by the RTDS and reverse micelle techniques. The RTDS and reverse micellar synthetic methods have the capability to produce different sizes and morphologies of iron containing catalysts depending upon the reaction conditions.

Iron bearing particle sizes determined by TEM and XRD generally agree for the highly crystalline materials produced. However, large differences are noted between the results of these analytical techniques for catalyst III which has a relatively small crystalline content as determined by dark field TEM and the weakness of the XRD pattern. The few crystallites present in catalyst III are large, >20 nm, which skews the XRD-based size results to larger sizes. Most of the materials produced by both particle formation methods have significant fractions which are not crystalline according to XRD or dark field TEM.

The iron-containing particles produced in the reverse micelle system are observed to be amorphous by both dark field TEM and XRD. Preliminary Mossbauer spectroscopy performed on the iron-oxides generated by the reverse micelle process reveals that α -FeOOH, β -FeOOH or α -Fe₂O₃ can be produced depending upon precipitation method and processing. The bulk aqueous chemistry of iron-oxide production¹² appears to be directly transferable to the reverse micellar system. Upon calcination of the reverse micelle produced iron-oxides at 450°C the primary phase becomes magnetite. The particle size of the materials produced can be as small as 1 nm. Surface area analysis of catalysts I, $S_g=164.77$ m²/g, and catalyst VIII, $S_g=150.68$ m²/g, as measured by the BET method are consistent with the small particle sizes determined by XRD and TEM.

The 298°K and 77°K Mossbauer spectra of catalyst I are shown in Figure 1. Using the methods developed by others, size distributions of the superparamagnetic hematite particles can be obtained with variable temperature Mossbauer.^{2,13-15} The size distribution for catalyst I is 52% > 8.5 nm, 31% between 8.5 and 5 nm and 17% < 5 nm if spherical geometry is assumed. These values agree well with the sizes of the particles determined by TEM and XRD (Table I). Mossbauer spectra of micelle produced α -FeOOH catalysts show no magnetic hyperfine structure even at 77°K. Care must be taken in using the Mossbauer results as a measure of particle size as the critical volume determined from Mossbauer spectroscopy can be due to "superparamagnetic clusters" and do not necessarily correspond to discrete particles.

The results of the catalyst testing are shown in Table II. These show that the materials produced by both RTDS and reverse micellar methods are good, selective, catalysts for carbon-carbon bond scission. While others have discussed the importance of hydration for iron catalysts² we have not attempted to optimize the degree of hydration in our materials. Our materials were tested as produced except for calcination of catalysts VII and VIII. We have found that iron containing materials contaminated with the surfactants from the reverse micelle synthetic method are not good catalysts. Commercial ferric-oxides, such as magnetite, were found not to catalyze the model reaction as well as our magnetite. Conversions of the model compound were typically 20-30%, with selectivity below 80% for commercial magnetite. Some of the best catalyst results are from micellar produced ferric-sulfides without the addition of sulfur, catalysts X and XIII. The structural phase of these ferric sulfides has not yet been determined. They are amorphous by XRD, and their catalytic activity varies with the precipitation technique used.

SUMMARY

Both the RTDS and the reverse micellar techniques can be used to produce catalytic iron containing compounds. The sizes and morphologies of the particles produced by both techniques can be controlled through experimental parameters. In addition, both techniques can produce large quantities of materials. We can produce grams of material in minutes with the RTDS technique, and with the reverse micelle technique we are currently producing greater than 11 grams of material per liter of organic solvent. The amount of material produced per liter is substantially more than the amounts which have been produced in other reverse micelle systems.¹⁶⁻¹⁹

ACKNOWLEDGEMENTS

We thank Dr. Paul Dowd of the University of Pittsburgh for disclosing his synthetic preparation of the model compound and the U.S. Department of Energy, Office of Fossil Energy for supporting this work under contract DE-AC06-76RLO 1830.

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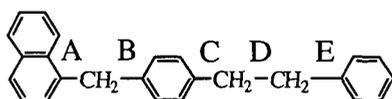
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Table I
Sizes and Morphologies of Representative Iron Catalysts
Produced by RTDS and Reverse Micelle Methods

Catalyst Number	Iron Compound	Phase	Average Particle Size (nm)	
			TEM	XRD
<u>RTDS Derived</u>				
I	Fe ₂ O ₃	Hematite	10-30	11 ± 2
II	Fe ₂ O ₃	Hematite	15-40	23 ± 2
III	Fe ₂ O ₃	Hematite	5-15	44 ± 4
IV	Fe ₂ O ₃	Hematite	30-50	42 ± 4
V	Fe ₃ O ₄	Magnetite	nd	29 ± 3
VI	Fe	α-Iron	nd	6 ± 4
<u>Reverse Micelle Derived</u>				
VII	Fe ₃ O ₄	Magnetite	5-10	10 ± 2
VIII	Fe ₃ O ₄ FeOOH/Fe ₂ O ₃	nd	4-10	nd
IX	FeOOH/Fe ₂ O ₃	nd	4-8	Amorphous
X	Fe ₂ S ₃	nd	8-15	Amorphous
XI	FeOOH/Fe ₂ O ₃	nd	10-20	Amorphous
XII	FeOOH/Fe ₂ O ₃	nd	10-20	Amorphous
XIII	Fe ₂ S ₃	nd	nd	Amorphous

nd- Not determined

Table II
Selected Results of Catalyst Testing Using
the Model Compound :



Naphthyl Bibenzylmethane

Catalyst	% Conversion ^a (±3%)	Selectivity ^b (±3)
None	2-5%	20-60
II	61%	98
III	49%	95
IV	23%	83
VII	67%	92
VIII	77%	89
X	68%	96 ^c
XI	51%	91
XII	70%	94
XIII	70%	98 ^c

a) Conversion is based on the model compound consumed. b) Selectivity is defined as the amount of products arising from cleavage of bonds A or B vs. the total amount of products. $([A]+[B])/([A]+[B]+[C]+[D]+[E])$ c) No sulfur added.

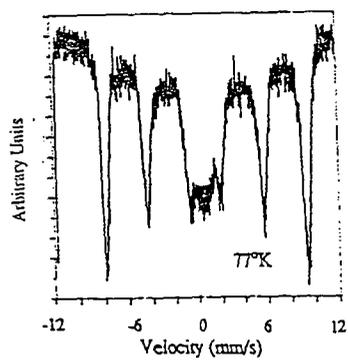
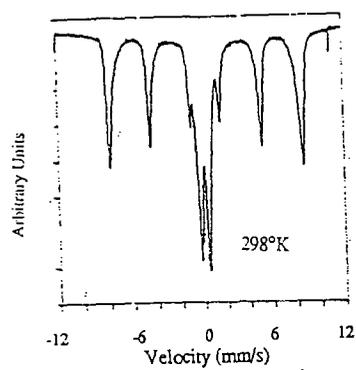


Figure 1. The Mossbauer spectra of catalyst I at room temperature and 77°K.