

DIRECT COAL LIQUEFACTION: A POTENTIAL ROUTE TO THERMALLY STABLE JET FUEL

Caroline E. Burgess and Harold H. Schobert
Fuel Science Program, Department of Materials Science and Engineering
The Pennsylvania State University, University Park, PA 16802

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INTRODUCTION

The principal mechanism of fuel degradation at temperatures above 300°C is pyrolytic decomposition. Cycloalkanes are much more resistant to thermal degradation than are *n*-alkanes or alkylaromatics [1]. Indeed, decalin shows remarkable thermal stability even at 450° [1, 2]. Hydroaromatics, such as tetralin, are also quite stable at these temperatures when reacted neat [1, 2] and can suppress the thermal degradation of other compound classes, such as *n*-alkanes, in a process termed hydrogen-transferring pyrolysis [3, 4]. Thus high concentrations of cycloalkanes and hydroaromatics in a real fuel (which of course may contain dozens of components) could provide significant thermal stability.

Direct liquefaction of coal could potentially provide a facile route to liquids boiling in the jet range and containing the desired cycloalkanes and hydroaromatics. The key chemical steps in this process would be the liberation of the aromatic units by cleavage of whatever crosslinks or other interactions hold them in the coal structure, and the hydrogenation of the aromatics to cycloalkanes or hydroaromatics. Clearly, coals showing good reactivity during liquefaction are desirable. To facilitate liberation of the aromatic ring systems, it would be helpful to select coals containing a relatively low population of crosslinks. To minimize downstream processing, it would also be useful to select coals in which a preponderance of the aromatic structures are naphthalene derivatives, to allow direct hydrogenation to decalins and tetralins. Similarly, it would be desirable to have a low content of heteroatoms, also to minimize downstream treatment of the liquids. Not all of these features are available in coals of a given rank. High reactivity and small aromatic units are characteristics of coals at the low end of the rank range. Low crosslink density and relatively low heteroatom content are more likely to be found in the bituminous rank range. Thus the selection of potential feedstocks may involve a compromise to achieve a reasonable balance among these desired characteristics.

We are conducting an exploratory study to test the hypothesis that it is possible to form high yields of cycloalkanes and hydroaromatics boiling in the jet range by selection of feedstocks to contain a high proportion of small aromatic units and relatively few crosslinks; and by choosing catalyst and reaction conditions to liberate the desirable structural features of the coal. In the present paper we report results of reactions of two bituminous coals subjected to temperature-programmed liquefaction, particularly, the effects of coal, solvent, and catalyst on conversion, product slate, and product quality.

EXPERIMENTAL

The coals were obtained from the Penn State Coal Sample Bank and Data Base. The provenance and characteristics of the coals are shown in Table 1. The solvents, catalysts, and reagents used in this work were purchased from commercial vendors and used without further purification.

Liquefaction reactions were conducted in stainless steel microautoclave reactors of nominal 30 mL capacity. Pyrene and 9,10-dihydrophenanthrene (DHP) were used as liquefaction solvents. The reactors were charged with 4 g coal and 4g of the desired solvent. For those reactions in which a catalyst was used, coal was dried and impregnated with ammonium tetrathiomolybdate (ATTM) or NiCl₂ as described in previous work [5]. The

reactors were pressurized to 7 MPa with H₂ at ambient temperature. The concept of temperature-programmed liquefaction has been discussed elsewhere [5, 6]. Briefly, the reactor is immersed in a sandbath preheated to 200°C and held for 15 min. The temperature is then ramped to 425° at 7°/min, and is held at 425° for 30 or 60 min. At the end of a reaction, the reactor is quenched by immersion in cold water.

Products were emptied from the tubing bomb into a dry tared thimble using dichloromethane (DCM) and extracted with DCM for about 36-48 h until the extracted solvent appeared clear. The products were then extracted with tetrahydrofuran (THF) for about 24-36 h until the extracted solvent appeared clear. The DCM was rotoevaporated from the DCM-solubles, and then the sample was extracted with hexane. The THF-insoluble portion was rinsed with acetone and pentane and dried at 100°C for 12 h. The THF-soluble fractions were dried for 1 h at 60°C. The hexane-soluble fractions were analyzed by GC/FID and GC/MS. The conditions of the GC used were a rate of 4 °C/min from 40 to 280 °C.

RESULTS AND DISCUSSION

The principal experimental results are summarized in Table 2. The DCM-solubles include gas yields, and gas yields were ≤5% for all reactions. The principal compound classes identified in the hexane-soluble portions of the DCM-soluble products are summarized in Table 3. For convenience, we will occasionally refer to three ratios: a) THF-solubles to the sum of the DCM-solubles expressed as THF/DCM; b) aromatic compounds of one ring to those with two rings or more, (i.e., benzenes + phenols to naphthalenes + phenanthrenes + polynuclear aromatics) expressed as B+P/≥2-ring; and c) the total aromatic compounds to alkanes, expressed as ΣAro/ΣAl.

For reactions without catalyst, conversions to DCM-solubles depend mainly on solvent. For a given solvent, conversions of the two coals are similar. However, DHP is clearly superior to pyrene for increasing conversions. Even though pyrene is well known as a hydrogen shuttler [7], DHP is a potent hydrogen donor [8]. Furthermore, in non-catalytic reactions, most of the hydrogen consumption comes from the solvent rather than gas-phase H₂ [8], so it is not surprising that substantially higher conversions are achieved in DHP. Although the conversions of the two coals in a given solvent are comparable, and the comparative effects of pyrene versus DHP are comparable, the change in product slates with increased conversion is quite different between the two coals. With DECS-6, the increased conversion effected by DHP comes largely via formation of THF-solubles. THF/DCM increases from 0.23 for reaction in pyrene to 0.64 for reaction in DHP. In contrast, THF/DCM is essentially unchanged (and in fact slightly decreases from 0.37 to 0.33) for reactions of DECS-12 in these solvents. DHP reduces the proportion of aromatics with ≥2 rings in the DCP-solubles, and increases the proportion of total aromatics relative to alkanes, relative to results obtained using pyrene. For DECS-6, the B+P/≥2-ring ratio is 0.98 for reaction in pyrene, and 0.73 for reaction in DHP. ΣAro/ΣAl increases from 1.46 to 1.80 for reaction in pyrene and DHP, respectively. The effect of solvent on the B+P/≥2-ring ratio for DECS-12 is quite similar, 1.19 for reaction in pyrene decreasing to 0.83 when DHP is used. A remarkable difference is seen in the ΣAro/ΣAl ratio for DECS-12 relative to DECS-6. For both coals, reaction in DHP increases this ratio relative to reaction in pyrene, but the products from reaction of DECS-12 have so fewer *n*-alkanes that there is an order-of-magnitude difference in the ΣAro/ΣAl ratios. Characterization of these two coals by flash pyrolysis GC/MS has shown the preponderance of *n*-alkanes in DECS-6 relative to DECS-12 [9].

For reactions in pyrene, the addition of catalyst not unexpectedly enhances conversion of both coals. Using either MoS₂ or NiCl₂, the conversion of DECS-6 increases by about 30 percentage points (Table 2). Both catalysts increase the conversion in the hydrogen-shuttling solvent pyrene to the same level as obtained by using the strong hydrogen donor solvent DHP without catalyst. However, the two catalysts have quite different effects on the product slate. MoS₂, which could be considered to be a hydrogenation catalyst [10-12], provides a very high yield of light products, THF/DCM being only 0.06. In comparison, NiCl₂, a cracking

catalyst [12-13] provides almost the same conversion, but a higher yield of preasphaltenes than attained with MoS_2 . Using NiCl_2 catalyst, the THF/DCM ratio is about the same as obtained in pyrene but without catalyst, i.e., 0.19 vs. 0.23, respectively. Thus NiCl_2 appears to increase the depolymerization of DECS-6, but not to alter the relative proportion of products; in comparison, MoS_2 seems both to increase the depolymerization and shift the product slate toward lighter products.

However, when deductions are drawn based on conversion data, it is important not to lose sight of the fact that these product classifications are based on solubility behavior, which potentially could mask differences in molecular composition. For NiCl_2 /pyrene reaction of DECS-6, there is a substantial increase in the amount of naphthalenes in the DCM-solubles relative to the MoS_2 -catalyzed reaction, which actually decreases the B+P/ ≥ 2 -ring ratio, from 1.87 for MoS_2 catalysis to 1.32 with NiCl_2 . With DECS-12, catalytic reaction in pyrene also increases conversion to about the same value as obtained in non-catalytic reaction in DHP. Use of MoS_2 shifts the product slate to lighter products, as occurred with DECS-6, although the effect is not quite so pronounced for DECS-12, THF/DCM decreasing from 0.37 to 0.23. With NiCl_2 , however, the proportion of preasphaltenes in the product is actually enhanced relative to reaction without catalyst. In this case the effect of NiCl_2 catalysis is quite different for the two coals. However, when product composition is examined, a reduction of the B+P/ ≥ 2 -ring ratio is observed for NiCl_2 -catalyzed reaction of DECS-12 in pyrene relative to MoS_2 , which can, as in the similar case of DECS-6, be attributed to a large increase in naphthalenes and a loss of phenols in the DCM-solubles. It is possible that the reduction of phenols and the concurrent increase in THF/DCM ratio could mean that retrogressive reactions are promoted by the NiCl_2 cracking without the stabilization of hydrogen from an H-donor or hydrogenation catalyst.

The effect of reaction time was evaluated only for DECS-6, by comparing reactions with high-temperature holding times of 30 and 60 min for both MoS_2 and NiCl_2 in pyrene. Little change was observed in either conversion or product slate. It is unlikely that the slight changes in conversion or product slate observed after 60 min would repay the additional processing costs associated with a doubling of the residence time at 425°.

The combination of the MoS_2 hydrogenation catalyst and DHP donor solvent in reaction of DECS-6 provided the highest conversion observed in the present work, 95%. The product slate was about the same as that obtained for MoS_2 and pyrene, with THF/DCM of 0.06. Liquefaction of DECS-6 in DHP without catalyst actually increased the THF/DCM ratio relative to non-catalytic reaction in pyrene. The catalytic effect of the added MoS_2 thus seems important for shifting the product slate to lighter—on the basis of solubility classifications—products, regardless of whether a hydrogen donor or hydrogen shuttler is used as solvent. Using DHP with NiCl_2 produced no increase in conversion relative to that of NiCl_2 and pyrene. There is, though, a shifting of the THF/DCM ratio to 0.15, compared with 0.19 for NiCl_2 /pyrene, and 0.23 for non-catalytic reaction in pyrene. It is noteworthy that the combination of catalyst and donor solvent produces the lowest values of the B+P/ ≥ 2 -ring ratio observed for this coal, 0.46 for MoS_2 -catalysis and 0.53 for NiCl_2 . Thus 40-43% of the DCM-solubles from DECS-6 for catalytic reaction in DHP are naphthalene derivatives.

For liquefaction of DECS-12 in pyrene, NiCl_2 provided higher conversions than MoS_2 , 84 vs 77%, respectively. The same superiority of NiCl_2 is observed when DHP is used as the solvent, the conversions being 89 and 85%, respectively. For both coals, a change of solvent from pyrene to DHP when MoS_2 is used as the catalyst produces essentially the same effect: an additional 6-8 percentage points of conversion, and a reduction of THF/DCM to 0.06. On the other hand, the change of solvent has different effects for the coals when NiCl_2 is used as the catalyst. We discussed the DECS-6 case above; for DECS-12, an increase in conversion and significant shift of THF/DCM is observed when DHP is used instead of pyrene. The combination of a catalyst and donor solvent causes significant reductions in the B+P/ ≥ 2 -ring ratio, as was seen for DECS-6. Indeed, nearly 50% of the DCM-solubles from MoS_2 /DHP reaction of DECS-12 are naphthalene derivatives.

An additional aspect of NiCl_2 catalysis is its ability to reduce yields of phenols relative to similar reactions in the presence of MoS_2 . For all but one coal/solvent combination, the concentration of phenols in the DCM-solubles is lower for the NiCl_2 -catalyzed reaction relative to MoS_2 , the single exception being DECS-6/DHP. But if there is a reduction in phenols when using NiCl_2 , and a concurrent increase in THF/DCM, it could be the lost phenols are participating in retrogressive reactions by crosslinking to THF-solubles. Solomon et al. [14] have suggested that functional groups containing oxygen participate in retrogressive reactions. It is also apparent these crosslinking reactions are repressed when a donor solvent or a good hydrogenation catalyst is used.

Attaining the highest conversion with either coal under these reaction conditions clearly requires the presence of the donor solvent in addition to a catalyst. For DECS-6, 95% conversion is achieved for MoS_2 /DHP reaction. Any other combination of solvent, catalyst, or both provides conversions in the range 83–89%. For DECS-12, the highest conversion, 89%, was obtained in NiCl_2 /DHP reaction; the other combinations of solvent and catalyst gave conversions of 77–85%. For either coal and either solvent, the lowest values of THF/DCM are invariably obtained with MoS_2 catalysis. THF/DCM ratios of 0.06 can be achieved for either coal with this catalyst, along with conversions in the 85–95% range. Furthermore, MoS_2 /DHP liquefaction produces DCM-solubles that are 40–50% naphthalene derivatives. The subsequent hydrogenation of this product could, in principle, provide a liquid that contains ~50% of the desirable, high-thermal-stability decalins and tetralins.

SUMMARY AND CONCLUSIONS

This paper reports preliminary results of work still in progress. We have so far shown that, with careful selection of the feedstock, it is possible to achieve 85–95% conversions, with THF/DCM ratios <0.1 and 40–50% of the DCM-solubles being naphthalenes. We have not yet attempted to improve these results by optimizing reaction conditions. The DCM-solubles are highly aromatic, with $\Sigma\text{Aro}/\Sigma\text{Alk}$ approaching 30 for some reactions of DECS-12. It is clear that both a hydrogenation of the product and a hydrodeoxygenation to remove phenols, neither of which is an insignificant operation, still must be investigated. Nevertheless, if these two further transformations can be effected, either by some alteration of reaction strategy such as "reverse temperature staging" [15] or by separate subsequent reactions, the prospect exists for direct conversion of bituminous coals to high yields of liquids containing high concentrations of desirable decalins and tetralins. Such a product could be the foundation of a jet fuel with excellent high-temperature stability characteristics.

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Table 1: Properties of coals.

Coal Number	DECS-6	DECS-12
Seam, State	Blind Canyon	Pittsburgh #8, PA
Rank	hvA b	hVA b
%C	81.72	84.75
%O	10.10	7.37
%H	6.22	5.66
%S	0.40	0.83
%N	1.56	1.40
%Mineral Matter	6.67	11.88
H/C	0.905	0.794

Table 2: Liquefaction conversion data for DECS-6 and DECS-12.

Expt #	Temp	Catalyst	Solvent	TC	THF-Sol	DCM-Sol	THF/DCM
tb 6-8	TPL, 425-30	none	pyrene	55.2	10.5	44.7	0.235
tb 6-9	TPL, 425-30	none	DHP	83.0	32.5	50.5	0.644
tb 6-3	TPL, 425-30	MoS ₂	pyrene	89.3	5.1	84.2	0.061
tb 6-4a	TPL, 425-30	NiCl ₂	pyrene	83.0	13.1	69.9	0.187
tb 6-10	TPL, 425-30	MoS ₂	DHP	95.0	5.7	89.3	0.064
tb 6-11	TPL, 425-30	NiCl ₂	DHP	83.2	11.0	72.2	0.152
tb 6-6	TPL, 425-60	MoS ₂	pyrene	88.2	3.6	84.6	0.043
tb 6-7	TPL, 425-60	NiCl ₂	pyrene	87.3	12.7	74.6	0.170
tb 12-5	TPL, 425-30	none	pyrene	51.9	14.0	37.9	0.369
tb 12-6	TPL, 425-30	none	DHP	81.7	20.1	61.6	0.326
tb 12-3	TPL, 425-30	MoS ₂	pyrene	76.8	14.5	62.3	0.233
tb 12-4	TPL, 425-30	NiCl ₂	pyrene	84.2	28.3	55.9	0.506
tb 12-7	TPL, 425-30	MoS ₂	DHP	85.4	5.1	80.3	0.064
tb 12-8	TPL, 425-30	NiCl ₂	DHP	88.7	13.1	75.6	0.173

TC = total conversion

DCM-Sol = DCM-Solubles + Gas Yield

THF/DCM = ratio of THF-Solubles to DCM-Solubles

Table 3: Percent area of major compounds in GC of hexane-solubles.

Expts	Benzenes	Phenols	2-Ring	3-Ring	4-Ring +	Alkanes	B+P/2-Ring	ΣAro/ΣAli
tb 6-8	3.7	25.6	27.7	2.3	0.0	40.6	0.98	1.46
tb 6-9	8.9	18.2	35.4	n.d.	1.8	35.8	0.73	1.80
tb 6-3	14.6	30.6	21.0	3.2	0.0	30.5	1.87	2.28
tb 6-4	19.2	25.8	29.4	3.8	0.9	21.0	1.32	3.77
tb 6-10	0.5	19.4	40.5	n.d.	3.1	36.6	0.46	1.73
tb 6-11	2.6	20.5	43.4	n.d.	0.0	33.4	0.53	1.99
tb 6-6	2.7	44.7	22.8	3.9	2.9	23.0	1.60	3.35
tb 6-7	8.6	29.5	34.5	3.9	0.0	23.5	0.99	3.26
tb 12-5	8.3	41.8	20.7	20.8	0.6	7.8	1.19	11.8
tb 12-6	15.4	28.3	46.7	n.d.	6.2	3.3	0.83	29.3
tb 12-3	5.0	46.4	29.2	2.2	4.5	12.8	1.43	6.82
tb 12-4	6.3	32.2	38.6	6.6	4.4	11.9	0.78	7.40
tb 12-7	2.4	30.1	48.1	n.d.	10.4	9.1	0.56	10.0
tb12-8	2.6	23.4	39.5	n.d.	31.1	3.4	0.37	28.4

2-Ring = alkylated aromatics and hydroaromatics composed of two rings

3-Ring = alkylated aromatics and hydroaromatics composed of three rings

4-Ring = alkylated aromatics and hydroaromatics composed of four rings and other polynuclear aromatics

n.d. = not determined

B+P/2-Ring = Benzenes + Phenols/2-Ring + 3-Ring + 4-Ring+

ΣAro/ΣAli = Total Aromatics/ Total Alkanes

UPGRADING OF DISTILLATE PRODUCTS FROM COAL LIQUEFACTION AND COAL/BITUMEN COPROCESSING

Michael F. Wilson

CANMET, Energy Research Laboratories, Energy, Mines and Resources Canada
555 Booth Street, Ottawa, Ontario K1A 0G1

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INTRODUCTION

Upgrading of heavy coal liquids involves first-stage hydrotreating with the objective of removing heteroatomic species, particularly nitrogen, which can be a serious poison for catalysts in second-stage hydrocracking or FCC. Hydrotreating also achieves molecular weight reduction and increases the hydrogen content of the coal liquid prior to cracking to lighter products suitable for use as transportation fuels.

A major problem in coal liquids upgrading is deactivation of hydrotreating catalysts through fouling of the catalyst surface. Deactivation has been attributed to the strong adsorption of certain feedstock nitrogen and oxygen containing components at acidic catalyst sites, as well as fouling by asphaltenic materials and polynuclear aromatic hydrocarbons. The adsorbed species are believed to act as precursors for the formation of carbonaceous deposits which result in loss of surface area and plugging of catalyst pores. These aspects of coal liquids upgrading have been adequately reviewed by Derbyshire (1). Previous work was undertaken by Chevron Research Company, notably Sullivan and Frumkin (2,3), who identified feedstock properties which were found to most influence the ease of upgrading: boiling point distribution, distillation end-point, heteroatom content and hydrogen content.

The objectives of this work were to undertake experimental hydrotreating of two gas oil feedstocks derived respectively from liquefaction of coal and coprocessing coal/bitumen. The purpose was to compare the upgradeability of the coal derived liquids for use as transportation fuels and to identify solutions to the problem of catalyst fouling and deactivation.

EXPERIMENTAL

The feedstocks used in the program were: Nedol process spent donor solvent, supplied by Sumitomo Metal Mining Co. Ltd., Ichikawa, Japan, and a CANMET coal/bitumen coprocessed heavy gas oil fraction. The latter feedstock was derived from coprocessing 70% Cold Lake bitumen and 30% Forestburg coal. The feedstocks represent two different sources and processing technologies for production of transportation fuels from coal. In both cases the materials require extensive upgrading to produce distillates which meet the required specifications as liquid fuels. The boiling range of both feedstocks was between 200°C-550°C. Approximately 2 wt % of the Nedol process spent donor solvent boiled above 525°C, and the amounts of asphaltenes and preasphaltenes were found to be 4.15 wt % and 0.86 wt % respectively. For the coprocessed gas oil, the +525°C fraction was 1.4 wt % and asphaltenes and preasphaltenes were 1.68 wt % and 0.11 wt %. Since the sulphur content of the spent donor solvent feedstock was low, 3 wt % butanethiol was added to maintain MoS₂ based catalyst activity during screening, following the procedure of Inoue et al. (4).

An automated microreactor unit was used to hydrotreat the coal liquid feedstocks and study the effects of catalyst deactivation. Time on stream catalyst deactivation runs were carried out to establish the extent of fouling by problematical feedstock components. A fixed bed stainless steel tubular reactor, 0.305 m long, 0.635 cm I.D., was operated in the continuous upflow mode. The catalyst bed was 0.14 m long and of volume 4.50 cm³. The catalyst was presulphided in situ with a mixture of 10% H₂S

in H_2 . Operating conditions for carrying out the catalyst deactivation experiments were: temperature $380^\circ C$, hydrogen pressure 10.3 MPa (1500 psig), LHSV 1.00, and hydrogen flowrate 1000 L H_2/L liquid feed (5500 scf/bbl).

Hydrotreating experiments were also carried out using a Robinson-Mahoney gradientless stirred tank reactor (5) to determine conversion of heteroatoms and aromatics in coprocessed liquid. The reactor is a continuous flow unit equipped with an annular catalyst basket and internal recycle impeller. The internal reactor volume was approximately 50 cm^3 and the catalyst bed 6.0 cm^3 . The catalyst was first presulphided using a mixture of 3 wt % butanethiol in diesel fuel and was then de-edged for three days (72 h) using the same feedstock. De-edging conditions were: temperature $380^\circ C$, hydrogen pressure 10.3 MPa (1500 psig), WHSV 0.75 and gas flowrate 1000 mL H_2/mL liquid feed. The coprocessed heavy gas oil was introduced into the reactor and the internal recycle impeller rate was set at 2500 rpm. For each of the catalysts tested, the operating temperatures were $300^\circ C$, $340^\circ C$, $360^\circ C$ and $380^\circ C$ at WHSV 0.75. Three Ni-Mo catalysts were used: AKZO KF-153S, CANMET CER 20 and CANMET CER 24. The physical properties of the catalysts are presented in Table 1.

RESULTS AND DISCUSSION

Feedstock Properties

Figure 1 compares the heteroatom and aromatic content of the two feedstocks. The coprocessed liquid had a significantly lower aromaticity, i.e., $f_a = 0.40$ compared with 0.58 for the spent donor solvent. There was also a large difference in elemental sulphur. Coprocessed gas oil had a very high sulphur content, i.e., 2.29 wt %, compared with 0.069 wt % for the spent donor solvent. The amounts of elemental nitrogen were about the same, but the coprocessed material had a somewhat lower oxygen content, i.e., 0.80 wt % compared with 1.60 wt % for the Nedol coal liquid. Further characteristics of coprocessed products are given by Rahimi et al. (6).

Catalyst Deactivation Runs For Hydrotreating Coal Liquids - Nitrogen Conversion (Effect of time on Stream)

Commercial catalyst AKZO KF-153S was used to hydrotreat the coal derived liquids at the prescribed operating conditions for between 200-300 h time on stream. Since sulphur was added to the spent donor solvent and oxygen content was difficult to analyze, the two parameters monitored were nitrogen and aromatics conversion. The catalyst was de-edged using the coal derived liquid feedstocks over 80 h time on stream. Plots of per cent nitrogen conversion versus catalyst time on stream are presented in Fig. 3. For both feedstocks the nitrogen conversion declined during the initial 80 h period. The commercial catalyst continued to show a steady decline in activity for the spent Nedol process donor solvent up to 200 h. For this feedstock the catalyst initially demonstrated a nitrogen conversion of greater than 80%. The effect of time on stream on nitrogen conversion in the coprocessed liquid, also plotted in Fig. 3, shows an interesting phenomenon which is observed over the first 200 h. The nitrogen conversion appears to decline during the first 80 h of the experimental run, but then recovers and rises to a maximum at approximately 130 h. Thereafter the catalyst activity appears to stabilize. An examination of this phenomenon suggests that during hydrotreating there is a transition from one type of catalytic site to another. Thus, at first, deactivation of active sites appears to occur, then in situ regeneration of the catalyst appears to take place. This may be the result of accumulation of H_2S in the reactor over the first 80 h, leading to regeneration of the catalyst. For the coprocessed gas oil, between 200-300 h time on stream, the activity of the AKZO catalyst appears to decline slowly.

Aromatics Conversion (Effect of Time on Stream)

The other indicator of catalyst deactivation relates to hydrogenation of aromatic type ring structures in the feedstocks. The fraction of aromatics, f_a , in the feed and products was determined by ^{13}C NMR. Figure 4 plots f_a versus time on stream for hydrogenation of the feedstocks over the commercial

catalyst. For Nedol process spent donor solvent, the catalyst showed a steady rate of deactivation over 200 h. In the case of coprocessed gas oil, the AKZO catalyst showed good hydrogenation activity with some scatter of experimental data but little deactivation. It is important to note that the cyclical deactivation/regeneration phenomenon shown in Fig. 3 for the HDN reaction was not observed in this case. This suggests that different catalytic sites are involved for the hydrogenation reactions and these were unaffected throughout the experimental run.

Determination of Heteroatom and Aromatics Conversion in Coprocessed Gas Oil Using a Gradientless Reactor

To determine meaningful conversion data for hydrotreating the coprocessed heavy gas oil feedstock, experimental runs were carried out using the gradientless stirred tank reactor (5). An insufficient amount of Nedol process spent donor solvent was available, therefore it was not possible to carry out corresponding determinations on that material. Because the gradientless reactor permits determinations under isothermal conditions with uniform reactant concentrations, it provides a means of accumulating reliable feedstock conversion data. Hydrotreating catalysts used were the high surface area commercial catalyst AKZO KF-153S and CANMET catalysts CER 20 and CER 24 for aromatics and heteroatom conversion respectively (see Table 1).

Determination of Nitrogen and Sulphur Conversion in Coprocessed Heavy Gas Oil

Figure 5(i) presents plots of per cent nitrogen conversion in coprocessed gas oil versus reaction temperature over catalysts AKZO KF-153S and CER 24. Both catalysts had high surface areas and reasonably good agreement is observed for nitrogen removal. At the maximum operating temperature, 380°C, the nitrogen conversion was approximately 80%. Plots of per cent sulphur conversion for the coprocessed gas oil versus reaction temperature are presented in Fig. 5 (ii). Again, high conversions (approximately 94%) were obtained at the maximum operating temperature. It is also shown that, at low sulphur conversions, a significant difference in conversion was found for the two catalysts tested. It is apparent from the general trends of the two curves plotted, that catalyst AKZO KF-153S had a higher chemical reaction rate at the lower temperatures. However, as the temperature is increased to the maximum, the two plots are seen to converge to a single point. This phenomenon is attributed to the HDS reaction being diffusion controlled at the higher temperatures. Catalyst AKZO KF-153S has a significantly higher surface area and pore volume than CER 24. However, this advantage is lost when the rate of diffusion of sulphur containing molecules into the catalyst pores becomes rate determining and it is observed that the sulphur conversion became the same for both catalysts.

Determination of Aromatics Conversion in Coprocessed Gas Oil

Input of additional hydrogen into the coprocessed liquid should facilitate second-stage upgrading to naphtha and middle distillates by improving product quality and reducing the amount of coke formed on cracking catalysts. Plots of per cent conversion of coprocessed gas oil aromatic carbon (¹³C NMR) over catalysts AKZO KF-153S and CER 20 versus reaction temperature are presented in Fig. 5(iii). Again, the curvature and convergence of the two plots indicates that aromatics hydrogenation over the Ni-Mo catalysts became diffusion controlled at the higher operating temperatures. These diffusion control effects in coprocessed gas oil were also confirmed by constructing Arrhenius plots for the hydrotreating reactions. As expected, the plots showed curvature in the high temperature region.

CONCLUSIONS

Time on stream hydrotreating runs showed that an overall higher rate of catalyst deactivation occurred during upgrading of the product from coal liquefaction. The limited amount of deactivation shown by the coprocessed liquid is considered acceptable for commercial operations. However, it was also shown that, at the higher operating temperatures, reactions were diffusion controlled.

Figure 2 compares final properties of hydrotreated products in terms of heteroatom and aromatics

content. It is shown that the regenerated Nedol process donor solvent had a significantly higher aromatic content (46.0%) than the corresponding coprocessed liquid product (25.0%). This difference is also reflected in the product atomic H/C ratios which were 1.32 and 1.69 respectively. Concerning nitrogen content, which is a key performance indicator for hydrocracking operations, both coal liquid products had about the same concentration, i.e, 1000-1200 ppm. No final measurements of elemental oxygen content were made, but experience has shown that oxygen is easier to convert. Similarly, Fig. 2 shows that sulphur conversion is not a problem. In summary, since hydrocracking operations usually require a final product nitrogen specification of approximately 10 ppm, and further hydrotreating was shown to consume excessive amounts of hydrogen, problems are anticipated in meeting the hydrocracking specification for both feedstocks. It is therefore concluded that fluid catalytic cracking is a better option than hydrocracking for converting coal derived and coprocessed heavy gas oils to lighter products.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the contributions of personnel from CANMET Catalytic Processing Section, the Fuels Characterization Research Laboratory, and financial support from Sumitomo Metal Mining Co.Ltd. and the Federal Panel on Energy Research and Development.

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Table 1 - Physical Properties of Ni-Mo Hydrotreating Catalysts

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)
AKZO KF-153S	286	0.43
CANMET CER 20	166	0.21
CANMET CER 24	230	0.34

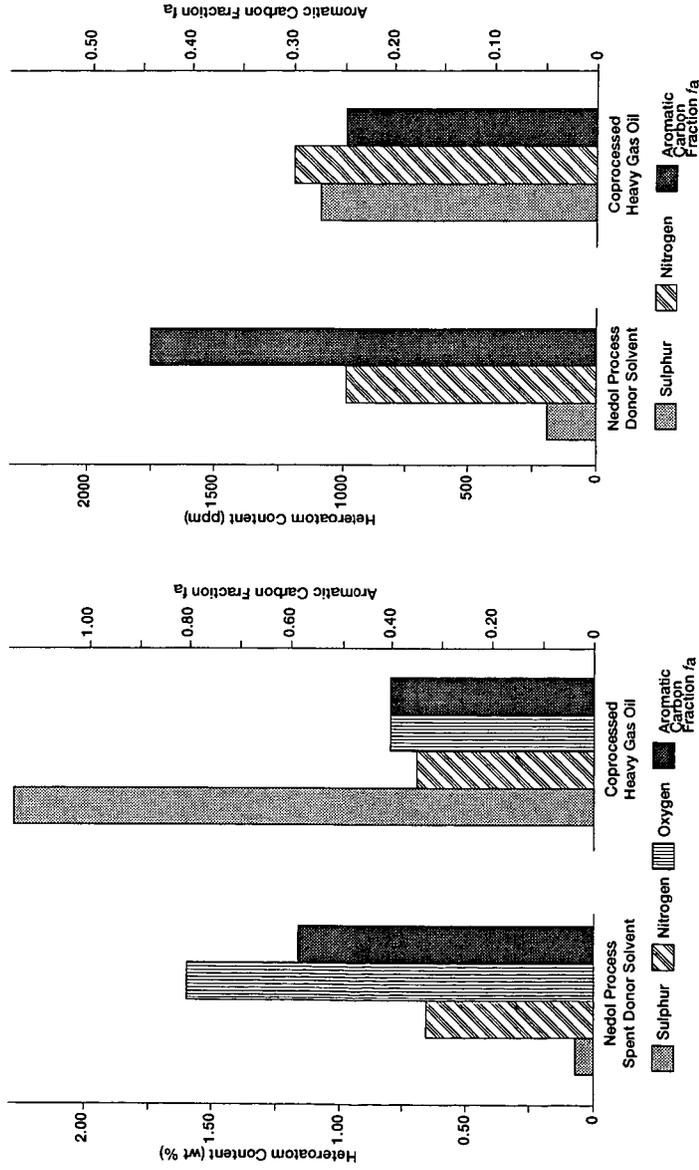


Figure 1 - Heteroatom and Aromatic Content of Coal Derived and Coprocessed Liquid Feedstocks

Figure 2 - Heteroatom and Aromatic Content of Hydrotreated Products

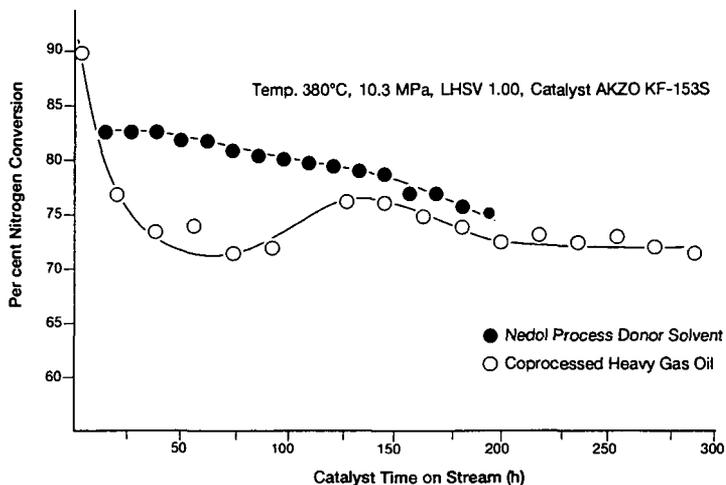


Figure 3 - Nitrogen Conversion in Hydrotreated Products as a Function of Time on Stream

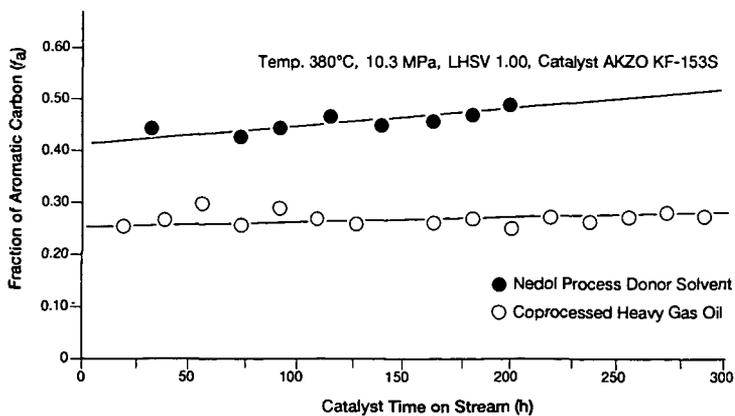


Figure 4 - Hydrotreated Product Aromacity as a Function of Time on Stream

Hydrogen Pressure 10.3 MPa, WHSV 0.75

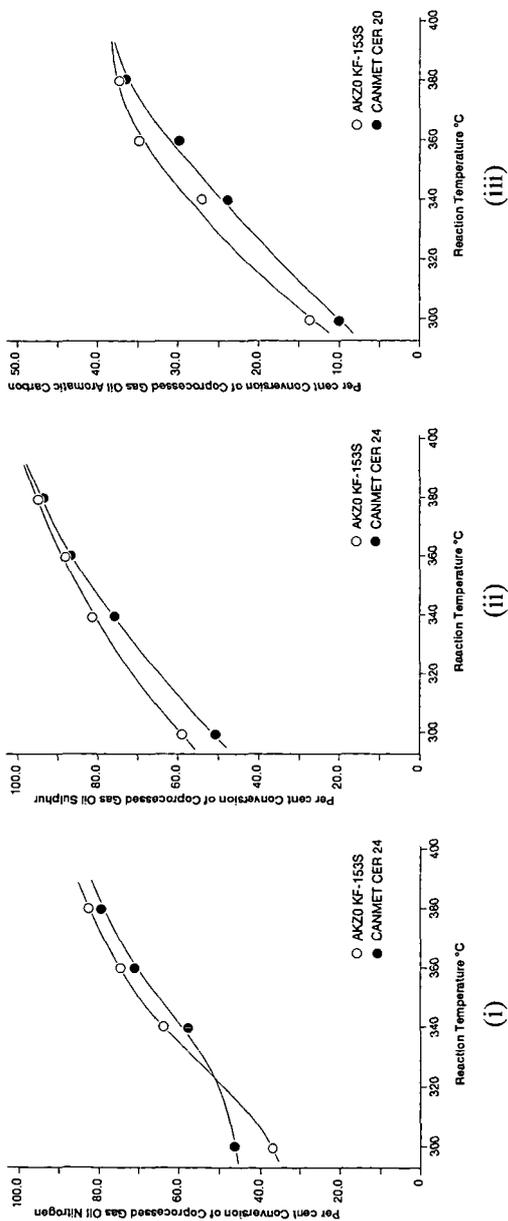


Figure 5 - Effect of Temperature on Conversion of Coprocessed Gas Oil Nitrogen, Sulphur and Aromatic Carbon over Ni-Mo Catalysts Using a Gradientless Reactor

CATALYTIC HYDROTREATMENT OF COAL-DERIVED NAPHTHA USING FIRST ROW TRANSITION METAL SULFIDES

Shuh-Jeng Liaw, Ajoy Raje and Burtron H. Davis

Center for Applied Energy Research
University of Kentucky
3572 Iron Works Pike
Lexington, KY 40511-8433

Keywords: Coal-derived Naphtha, Catalytic Hydrotreatment

ABSTRACT

This study is designed to define the possibility of increasing the rate of heteroatom removal from coal-derived naphtha by an order of magnitude greater than the current hydrodesulfurization catalysts. For the unsupported first row transition metal sulfide catalysts, maxima HDS activity is obtained for chromium sulfide and the minimum HDS activity is obtained for manganese sulfide. This is similar to the results presented by Chianelli et al. for hydrodesulfurization of dibenzothiophene. The maximum HDN activity is obtained for chromium sulfide and the minimum HDN activity is obtained for cobalt sulfide. The effect of substituents on the conversion of nitrogen compounds in the naphtha varied. The HDN of alkyl-substituted pyridine and aniline is dominated by an electronic, rather than a steric, effect. The effect of alkyl-substitution on the reactivity of quinoline is relatively small.

INTRODUCTION

Exxon workers(1) showed that some metal sulfides of the second and third row transition metals were more than 10 times as active as MoS_2 for the hydrodesulfurization of dibenzothiophene. Our study is designed to define the possibility of increasing the rate of heteroatom removal by an order of magnitude over the rate attainable with current Co-Mo-alumina or Ni-Mo-alumina catalysts. It is also designed to define whether heteroatom removal has a common rate for all compounds in each heteroatom class or whether some heteroatom compounds are especially difficult to convert. To characterize a catalyst in terms of its selectivity for individual heteroatom removal reactions for individual compounds in a coal-derived naphtha, methods to determine the amount of each sulfur and nitrogen compounds present in the feed and hydrotreated naphtha is needed. Recently instrumentation with the potential to sample directly from a flame ionization detector to determine the amount of sulfur present in the effluent from a capillary gas chromatograph has become available. Likewise, a nitrogen sensitive GC detector can be utilized for a quantitative determination of individual nitrogen compounds. Thus, the naphtha can be analyzed for composition using a high resolution capillary column gas chromatography.

EXPERIMENTAL

Hydrotreatment of the III. # 6 naphtha sample was carried out using the first row unsupported transition metal sulfides at temperatures of 350 and 400°C. The temperature was varied while holding constant the total pressure (660 psig) and weight hourly space velocity (WHSV = 1 g of feedstock / g of catalyst / hour). For each experiment, 3 grams of the row 1 unsupported transition sulfide was used.

Individual nitrogen compounds of the hydrotreated III. #6 naphtha were analyzed using a Thermionic Specific Detector (TSD) coupled with an Varian 3700 gas chromatograph containing a carbowax column. Sulfur compounds were analyzed using a Sievers Model 350B Chemiluminescence Sulfur Detector (CSD) coupled with an HP 5890 Series II gas chromatograph containing a SPB-1 column. Identification of the nitrogen and sulfur compounds was accomplished by comparison of the retention time to a standard compound.

RESULTS

The conditions and results for the preparation of the transition metal sulfides are given in Table 1. Transition metal sulfides with intermediate to high surface areas were obtained; these are comparable to the earlier Exxon work. The nitrogen and sulfur content of products and the % HDN and % HDS are shown in Table 2. These catalysts do not exhibit an especially high activity for the removal of sulfur and nitrogen, compared to Ni-Mo-alumina and Co-Mo-alumina catalysts.

For the HDS reaction, the maximum % HDS activity, based on three grams of catalyst, is obtained for chromium sulfide (Figure 1). Increasing the temperature from 350°C to 400°C results an increase of approximately 25 % for sulfur removal. Chianelli et al.(1) reported that chromium sulfide has the highest activity for HDS of dibenzothiophene and manganese sulfide has the lowest activity for the first row transition metals.

The % HDN based on catalyst weight is approximately the same for all of the catalysts, about 40 % (Figure 2). Increasing the temperature from 350 to 400°C results an increase of approximately 10 % for nitrogen removal.

A comparison of the % HDN vs % HDS based on catalyst weight shows that sulfur removal varies while nitrogen removal remains nearly constant (~40%) (Figure 3).

Conversion of Individual Nitrogen Compounds:

The conversion of individual nitrogen compounds was studied at 350°C, 660 psig and a weight hourly space velocity of 1 g/g/hr.

Pyridines

Figure 4 shows the results, as a typical example, for the conversion of compounds in the pyridine class using an iron sulfide catalyst. For this class, pyridine is the easiest compound to convert for all of the catalysts. The rate of conversion of pyridine substituted by a methyl or ethyl group decreases in the order: unsubstituted > 4- > 2- > 3- for all catalysts. Similar results were observed for the commercial Co-Mo-Alumina and Ni-W-Alumina catalysts. Pyridines with substituents of 2 or more carbons are harder to convert than pyridine with a one carbon substituent.

Anilines

The conversion of compounds in the aniline class, using iron sulfide (Figure 5), as a typical example, shows that unsubstituted aniline is the easiest compound to convert; this is analogous to the pyridine class where the unsubstituted compound is easier to convert. For all catalysts, anilines substituted with 2 to 4 carbons are harder to convert than anilines with only a one carbon substituent. These figures also show that the conversion of nitrogen compounds depends on the position the group(s) substituted on the ring. The rate of conversion for the mono-methyl or mono-ethyl substituted anilines are: unsubstituted > 4- \approx 2- > 3-. This is the case for all catalysts. However, the conversion of mono-methyl and mono-ethyl aniline is not as dependent on substituents or their ring position as the pyridines were.

Quinolines

Figure 6 shows results of the conversion of compounds in the quinoline class using iron sulfide as a typical example. The data show that quinoline is harder to convert than the pyridines were. Unsubstituted quinoline, is converted at about the same rate as one carbon alkyl substituted quinoline with the all catalysts.

DISCUSSION

In general, hydrotreatment of the heavy fractions of coal derived materials is complicated by the molecular weight, and the corresponding large size, of the molecules converted. The large size introduces severe diffusional problems during processing. However, this is not a problem in the hydrotreatment of coal derived naphtha, since the dominant fraction of the material contains only one ring of five or six carbons; two ring components are the largest molecules that will be encountered and these represent only approximately 10 % of the nitrogen compounds and approximately 24 % of the sulfur compounds. Thus, diffusion limitations due to size exclusion should not be a problem in this study.

Alkyl-substituted heterocyclic compounds were found in the Illinois #6 naphtha. The position of the substituent influences the rate of HDN. For the first row unsupported transition metal catalysts, HDN reactivities of pyridine, aniline and quinoline varies according to the position of substituent added as follows:

pyridine > 4-R-pyridine > 2-R-pyridine > 3-R-pyridine,
Aniline > 4-R-Aniline \approx 2-R-Aniline > 3-R-Aniline, and
Quinoline \approx 3-Methyl-Quinoline \approx 4-Methyl-quinoline,
where R = methyl or ethyl group. 2-Methylquinoline is present in the naphtha in such small quantities that its conversion could not be followed.

Many publications(2-5) have reported that steric and electronic effects may play an important role for the HDS of a number of sulfur compounds. From the point view of steric hindrance by a substituent group, the order of reaction rates for HDN should be 4 > 3 > 2. However, from the point view of electronic effect, the rates should be 4 \approx 2 > 3. HDN of alkyl-substituted anilines and pyridines show the order expected for an electronic effect. The effect of alkyl substituents on the reactivity of quinoline is relatively insignificant. Gates et. al.(5) reported that HDN conversion of 2,6-, 2,7-, and 2,8-dimethylquinoline is approximately the same as that of quinoline.

ACKNOWLEDGMENT

This work was supported by the DOE contract #DE-AC22-90PC91058 and the Commonwealth of Kentucky. The authors also thank the personnel at the Wilson liquefaction facility for providing the naphtha samples.

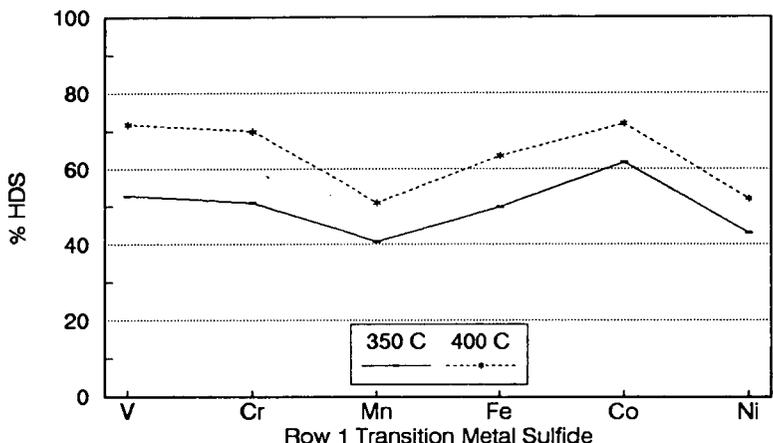
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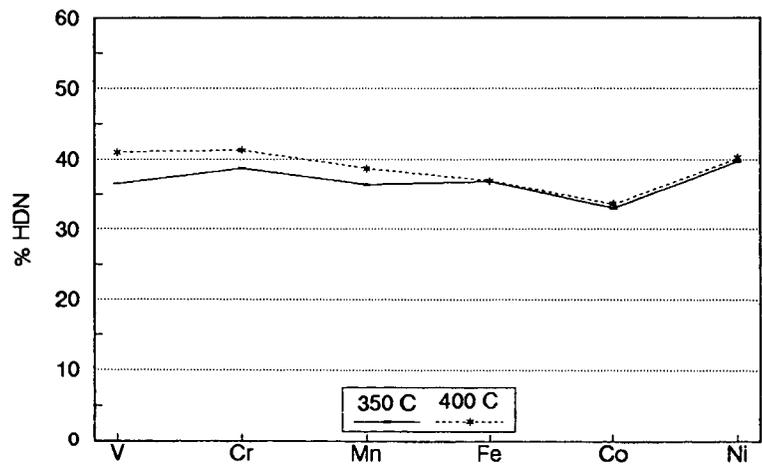
Table 1							
Row 1 Transition Sulfide Preparation Conditions and Results							
	Ti	V	Cr	Mn	Fe	Co	Ni
Metal	20g	20g	25g	25g	25g	30g	25g
Chloride	TiCl ₄	VCl ₄	CrCl ₃	MnCl ₃	FeCl ₃	CoCl ₂	NiCl ₂
Li ₂ S	9.70g	9.53g	10.88g	10.68g	10.83g	5.79g	8.86g
EA, mL	None	None	None	800	800	800	800
THF, mL	800	800	800	None	None	None	None
S _a , m ² /g	4.4	25.82	13.02	1.7	10.18	9.34	1.99

EA = Ethyl Acetate
 THF = Tetrahydrofuran
 S_a = Surface Area

Table 2						
Nitrogen and Sulfur Content of Products from the Hydrotreatment of Illinois #6 Naphtha						
Temp. °C	Pressure, psig	Catalyst	Nitrogen, Wt. ppm	Sulfur, Wt. ppm	Nitrogen % HDN	Sulfur % HDS
350	660	VS _x	1030	370	36.6	52.8
350	660	CrS _x	996	385	38.7	50.9
350	660	MnS _x	1058	465	36.4	40.7
350	660	FeS _x	1049	393	36.9	49.9
350	660	CoS _x	1113	301	33.1	61.6
350	660	Ni ₂ N	977	446	39.8	43.1
400	660	VS _x	958	223	41.0	71.6
400	660	CrS _x	953	237	41.3	69.8
400	660	MnS _x	995	385	38.7	50.9
400	660	FeS _x	1047	288	37.0	63.3
400	660	CoS _x	1103	220	33.7	71.9
400	660	Ni ₂ N	970	376	40.3	52.0



Row 1 Transition Metal Sulfide
 Figure 1. HDS of Illinois #6 Naphtha



Row 1 Transition Metal Sulfide
 Figure 2. HDN of Illinois #6 Naphtha

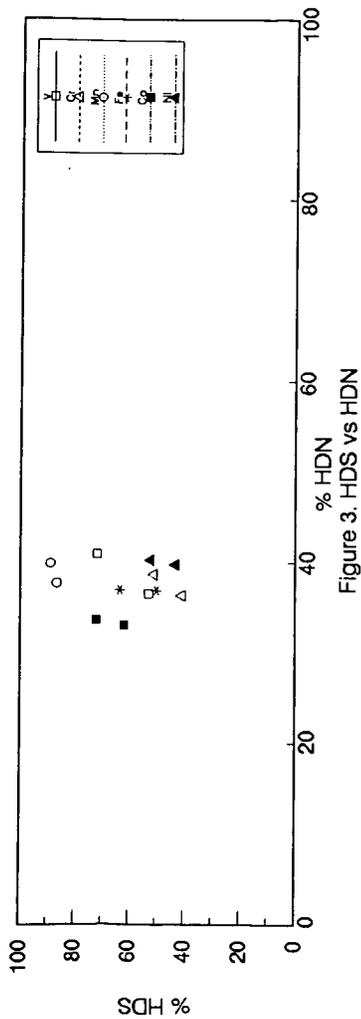


Figure 3. HDS vs HDN

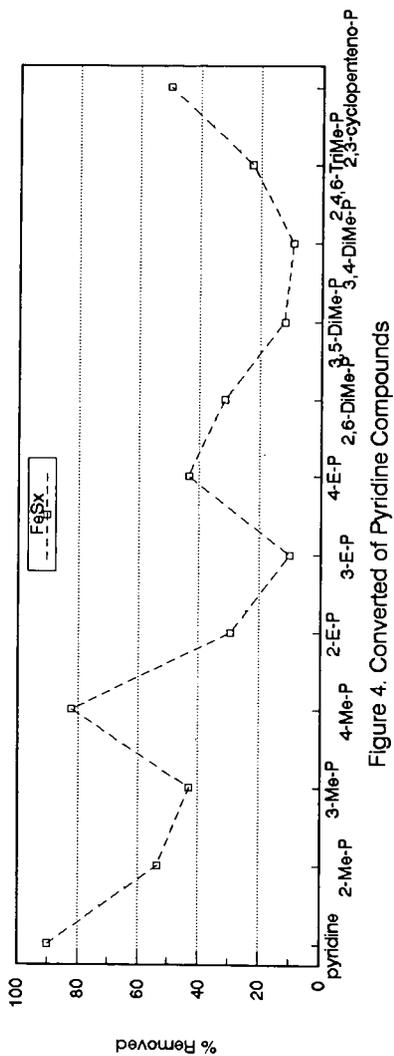


Figure 4. Converted of Pyridine Compounds

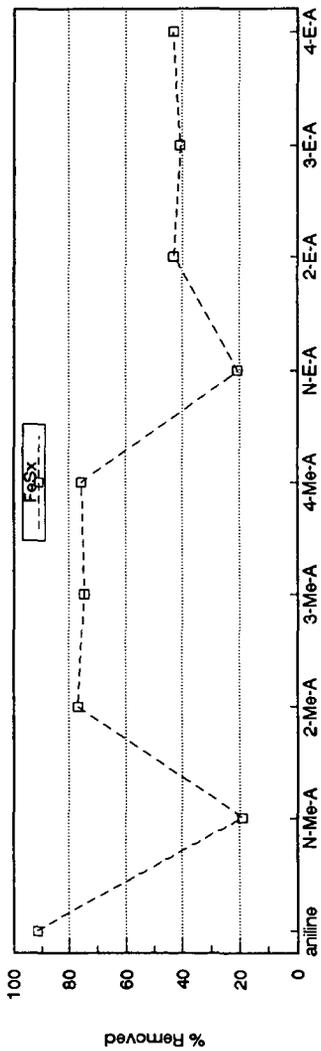


Figure 5. Conversion of Aniline Compounds

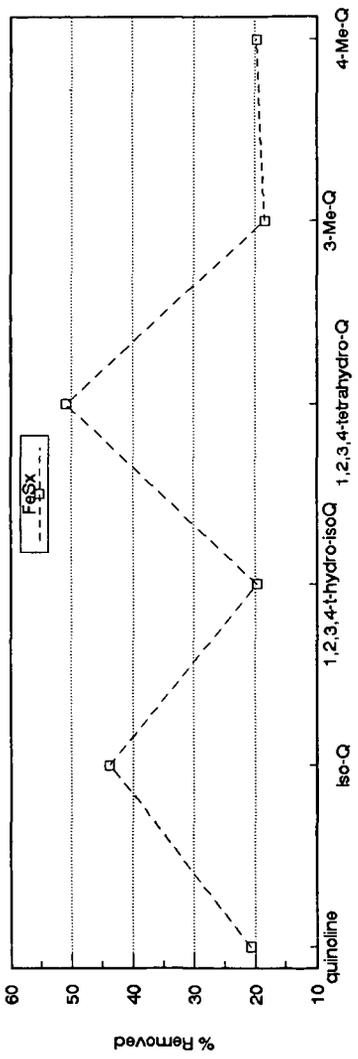


Figure 6. Conversion of Quinoline Compounds

**CATALYTIC MULTISTAGE LIQUEFACTION OF BLACK THUNDER MINE COAL
USING BOTH SUPPORTED AND SLURRY CATALYSTS.**

R. H. Stalzer, A. G. Comolli, L. K. Lee, V. Pradhan
Hydrocarbon Research Inc.
100 Overlook Center, Suite 400
Princeton, NJ 08540

KEYWORDS: Coal Liquefaction, Molybdenum, Iron Impregnated Coal

ABSTRACT

Catalyst cost has a significant impact on the economics of direct coal liquefaction. The catalyst cost is determined by its activity and deactivation. The use of an active slurry catalyst in low concentration, which gives equivalent performance to supported catalyst systems, would be potentially attractive. A slurried molybdenum catalyst, used with both iron impregnated coal and untreated coal, has been found to be an effective catalyst for the liquefaction of a sub-bituminous coal in HRI's Catalytic MultiStage Liquefaction process. The efficacy of the combined molybdenum/iron catalyst system in the first stage was investigated in HRI's ebullated bed bench unit. The combined catalyst system of molybdenum/iron (300 ppm Mo & 5000 ppm Fe) performed better than either iron or molybdenum alone in the first stage. The slurried catalyst, at these low concentrations, appeared to do as well a job of converting coal into liquids as a conventional supported catalyst (Ni-MO/Al₂O₃) in the first stage.

INTRODUCTION

The process performance parameters such as total coal conversion, 975+°F resid conversion and c4-975°F distillate yield can be used successfully as a measure of hydrogenation/hydrocracking activities of different catalyst systems. The catalyst activity and its deactivation-behavior can be compared for different catalyst systems by examining the resid conversion and the resid content of the heavy oil products as a function of catalyst age.

EXPERIMENTAL

This paper compares the results of three different bench-scale tests all run with Black Thunder Mine coal. The first test uses supported catalyst in both stages of a two reactor system. The other two tests use supported catalyst in the second stage and two different slurry catalyst additives in the first stage. The iron catalyst precursor was impregnated on the coal matrix using an incipient wetness technique developed by Pittsburgh Energy Technology Center¹ and previously scaled up by HRI for bench run CC-15². Black Thunder Mine coal was impregnated with hydrated iron oxide (FeOOH) at 5000 ppm of iron using this technique. The molybdenum catalyst was added as a 5 wt% solution of ammonium heptamolybdate at 300 ppm of coal.

HRI, Inc's Catalytic MultiStage Liquefaction (CMSL) technology was used as a basis for this test program. The reactor configuration consisted of an initial pre-treater stage, followed by a backmixed slurry reactor and then an ebullated bed reactor. The iron and molybdenum catalyst precursors were first activated to a sulfided form in the pre-treater stage prior to the two liquefaction stages. The first liquefaction stage operated as a slurry reactor (containing no supported catalyst) and the second stage as an ebullated bed containing Shell S-317 1/32" extrudate. Downstream product separation was accomplished by a hot separator and a cold separator. The bottoms from the hot separator were further processed off-line by batch pressure filtration. The pressure filter liquid (PFL) was used to slurry the feed coal and as a flush oil. The two catalyst precursors were activated with H₂S (3 wt% coal) at 300 °C in the pre-treater stage.

RESULTS AND DISCUSSION

Three runs with five different first stage catalyst conditions were compared; second stage catalyst always consisted of Shell S-317 1/32" extrudates (Table 1). Run CMSL-1 used both the slurry molybdenum catalyst with the iron impregnated coal as well as just the slurry molybdenum catalyst. Run CC-15 examined the use of both the iron impregnated coal and using no catalyst additive so that the first stage would be just a thermal reactor. Run CC-1³ is a base case for a catalytic/catalytic CTSLTM operation. Since each run consisted of a number of operating conditions, the exact periods chosen for comparison were based upon comparable second stage catalyst ages and similar high/low temperature staging of the final two reactors. The major significant difference among the runs is that CMSL-1 was run at a much higher space velocity, 1.45-1.66 times the base condition, giving only 60-69% of the nominal residence time of the base condition. This would normally lead to poorer performance in terms of coal conversion, resid conversion and total distillate yield and a higher level of resid in the pressure filter liquid.

The coal conversion for the four systems using a first stage catalyst are all roughly equal, within 1.5% (Figure 1). The conditions using the slurried molybdenum catalyst actually have the highest conversion, and the run with only a molybdenum additive has a higher conversion than when the iron is also present. All three slurry catalyst systems, the molybdenum/iron, the molybdenum alone and the iron alone, give favorable coal conversion compared to the base condition with the supported catalyst.

The resid conversion for the four catalytic systems also show only a small variation, with the molybdenum/iron system having the highest conversion and the iron system with the lowest (Figure 1). Both of the systems using the molybdenum additive show at least as good resid conversion as the base system does. Since the resid conversion is strongly dependent on the catalyst age, it is not surprising that the molybdenum/iron system, with a lower catalyst age by almost 1/2, has a higher conversion than the molybdenum

system does.

The total distillate yield (C4-975+F) also shows only small differences among the four catalytic conditions (Figure 1). This is the only measure of performance for which either of the molybdenum containing systems is worse than the base condition, and even then the molybdenum system is only 1.6 WT% lower than the supported catalyst; while the molybdenum/iron system is 1.2 WT% higher.

These three parameters, coal conversion, resid conversion and distillate yield, can be used to determine the performance of a catalyst in the CMSL process. The resid conversion and the total distillate yield being the two more catalyst dependent variables, but the coal conversion is not entirely independent of catalyst. For these three parameters there is little difference among the four different catalytic systems, the condition using no catalyst at all in the first stage having the poorest performance, as would be expected. These four conditions show equivalent performance even though the molybdenum/iron system was run at 1.66 times the reference space velocity and the molybdenum system was run at 1.45 times the reference space velocity. Also, there is little difference in the performance between the run with just a molybdenum catalyst and the run with the molybdenum and iron catalysts.

Another measure of catalyst performance is the distribution of the final products (Figure 2). The molybdenum/iron system gives the best overall product distribution with the highest light distillate yield and the lowest resid yield. Both the iron system and the molybdenum system compare well with the supported catalyst system, demonstrating higher light distillate yields with lower heavy distillate yields while the naphtha and resid yields are very close. The molybdenum and the molybdenum/iron systems both give better distillate distribution than the supported catalyst even though they are at a much higher space velocity, 1.45 and 1.66 times the reference space velocity respectively.

The activity and deactivation of a catalyst system is also critical to the long term operation of a liquefaction process. Figure 3 shows one measure of catalyst deactivation in terms of the resid conversion as a function of catalyst age. The CMSL-1 run using the molybdenum catalyst always gives a higher resid conversion than does CC-15 with the iron catalyst. Additionally the rate of deactivation as measured by the slope of the graph is also lower for the molybdenum system by 54%.

One of the more noticeable effects catalyst has is on the quality of the pressure filter liquid (PFL) used as a recycle oil to slurry the fresh coal feed. This is taken as the liquid bottoms from an atmospheric flash vessel usually operated at 315 °C. The better a catalyst is as a hydrocracker, the slower will the resid content of the PFL increase as the catalyst ages. Figure 4 shows the resid content as a function of catalyst age for the three runs. Run CC-1

data is not appropriate to this comparison past a catalyst age of 168 lbs dry coal/lb catalyst due to various recycle schemes that were used. Both CC-15 with the iron catalyst and CC-1 with the supported Shell S-317 catalyst show the same trend of resid buildup in the PFL. Run CMSL-1 with the molybdenum catalyst initially shows this same trend until a catalyst age of 300 lbs dry coal/lb catalyst is reached. At this point the resid content of the PFL is constant at 27 WT%. The molybdenum catalyst system achieves a steady level of resid content in the PFL sooner and at a lower level than does the iron system. The molybdenum system performs as well as either the supported catalyst system or the iron system does and at a much higher space velocity.

CONCLUSIONS

It has been shown that at comparable operating conditions the use of combined molybdenum/iron slurried catalysts in the first stage of the CMSL process results in an improved process performance for liquefaction of a sub-bituminous coal over that obtained from the use of either iron or molybdenum catalyst alone or the use of the supported Ni-Mo/Al₂O₃ catalyst in the first stage. The slurried catalysts, as compared to the supported catalyst (in the first stage) not only resulted in improvements in coal and resid conversion and C4-975+F distillate yield, they also subsidized the deactivation of the second stage supported catalyst, probably by maintaining the quality of the recycle oil in the first stage. This similar, if not better, overall performance was achieved while maintaining a 66% higher throughput.

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TABLE 1: OPERATING PARAMETERS FOR COMPARISON RUNS						
RUN ID#		CMSL-1	CMSL-1	CC-15	CC-15	CC-1
PERIOD (DAY)		7	14	8	11	16
CATALYST AGE (LB COAL/LB CAT)		168	317	228	316	384
CATALYST 1 ST STAGE		MOLY & IRON	MOLY	IRON	NONE	SHELL S-317
2 ND STAGE		SHELL S-317	SHELL S-317	SHELL S-317	SHELL S-317	SHELL S-317
TEMP (°C) (°F)	RXN 1	444 (832)	440 (824)	427 (801)	427 (801)	436 (817)
	RXN 2	413 (775)	413 (775)	412 (774)	413 (775)	408 (767)
SPACE VELOCITY (SV _{REF} = 1.0)		1.66	1.45	0.91	0.96	1.00

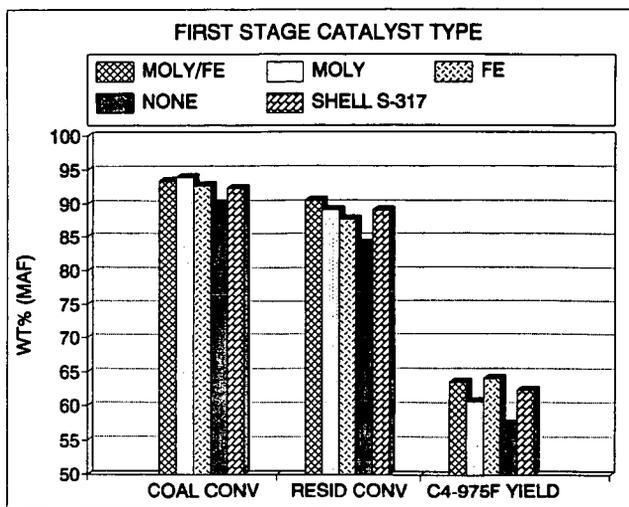


Figure 1. Process performance.

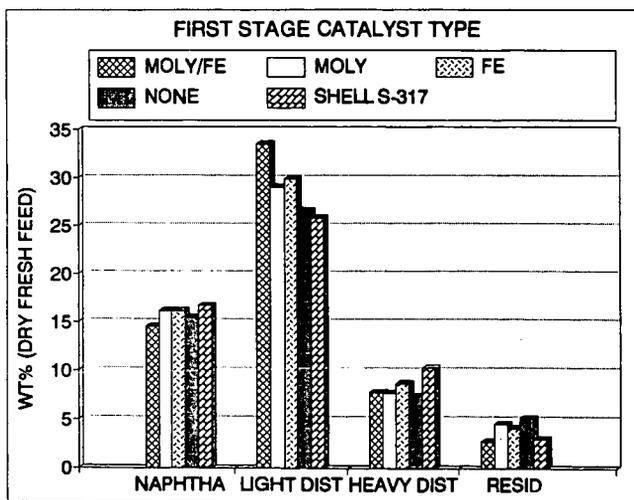


Figure 2. Final Product Distribution.

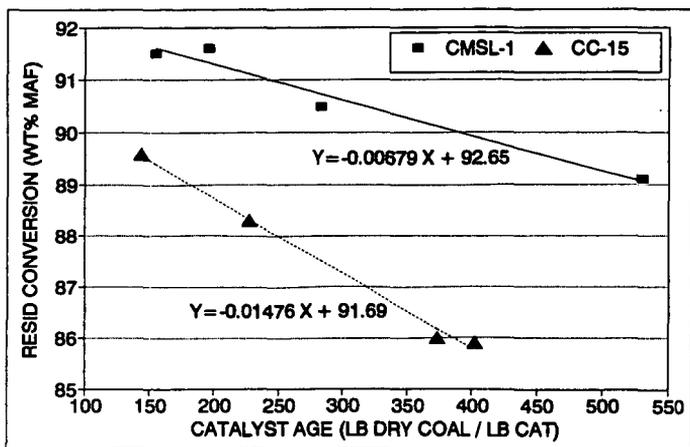


Figure 3. Resid conversion as a function of catalyst age for CMSL-1 and CC-15.

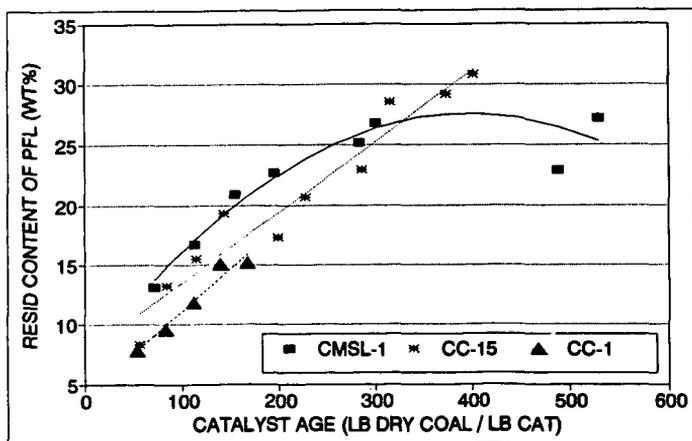


Figure 4. Resid content of the pressure filter liquid as a function of catalyst age.

A NOVEL SHORT TIME REACTOR SYSTEM FOR STUDYING THE INITIAL STAGES OF DIRECT COAL LIQUEFACTION

He Huang, William H. Calkins*, and Michael T. Klein
Department of Chemical Engineering
University of Delaware, Newark, DE 19716

Keywords: short contact time reactor, DBE conversion, coal liquefaction

ABSTRACT

Study of direct coal liquefaction at short contact time can provide insight into the chemical and physical processes involved at low conversions, before the occurrence of significant secondary degradative and retrogressive reactions of the liquefaction products. However, it has been difficult in the past to produce well-defined, short reaction time samples for in-depth analysis. To achieve this, a novel bench scale reactor was designed and built. The characteristics of the reactor system are as follows. The coal-organic solvent liquid slurry is driven into a reactor, which is already at reaction temperature, through preheater tubing using a high-pressure gas. Preliminary tests show that this can be accomplished in less than one second, and the desired reaction temperature of the process stream is achieved within approximately 0.3 seconds. The injected slurry is agitated by gas bubbles introduced through the slurry from the bottom of the reactor. The quenching process is performed in a similar way and accomplished in less than one second. The product stream cools down to about 25 °C in approximately 0.3 seconds. The preliminary operating results on this unit for conversion of model compound, direct coal liquefaction, and conversion of coal-derived resids have been reported in this paper.

INTRODUCTION

In the liquefaction of coal, as in many other high-pressure and high-temperature reactions, important information concerning the controlling chemical and physical processes can be obtained through study at the very early stages, before complicating secondary reactions occur. The major experimental challenge is to bring the system up to the reaction temperature and pressure in a time frame less than that required for the physical and chemical processes to start to occur. It is also important to choose an appropriate method to agitate the reactor contents to maintain uniforms of temperature and concentration.

In most laboratory high pressure equipment used to run direct coal liquefaction, such as tubing bombs or autoclaves, the heat up and cool down times of the massive equipment required to hold the pressure are long compared to the times involved in the reactions themselves. A representative temperature profile for the tubing-bomb reactor is shown in Figure 1. The resulting long heat up and cool down times obscure fundamental interpretation of the results, and do not allow practical process studies to be made at short reaction times. The common ways to agitate the reactor system are either stirring or shaking. To do this requires complicated and expensive equipment, particularly on a very small laboratory scale (ca. 30 grams). This also makes rapid sampling difficult. Thus, a reaction system at constant temperature and pressure, capable of sampling at very short reaction times (a few seconds up to 30 minutes or longer) and agitating in a simple way, is needed. Such a novel Short Time Batch Reactor (STBR) has been devised and built in our

laboratory, and tests of this apparatus for studying conversion kinetics of model compounds, coal-derived resids, and coal liquefaction are underway. Herein we report on the preliminary operating results of this unit.

EXPERIMENTAL

Apparatus

An empty batch reactor illustrated in Figure 2 is immersed in a sand bath and brought up to the desired reaction temperature. Using high pressure gas, the reaction mixture under study is driven into the reactor from a small blow case through preheater tubing, which is also at reaction temperature. Tests show that this can be accomplished in less than one second. Because only small quantity (about 30 grams in our present unit) of the reaction mixture is heated during injection in the relatively massive preheater tubing, the desired reaction temperature is achieved within approximately 0.3 seconds. The reaction mixture is then agitated by gas bubbles injected through the slurry from the bottom of the reactor. The degree of agitation is controlled by the exit gas flow rate from the top of the reactor. At a selected time, the reactor contents are driven out of the reactor into a cold receiver through a precoolers with high pressure gas. Both the receiver and precoolers are immersed in a water bath. This process is also accomplished in less than one second, and the cooling of the product mixture to about 25°C is achieved in approximately 0.3 seconds.

The details of the reactor system are shown in Figure 3. The heating bath used is a Techne IFB-52 industrial fluidized sand bath, which maintains a reaction temperature of $\pm 2^\circ\text{C}$. The 30 cm³ reactor is capable of containing 17 MPa (2500 psi) pressure at temperatures up to 550 °C. The tubing used for preheater and precoolers was 1/4" 316 stainless steel with wall thickness at 0.035". The lengths of the preheater and precoolers were both about 21 feet. Since a gas (e.g. hydrogen or nitrogen) is bubbled through the reaction mixture under pressure and out through a let-down valve, a small, water-cooled condenser above the reactor and a disengaging space above it before the let-down valve are necessary to avoid loss of solvent or other low boiling components.

Reaction Temperature Profile

A time-temperature profile for a mixture of 89% tetralin, 1% biphenyl, and 10% dibenzylether (DBE) is shown in Figure 4. At the time of injection, the reactor temperature dropped 5 - 8 °C, but it recovered to sand bath temperature within 30 seconds. This temperature drop may be reduced by longer preheater tubing.

The excellent time-temperature profile of Figure 4 is due to the preheating of the comparatively massive empty reactor and the preheater tubing and fittings prior to $t = 0$. This allows the only thermal transient to be focused on the reaction mixture.

Sample Recovery

The amount of material recovered from the reactor when it is driven from the system depends on the surface area of the entire apparatus. This is because surface holds up liquid for wetting. The surface areas of the preheater and precoolers are the bulk of that involved, and therefore there is a trade off between the reaction temperature drop on injection and the degree of recovery. For that reason, the longer the preheater, the smaller the reaction temperature drop on injection, but the lower the recovery. The viscosity or fluidity of the sample stream also influences the recovery. For the process streams studied thus far, recoveries have varied from 75 to 85 %. Because of the hold-up of some of the reaction mixture on the walls of the reactor and preheater and precoolers tubings, 100% recovery of the reaction mixture is not practical. This means that analytical methods must be available

to follow the course of the reaction with aliquots. This has not been a limitation for the reactions studied thus far. However, if better material balances are required, the first sample can be supplemented with solvent washes of the system, and further quantities of the reactant recovered by solvent removal in a rotovapor.

Cleaning System

The reactor system can be cleaned in place by a series of suitable solvent washes. The number of the washes required will depend on the reactions being studied.

PRELIMINARY RESULTS

Conversion of Model Compound

Solutions of model compounds, such as dibenzylether in tetralin, have been run in this equipment to investigate its performance. A temperature profile of the reaction has already been shown as Figure 4. Approximately 85% of the reaction mixture was recovered. Benzaldehyde, benzyl alcohol and toluene were the principal products as shown by GC-MS. A kinetic curve for the reaction under 1000 psi N_2 at 375 °C is shown in Figure 5. Excellent fit to first-order kinetics with $k_{DBE} = 8.78 \times 10^{-4} \text{ s}^{-1}$ was found.

Coal Liquefaction

Mixtures of 25% Wyodak Black Thunder coal in tetralin were run in this apparatus to begin to study the liquefaction process itself at very low conversions. A typical temperature profile at 380°C over a two minute interval is shown in Figure 6. Samples could be taken at as short a reaction time as 10 seconds, with confidence that the desired reaction time at temperature was achieved. No difficulty was encountered in driving the reaction mixture in and out of the reactor. Recovery of the reaction mixture was about 80%.

Conversion of Coal-Derived Resid

Initial studies with this new reactor are being devoted mainly to investigation of the conversion kinetics of coal-derived resids. The compositions of the coal derived resids being studied are shown in Table 1. Mixtures of the resid, in various concentrations with tetralin, such as 1:2 and 1:3, and sometimes with added catalyst, are heated sufficiently to become fluid, and then charged to the blow case which is maintained sufficiently warm with heating tape to keep them fluid. They are also agitated in the blow case with bubbling hydrogen gas. The charge is then driven into the reactor with 1500 psi hydrogen and the reactor agitated again with bubbling hydrogen. The resids are solid materials at room temperature, and contain up to 20% mineral matter. They therefore present a rather viscous mixture, even when diluted with tetralin and heated to become relatively fluid. Reactions have been run at 1500 psi and 410 °C. Recovery of the reaction mixture has been about 75%.

SUMMARY AND CONCLUSIONS

This reactor system (STBR) should have broad applicability to fuel science problems and many other high-pressure, high-temperature reactions of organic or inorganic systems where small-scale experiments for kinetic measurements are needed. Complex reactions where secondary reactions set in at an early stage can be studied in this type of reaction system at very low conversions.

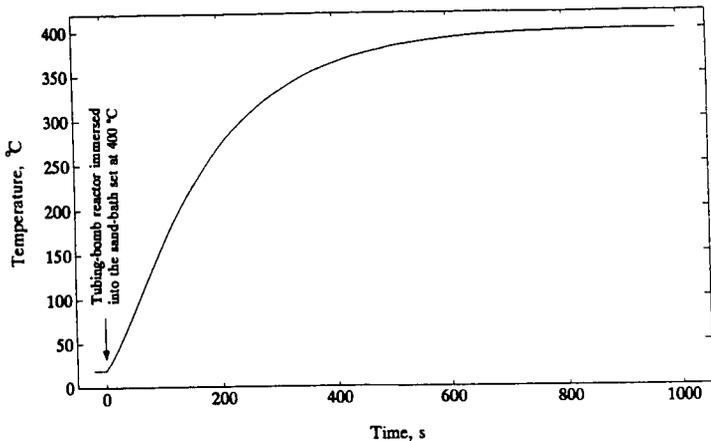


Figure 1 Time-Temperature Profile for a Tubing Bomb Reactor

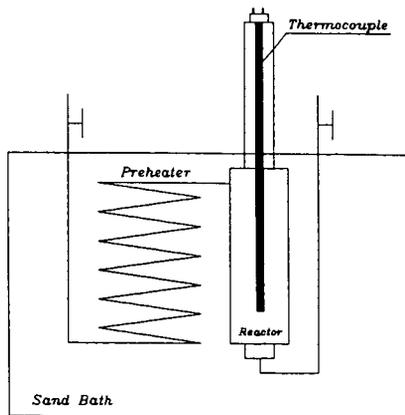


Figure 2 Batch Reactor (STBR) for Studying the Initial Stages of Direct Coal Liquefaction

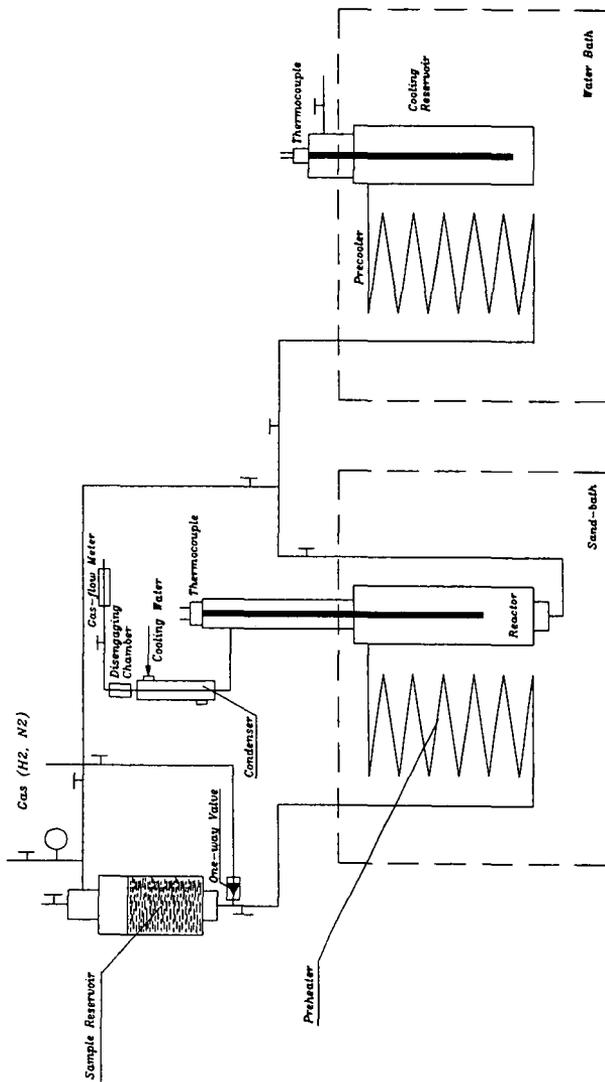


Figure 3 Apparatus for Direct Coal Liquefaction at Short Contact Times

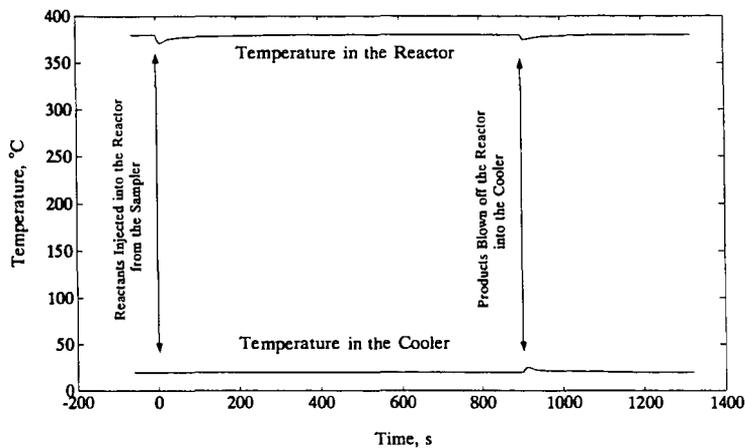


Figure 4 Time-Temperature Profile for a Typical DBE Conversion Run

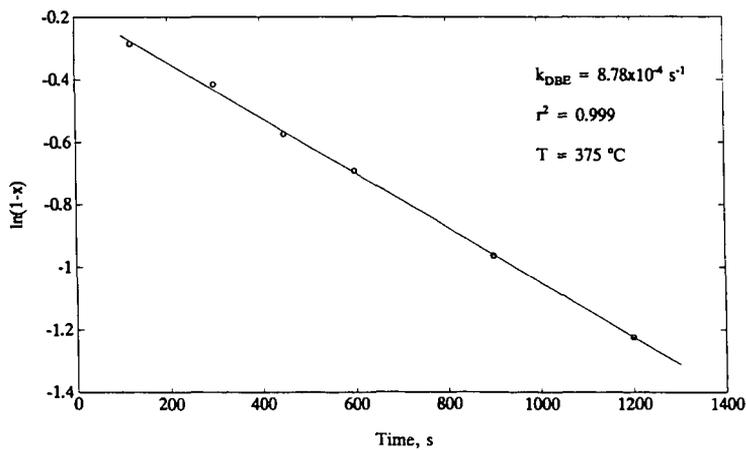


Figure 5 $\ln(1-x)$ vs. Time for DBE Conversion in Tetralin

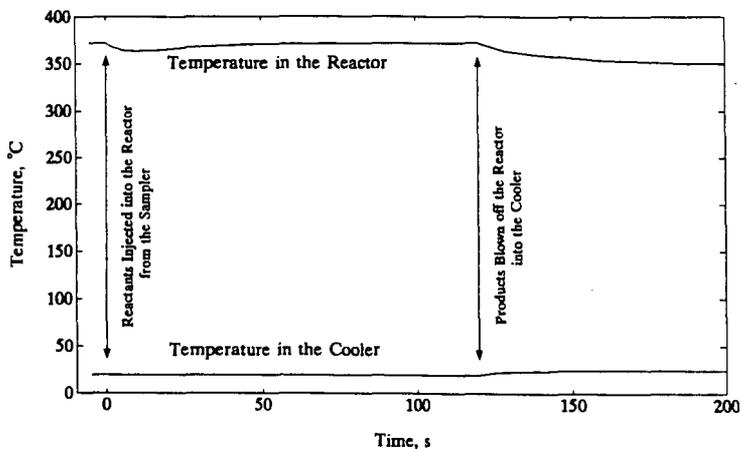


Figure 6 Time-Temperature Profile for a Typical Short Time Coal Liquefaction Run

Table 1 The Compositions of the Coal-Derived Resids

	Resid 1 ^{a)}	Resid 2 ^{b)}
Ultimate:		
Ash, wt%	10.21	16.67
C, wt% MAF	90.24	91.03
H, wt% MAF	6.39	6.56
N, wt% MAF	1.05	1.15
S, wt% MAF	1.49	0.09
O (by diff.), wt% MAF	0.83	1.17
Proton Distribution (% , pyridine-soluble basis):		
Condensed Aromatics	27.8	27.2
Uncondensed Aromatics	3.8	6.8
Cyclic Alpha	21.2	18.3
Alkyl Alpha	9.6	8.8
Cyclic Beta	15.5	13.6
Alkyl Beta	13.4	16.6
Gamma	8.7	8.7
Insoluble Organic Matter in Pyridine (wt%):		
	6.28	13.9

a) Feed coal: Pittsburgh seam Ireland mine, Wilsonville Run 259 of V1067 at 2nd stage product;

b) Feed coal: Wyodak abd Anderson seam Black Thunder mine, Wilsonville Run 260 of V1067 at 2nd stage product;

THE INFLUENCE OF PROMOTER METALS ON THE CATALYTIC ACTIVITY OF A NANOSCALE SULFATED HEMATITE FOR THE LIQUEFACTION OF A SUBBITUMINOUS COAL

G. T. Hager, E. N. Givens, F. J. Derbyshire, The Center for Applied Energy Research, University of Kentucky, 3572 Iron Works Pike, Lexington, KY 40511-8433

Abstract

Nanoscale sulfated hematites ($\text{Fe}_2\text{O}_3 \cdot \text{SO}_4^{2-}$) have been shown to have high catalytic activity both for coal liquefaction and coprocessing of coal with a petroleum resid. The addition of small amounts of molybdenum as a promoter metal significantly enhances this catalytic activity. In this study, several metal promoted hematites have been prepared and characterized. The promoter metals studied include molybdenum, nickel, tungsten, and titanium. Various techniques were utilized to define both the bulk and surface chemistry of these materials, including XRD, SEM, TEM and XPS. The activity of these catalysts for the liquefaction of a subbituminous coal in tetralin will be reported.

Introduction

Several groups have investigated the use of sulfated hematites ($\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$) for use as both coal liquefaction and coprocessing catalysts with promising results.[1-8] It is important to note that this formula does not represent a stoichiometric relationship between the sulfate and the iron but rather the sulfate may be considered as SO_3 chemisorbed on the surface of Fe_2O_3 . Tanabe et al.[8] found that the sulfated hematite exhibited the highest activity, similar to that of a $\text{Co/Mo/Al}_2\text{O}_3$ catalyst, for the liquefaction of a bituminous coal. A study by Yokoyama et al [2] showed that the activity of the sulfated hematite was independent of the rank of the coal, yielding high conversions for both bituminous and subbituminous coals. In addition to a high conversion, these catalysts also showed a relatively high selectivity to oils.[1]

More recent work by Pradhan et al. [5-7] has shown the high activity of sulfated hematite for both direct coal liquefaction and coprocessing of coal with a Maya resid. The addition of up to 2 wt% molybdenum as a promoter metal further was found to further increase the activity of the catalyst. The highest conversions were achieved in the presence of added elemental sulfur with the catalyst. The high activities reported were achieved at very low catalyst loadings of <0.4 wt% Fe. This high activity is, in part, due to the small particle size and the associated high dispersion. XRD and TEM have both shown that the average particle diameter is 10-30 nm. The small size of these particles allows better contact with the coal. In addition, the presence of the sulfate group on the surface may inhibit the tendency of the particles to sinter during the liquefaction process. The increased acidity associated with the sulfate group also enhances the activity of the catalyst

for certain reactions.

Experimental

The technique used for production of the sulfated hematite involves the aqueous precipitation of an iron salt in the presence of a source of sulfate ion. There are several techniques used for this purpose. For this project, a urea precipitation of ammonium ferric sulfate was utilized. In this process 25 g of urea were mixed with 17.5 g of iron alum $[(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}]$ in 500 ml of distilled deionized water. The initial pH of the solution was ~3. The solution, stirred continuously during the process, was heated to ~95°C and kept at temperature for ~2 hrs. During this time the urea caused the gradual precipitation of the iron and a neutral pH was attained indicating the completion of the reaction.

The precipitate was removed from the solution by vacuum filtration and washed with distilled deionized water to remove unbound sulfate groups. The filter cake was dried to remove any residual moisture. The original technique called for calcination of the filter cake in air at 500°C for ~1 hr. Subsequent testing showed that for the small samples (~3g) generated in each batch calcining at ~475°C for ~10 minutes was sufficient.

Promoter metals may be added to the sulfated hematite by addition of metal containing salts to the solution. Molybdenum has been used, in the form of ammonium molybdate, to produce a sulfated hematite doped with molybdenum. Various concentrations of molybdenum have been added to determine the effect of loading on the activity. Several other metals, including tungsten, nickel, and cobalt were also added using this method. In addition, this procedure may be modified to add multiple promoter metals to the sulfated hematite. Several combination promoted sulfated hematite have been produced by this technique including nickel/molybdenum, cobalt/molybdenum, and tungsten/molybdenum.

XRD was utilized to identify the phase of the precipitated iron particles, both before and after calcination. As shown in Figure 1 the XRD spectra of the as-formed particles closely matches the reported spectra of goethite ($\alpha\text{-FeOOH}$). Also clearly shown in the spectra are the 44.7° and 65.0° peaks identified with $\alpha\text{-Fe}$. The relatively poor resolution in the XRD spectra is due to both the extremely small size and poor crystallinity of the particles. After calcining, the XRD spectra of the particles, shown in Figure 2, can clearly be identified as hematite ($\alpha\text{-Fe}_2\text{O}_3$) with the continued presence of the $\alpha\text{-Fe}$ peaks at 44.7° and 65°. The sharpness of the peaks in the calcined particles may be attributed to an increase in both the crystallinity and average particle size.

The chemisorbed sulfate group has been reported to have several effects on the catalytic properties of the particles.[5] One of the purposed function is the attainment and maintenance of high dispersion. The sulfate group may inhibit the particle agglomeration and sintering. The quantity of sulfur present was determined by elemental analysis to be 3-5 wt %. There was little effect of calcination on the sulfur content. The slight increase in concentration is easily accounted for by the mass loss which occurs during calcination.

The average crystallite diameter of the particles may be estimated from the XRD spectra. Utilizing this technique, the average particle sizes were shown to be in the 5 - 30 nm range with

most particles ranging from 15-20nm. SEM on the particles reveal that the particles exist as an agglomeration of very small particles below the resolution of the instrument. While this does not directly confirm the estimates made from the XRD spectra, neither does it refute them. TEM on the particles is in progress to validate the XRD derived estimates.

In order to determine the effect of residence time at temperature during calcination on the particle phase and size, a single batch of goethite was split into 4 samples. Each sample was calcined for between 10 and 60 minutes. The resulting catalysts were analyzed by XRD and the spectra were compared to determine phase and particle size. It was found that the transformation from goethite to hematite is complete within 10 minutes. However, the continued exposure to this temperature appeared to have little effect on the average diameter of the particles. There is some loss of surface area associated with the calcination process. Nitrogen BET measurements showed a decrease of the surface areas of ~18% during the calcination process.

The addition of molybdenum to the sulfated hematite as a promoter metal has been reported to improve the activity of the catalyst.[5] It was therefore decided to attempt to add varying amounts of molybdenum to the sulfated hematite to act as a promoter metal. The doping of the sulfated hematite with molybdenum was achieved by addition of ammonium molybdate to the iron alum/urea solution. Elemental analysis of both the product and the waste water indicate that all but a trace amount of the molybdenum is incorporated in the catalyst.

It has been reported that the role of the molybdenum in the catalyst structure is to deposit on the surface as MoO_3 [9]. Consequently, elemental analysis shows that the addition of molybdenum results in a decrease in the amount of sulfate present. Since the sulfate group is located primarily on the surface, this further confirms that the molybdenum acts to displace the sulfate group on the surface of the hematite. Further, the XRD spectra indicate that, even at concentrations up to 10 wt% molybdenum, only the hematite and α -Fe spectra were present indicating that the molybdenum is present either in an amorphous phase or on the surface.

The addition of molybdenum had a moderate effect on the particle diameter as determined from XRD spectra. As shown in Figure 3, the increase in the amount of molybdenum added led to a gradual decrease in the particle diameter. However, as the error bars indicate, this trend is somewhat dubious. The significant error is due to inaccuracies associated with the estimation of particle diameter from XRD spectra and also to the amount of noise present in the spectra. The molybdenum promoted sulfated hematites also appear as a loose agglomeration of particles whose size was below the resolution of the SEM.

Surface areas of the molybdenum promoted sulfated hematites were measured by the nitrogen BET method. The effect of increasing molybdenum concentration was to increase the surface area of the particles, as shown in Figure 4. As expected, since there is little to no porosity associated with these particles, the trend in surface area agrees with the trend seen in the particle diameter estimation. The replacement of the sulfur with molybdenum on the surface may lead to further inhibition of agglomeration due to the relative size of the atoms. This would agree well with both the surface area measurements and particle diameter estimations.

The catalysts were tested for use in the liquefaction of a subbituminous Black Thunder coal.

The experiments were carried out in horizontal 50 ml. microautoclave reactors. The conversions were determined by solubility using THF and pentane, into IOM, preasphaltenes + asphaltenes, and oils. The gas yields were determined directly by GC. Two sets of reactions were carried out to determine the effect of severity on catalytic activity. The low severity experiments were conducted at 385°C for 15 minutes while the high severity conditions were carried out at 415°C for 60 minutes. All runs were done in duplicate to assure reproducibility. As shown in Table I, preliminary results indicate that, for a catalyst loading of 0.7 wt % Fe at high severity conditions, while all catalysts displayed similar total conversions (~89%), the use of molybdenum resulted in the greatest increase in conversion to oils (~39%). The nickel doped sulfated hematite showed a slightly higher total conversion (~90 %) but a lower selectivity to oils (~33 %). Tungsten and cobalt yielded similar total conversions (~89 %) and oil yields (~37 %). These results show that these catalysts compare favorably with a commercially available 30 Å superfine iron oxide, while their lower cost and ease of production make them economically more viable for scale up.

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Table I. Effect of Catalyst on Liquefaction Yields

	% Total Conversion	% PA&A	% Oils	% Gas
SFIO	87.0	45.2	34.6	7.2
1%Mo/Fe ₂ O ₃ /SO ₄ ²⁻	88.5	43.1	38.9	6.8
5%Co/Fe ₂ O ₃ /SO ₄ ²⁻	88.8	45.6	36.6	6.6
5%W/Fe ₂ O ₃ /SO ₄ ²⁻	88.9	45.3	36.8	6.8
5%Ni/Fe ₂ O ₃ /SO ₄ ²⁻	90.4	49.8	33.4	7.1

Figure 1. XRD Spectra of As-formed Particles with Goethite and alpha Fe

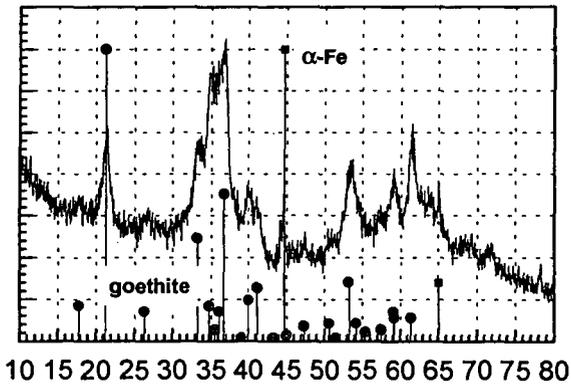


Figure 2. XRD Spectra of Calcined Particles with Hematite and alpha Fe

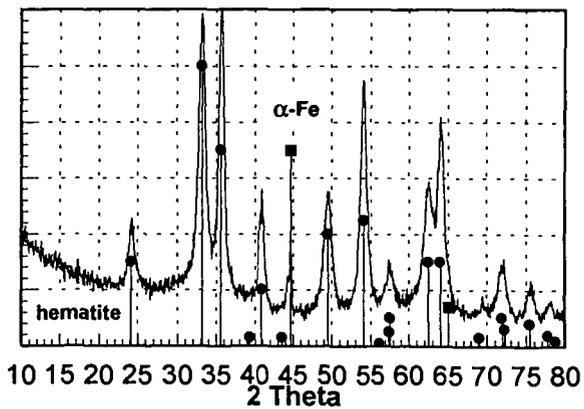


Figure 3. Effect of Molybdenum Concentration on Particle Diameter Estimated from XRD

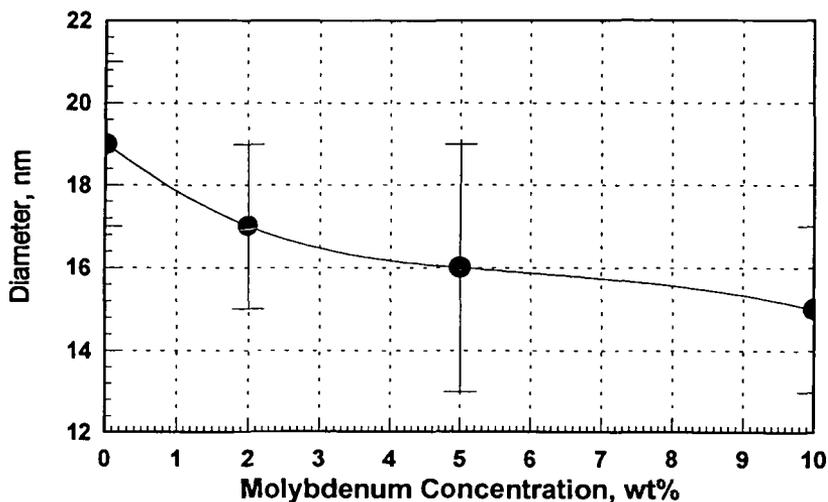
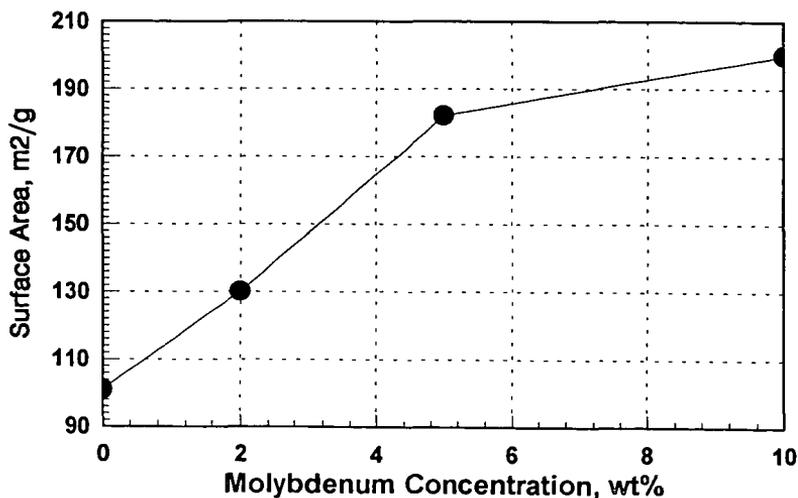


Figure 4. Effect of Molybdenum Concentration on Surface Area



EFFECTS OF SOLVENT AND CATALYST ON LIQUEFACTION CONVERSION AND STRUCTURAL CHANGES OF A TEXAS SUBBITUMINOUS COAL

Lili Huang, Chunshan Song, Harold H. Schobert
Fuel Science Program, Department of Materials and Engineering,
209 Academic Projects Building,
The Pennsylvania State University, University Park, PA 16802

Keywords: liquefaction, conversion, aromaticity

INTRODUCTION

Coal liquefaction involves an initial stage of coal macromolecular break-up driven by thermal energy [1, 2]. The result of this break-up is the formation of free radicals. If these free radicals are stabilized by hydrogenation, a liquid product is formed and the goal of liquefaction is achieved. On the contrary, if the radicals recombine with one another and form more stable and heavier product, the liquefaction has failed. Therefore, hydrogenation is the key in coal liquefaction. In fact, a recent study showed that the more hydrogen consumed in the reaction, the higher conversion would be obtained [3]. There are several ways often used to accelerate the rate of hydrogenation: to use a high pressure of H₂ [4], to use a hydrogen-donor solvent [5], and to use a catalyst.

In this study, a Big Brown Texas subbituminous (DECS-1) coal was used for liquefaction. A low-rank coal like this is characterized by low aromaticity, small ring clusters, abundant aliphatic and hydroaromatic carbon, and high oxygen content [6]. These structural features cause the thermal break-up of the coal over a wide temperature range [7-9], and thus the hydrogenation should be feasible in the same range. The purpose of this work is to investigate the liquefaction of DECS-1 at temperature range from 250°C to 450°C. Two kinds of solvent, a hydrogen-donor solvent (tetralin) and a non-donor solvent (1-methylnaphthalene) were used to compare with the reactions without solvent. An ammonium-tetrathiomolybdate-derived catalyst was used. Liquefaction results are presented to determine the solvent effect and the catalyst effect. The residues from tetrahydrofuran (THF) extraction of the reaction products were studied by CPMA¹³C NMR to obtain their aromaticities. Furthermore, the conversion and the aromaticity data were combined to calculate the amount of aliphatic and aromatic carbon that has reacted and has been removed from the coal during liquefaction.

EXPERIMENTAL

The coal sample was a Big Brown Texas subbituminous (DECS-1) obtained from the Penn State Coal Sample Bank. Its compositional data are summarized as the following on a dry and mineral matter free basis: 76.13% carbon, 5.54% hydrogen, 1.50% nitrogen, 1.05% organic sulfur and 15.78% oxygen (by difference). The reaction solvents were tetralin (Aldrich, 99%), and 1-methylnaphthalene (1-MN, Aldrich, 98%). The catalyst precursor was ammonium tetrathiomolybdate (ATTM, Aldrich, 99.97%). All the chemicals were used without further purification.

The catalyst loading was 1 wt% of Mo based on the dmmf coal. A THF/H₂O (1:1) mixture was used to make the solution of the catalyst precursor, because this binary mixture was superior to H₂O in terms of providing higher conversion and oil yield in subsequent liquefaction [10]. The catalyst precursor was first added to water, of just enough volume to dissolve the desired amount of the precursor. An equal volume of THF was then added to the H₂O solution. After being stirred to achieve a homogeneous mixture, the THF/H₂O/ATTM mixture was added to the dried coal to make a slurry. After 20 minutes of stirring at room temperature under N₂ atmosphere, the excess water and THF was removed by rotary evaporator. The "wet" sample (still containing some residual H₂O and THF) was then dried in a vacuum oven at room temperature for 20 hours, at 45°C for 5 hours and at 95°C for 4 hours, sequentially.

Liquefaction experiments were conducted in 25 ml microautoclaves in a fluidized sandbath. For each reaction, 4 grams of the coal sample and 4 grams of a solvent, if a solvent was applied, were loaded into a microautoclave. The reactor was purged three times with hydrogen and the final H₂ pressure was 1000 psi (7 MPa) at room temperature. For every reaction, the sandbath was preheated to a desired temperature, 250°C, 300°C, 350°C, 400°C, or 450°C. The microautoclave was then plunged into the sandbath and agitated at a rate of 200 cycles per minute. The total time in which a microautoclave was kept in the sandbath was 33 minutes, with 3 minutes being the time for rapid heat up. Finally, after reaction, the microautoclave was taken out of the sandbath and rapidly quenched by dipping into cold water.

After the microautoclave was cooled to room temperature, the reactor was vented, the volume of the gas was measured by the water displacement method, and a sample was collected for further analysis. The liquids and the solids in the microautoclave were washed into a tared ceramic thimble using hexane. Then the products were separated under a nitrogen atmosphere by Soxhlet extraction using hexane, toluene and THF sequentially. The soluble products are classified as oil, asphaltene and preasphaltene, respectively.

The THF insolubles were analyzed by ¹³C solid state NMR using cross polarization magic angle spinning (CPMAS) technique. All CPMAS spectra were obtained on a Chemagnetics NMR Model M100s. The ¹³C frequency was 25.15 MHz. The pulse delay was 1 second and the contact time was 1 ms.

RESULTS AND DISCUSSION

The results of liquefaction without catalyst are listed in Table 1. Conversions are in a large range, from 11.7% to 92.2%. At 250°C, the solvents do not show any significant effect on conversion or product distribution. As the temperature increases to 300°C, the solvents start showing their advantage by providing slightly higher conversions than the reaction without solvent. At 350°C, there is a remarkable increase in oil, asphaltene and preasphaltene yields when a solvent is used. This indicates that in this temperature range, the solvents play a role which enhances the conversion, but since there is no difference between the reaction with tetralin and the reaction with 1-MN, this role may not relate to hydrogen donation. In the temperature range from 350°C to 400°C, there is a drastic increase in conversion no matter whether a solvent is applied or not, suggesting that at this temperature range, thermal energy is enough to break down the coal macromolecular matrix. At 400°C, tetralin made a tremendous difference from 1-MN and no solvent. The conversion reaches 82.0%, composed of gas, 9.5%; oil, 36.7%; asphaltene, 16.6%; and preasphaltene, 19.2%. With 1-MN or without solvent, the conversions are much less, 55.5% and 45.0% respectively. The differences of conversion and product distribution imply that tetralin is active in donating hydrogen at temperatures higher than 350°C. 1-MN, on the other hand, shows a very slight advantage over no solvent in gaining higher conversion and oil yield, but as temperature increases to 450°C, this advantage almost disappears.

The results of catalytic liquefaction are presented in Table 2. In the presence of ATTM, the conversion of all experiments increase drastically as the temperature increases from 250°C to 400°C. Comparing the reactions with no solvent, tetralin or 1-MN with the corresponding non-catalytic reactions, the catalyst increased the conversion, especially at temperatures higher than 300°C, suggesting that ATTM was converted to an active catalyst at temperature between 300°C and 350°C [11]. Furthermore, the product distribution shows that the increasing conversion is accompanied by an increasing yield of light materials, such as oil, when the catalyst is added. The other comparison is among the three kinds of catalytic reactions. At temperatures between 250°C and 400°C, there is no significant difference in conversion and product distribution (though at 400°C the reaction without solvent seems to have higher oil yield). In this temperature range, the catalyst has a stronger effect than the solvents; thus any difference caused by the solvents is diminished. However, at 450°C, tetralin gave a slightly higher conversion while both 1-MN and no solvent actually gave a much lower conversion (almost 20 percentage units lower) relative to those at 400°C. In the case of 1-MN at

450°C, the yields of gas, asphaltene and preasphaltene are still very similar to those in tetralin, while the conversion is much lower. The sole cause of this conversion difference is the decrease of the oil yield. With tetralin at 450°C, yields of asphaltene and preasphaltene dropped by 9 percentage units and 17 percentage units respectively, while the yield of oil increased by 22 percentage units compared with that at 400°C. This suggests that at this temperature (450°C), in the presence of both catalyst and a H-donor solvent, the conversion from preasphaltene and asphaltene to oil, or from heavy products to light products, is favorable. With the presence of the catalyst but absence of a donor solvent (meaning with no solvent or a non-donor solvent), the conversion drops as well as all of the product yields, except gas, suggesting that retrogressive reactions take place and form heavier and more stable materials.

In coal liquefaction, once the free radicals are formed, the reactions that they undergo are the result of a competition between radical stabilization by hydrogenation to form light products and recombination of the radicals to form heavy products. Since the free radical formation is a pyrolytic break-up of coal matrix, it is a thermally driven reaction [1]. At low temperatures (up to 400°C), the rate of radical formation is so slow that the hydrogenation rate can catch up, regardless of whether the hydrogen radicals are from the donor solvent or from the gaseous H₂. However, at 450°C, radical formation from the coal is very fast, but the H radical from catalytic decomposition of gaseous H₂ is not as fast, and therefore radical recombination is more likely to take place. Since tetralin has intimate contact with these radicals and is able to donate H, hydrogenation can still take place to form light products.

The gas yields from all liquefaction experiments are plotted versus temperature in Figure 1. All the yields are in the range from 0% to 20%. Regardless of the solvents and the catalyst used in the reactions, they all fall on one line. Therefore, the amount of gas produced in the reactions is a function only of temperature. Since neither a solvent nor a catalyst has any effect, gas formation is a reaction driven by thermal energy.

Examples of the spectra of CPMAS ¹³C NMR of residues are shown in Figure 2. The spectra were curve-fitted using LabCalc program and the area of each peak was integrated. The aromaticities of the raw coal and the dried coal are both 0.48. This shows that before reaction, the aromaticity is not affected by vacuum drying at 95°C. The aromaticities of residues from all runs are summarized in Table 3. It is observed that as temperature increases, the aromaticity increases from 0.50 to 0.94. There are two possible explanations of this increase: one is that as reaction temperature increases, more and more aliphatic carbons are cracked from the macrostructure of the coal while the aromatic carbon may not react as much; the other is that dehydrogenation and condensation reactions take place during the reaction increasing the amount of aromatics in the coal. Comparing the aromaticities of the residues from the non-catalytic reactions, it is found that the solvents do not have a significant effect. Furthermore, in the case of catalytic reactions, the solvents have no significant effect either. In order to determine the influence of the catalyst on the aromaticities, all the data are plotted versus conversion in Figure 3. A general trend is that the aromaticities of residues increase with conversion, but the data fall into two separate sets: those from reactions with and without the catalyst, regardless of the solvent used. Generally, f_a of the residue from a catalytic reaction is lower than that from a non-catalytic reaction, and the difference between the two increases with increasing conversion. At the most severe conditions, 450°C with the catalyst, the aromaticities deviate from the line of catalytic reaction. The higher aromaticities are caused by more aromatic carbon, which indicates the retrogressive reactions at this temperature. In non-catalytic reactions, the use of tetralin at 400°C and 450°C results in lower aromaticities, suggesting that tetralin helps to convert aromatic carbons from coal to THF solubles.

To achieve a general idea on what kinds of structure have been converted to THF solubles, or what kinds of reactions are actually catalyzed by the catalyst during the liquefaction, the percentages of aliphatic and aromatic carbon that have been reacted are calculated from the amounts of dry, mineral-matter-free coal charged, aromaticity of the dried coal, the conversions, and the aromaticities of the residues. In Figure 4, the extent of reacted aliphatic carbon is shown as a function of temperature. At each temperature, the lowest point always corresponds to the reactions with no

solvent and no catalyst. As expected, these reactions with the worst liquefaction conditions result in the lowest conversion of aliphatic carbon. Comparing the effects of the solvents, the catalyst and temperature, the latter is shown to be the most significant by the fact that highest conversion of aliphatic carbon at one temperature is always lower than the lowest conversion at the next temperature (except that between 400°C and 450°C). Roughly speaking, all the points stay on one curve, regardless of the use of solvent or catalyst. The amount of reacted aliphatic carbon increases nearly linearly when the temperature increases, up to 400°C. At 400°C, about 90% of the aliphatic carbon has been converted to THF solubles. When the reaction temperature was further increased to 450°C, the increase of the reacted aliphatic carbon became insignificant, from 90% to about 95%. This study suggests that, like the yields of the gases, the conversion of aliphatic carbon from coal to THF solubles is a function mainly of temperature, neither solvent nor catalyst has any influence on it. In Figure 5, the amount of aromatic carbon converted to THF solubles is plotted versus the temperature. Unlike those in Figure 4, the data are much more scattered in Figure 5. In non-catalytic liquefaction reactions, tetralin made a remarkable difference from 1-MN and no solvent. When the temperature was 350°C or higher, much more of the aromatic carbon reacted in the presence of tetralin. At 450°C, the conversion of aromatics reached 86% with tetralin, while it only reached 15% and 10% with 1-MN and without solvent respectively. In catalytic liquefaction reactions, the difference caused by the solvents is diminished when the temperature increases to 400°C, indicating that the catalyst is sufficiently active in converting the aromatics into THF solubles and that solvent is no longer a major determining factor. However, when the temperature increased to 450°C, with the presence of the catalyst, reactions with 1-MN or without a solvent have a large decrease from 77% to 36% and from 93% to 42% respectively, while that with tetralin increased from 87% to 92%. At temperature as high as 450°C, the thermal cracking of the coal matrix is very fast, and the hydrogenation from the gaseous H₂ catalyzed by the added catalyst is no longer able to catch up. Therefore at 450°C in the presence of the catalyst, tetralin is no longer a minor factor. In fact, the only way to prevent the retrogressive reaction is to have a donor solvent, such as tetralin.

The study of reacted aliphatic and aromatic carbon helps to explain why a non-catalytic reaction always produces residues with higher aromaticity than a catalytic reaction even though the conversion can be the same. In the former case, the conversion is achieved by having more aliphatic carbon reacted and in the latter case, it is achieved by having a greater proportion of aromatic carbon reacted. For example, in experiment no. 331, the conversion is 44.0%, there is -8% aromatic (i. e. implying retrogressive aromatization reactions) and 79% aliphatic carbon reacted; while in experiment no. 327, the conversion is 45%, there are 23% aromatic and 63% aliphatic carbon reacted.

SUMMARY

Liquefaction of a Big Brown Texas subbituminous coal was studied in the temperature range from 250°C to 450°C. Tetralin and 1-MN were used as reaction solvents to compare with the reactions without solvent. Ammonium tetrathiomolybdate was used as the catalyst precursor. In thermal experiments, tetralin, a H-donor solvent, was beneficial not only in gaining high conversion but, most importantly, also in gaining high yield of oil at temperatures higher than 350°C. In catalytic experiments, conversions are very similar regardless of solvent used at temperatures up to 400°C, and tetralin does not have an advantage. However, at 450°C, conversions with 1-MN or with no solvent dropped while that with tetralin increased, as well as the oil yield. The gas yields appear to be independent of solvent and catalyst but dependent on temperature.

Cross polarization magic angle spinning of ¹³C NMR was performed to obtain aromaticities of reaction residues. It is found that in the plot of aromaticity versus conversion, the data fall into two sets: the non-catalytic reactions and the catalytic reactions. With the same conversion, a residue from a catalytic reaction always has lower aromaticity. This is because in a catalytic reaction, more aromatic carbon has been reacted. The study of the amount of aliphatic carbon converted from the coal to THF solubles shows that neither the catalyst nor the solvents has influence on it, but it is a function of temperature. In the case of conversion of aromatic carbon from coal to THF solubles, both the catalyst and the solvents have strong effects. For non-catalytic reactions, tetralin gave much

higher conversions of aromatic carbon than 1-MN or no solvent. For catalytic reactions, there is no difference among the solvents (or no solvent) at temperatures up to 400°C. At temperatures higher than 400°C, tetralin again gave a much higher conversion than the other two cases, indicating that the hydrogen donation by the solvent played a significant role. As for 1-MN and no solvent, compared with the results at 400°C, the conversion of aromatic carbon at 450°C did not increase, in fact it decreased drastically, suggesting that retrogressive reactions occur in these situations.

ACKNOWLEDGEMENT

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Table 1. Conversion and yield of non-catalytic reactions

Expt.#	Description	Conv.	Gas	Oil	Asph.	Preasph.
317	250C, NC, NS	11.7	1.9	8.2	0.8	0.8
318	250C, NC, TE	13.3	0.6	6.0	3.7	3.1
319	250C, NC, MN	11.9	2.8	5.6	2.4	1.2
335	300C, NC, NS	16.2	3.5	7.9	0.9	3.9
336	300C, NC, TE	20.8	3.5	9.8	3.5	4.0
337	300C, NC, MN	22.2	3.5	10.2	2.0	6.5
320	350C, NC, NS	19.1	6.5	7.4	1.2	4.1
307	350C, NC, TE	38.2	4.4	18.2	8.3	7.4
309	350C, NC, MN	33.8	5.0	14.8	7.4	6.7
331	400C, NC, NS	45.0	11.6	19.8	3.4	10.2
332	400C, NC, TE	82.0	9.5	36.7	16.6	19.2
334	400C, NC, MN	55.5	9.7	24.4	10.4	11.0
349	450C, NC, NS	51.5	17.6	28.8	0.9	4.2
350	450C, NC, TE	92.2	19.2	49.0	8.4	15.6
351	450C, NC, MN	57.0	16.3	31.8	4.3	4.6

Table 2. Conversion and yield of catalytic reactions

Expt. #	Description	Conv.	Gas	Oil	Asph.	Preasph.
322	250C, ATTM, NS	5.0	0.9	0.0	3.1	3.8
323	250C, ATTM, TE	3.8	0.9	0.0	2.3	1.7
324	250C, ATTM, MN	3.6	0.6	6.0	2.3	2.5
338	300C, ATTM, NS	17.2	2.5	9.3	1.8	3.6
339	300C, ATTM, TE	22.0	0.9	12.4	5.5	3.2
340	300C, ATTM, MN	22.9	2.4	10.2	6.0	4.3
325	350C, ATTM, NS	39.4	4.0	23.2	6.2	6.0
326	350C, ATTM, TE	46.6	3.7	23.9	11.4	7.6
327	350C, ATTM, MN	44.0	3.4	18.5	9.9	12.2
329	400C, ATTM, TE	92.0	6.8	44.3	19.3	21.6
330	400C, ATTM, MN	84.8	8.1	41.6	16.4	18.7
352	450C, ATTM, NS	69.4	18.0	44.6	5.2	1.6
353	450C, ATTM, TE	95.8	14.2	66.1	10.4	5.1
354	450C, ATTM, MN	67.2	16.1	37.4	8.4	5.3

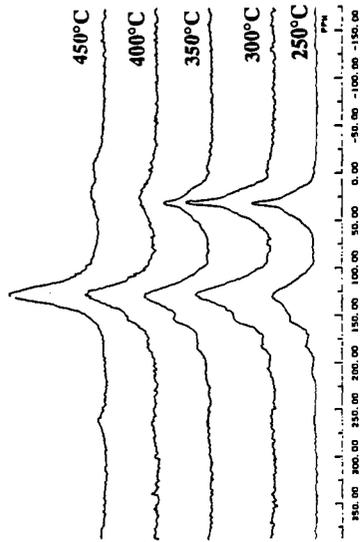


Figure 2. NMR spectra of residues from non-catalytic reactions with tetralin

Table 3. Aromaticity of residues from all liquefaction experiments

T (°C)	nc/ns	nc/tetr.	nc/l-mn	atm/ns	atm/tetr.	atm/l-mn
250.0	0.52	0.50	0.53	0.50	0.52	0.52
300.0	0.55	0.63	0.60	0.45	0.57	0.58
350.0	0.64	0.69	0.74	0.59	0.62	0.66
400.0	0.80	0.85	0.86	0.78	0.76	0.72
450.0	0.89	0.91	0.94	0.85	0.94	0.93

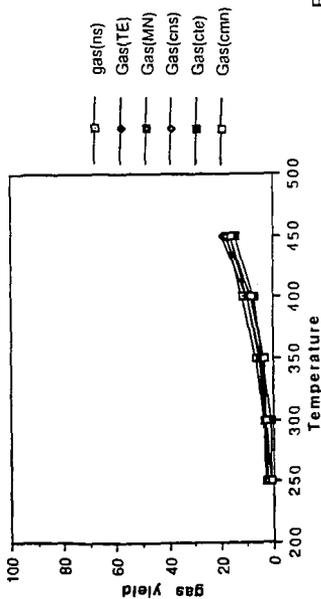


Figure 1. Gas yield of all liquefaction experiments

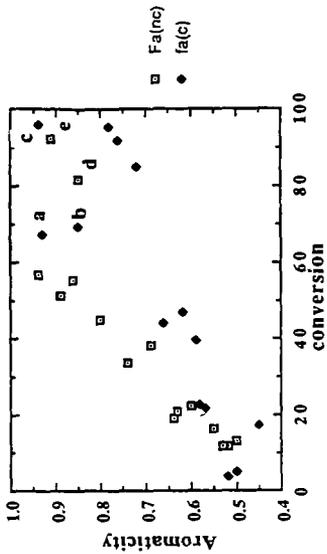


Figure 3. Aromaticity of residues from all experiments as a function of conversion a, b, c, aromaticities of catalytic reaction at 450°C with 1-MN, no solvent and tetralin respectively; d, e, aromaticities of residue from non-catalytic reactions with tetralin at 400°C and 450°C.

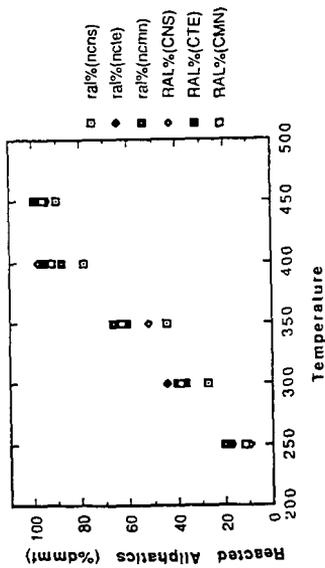


Figure 4. Reacted aliphatic carbon as a function of temperature

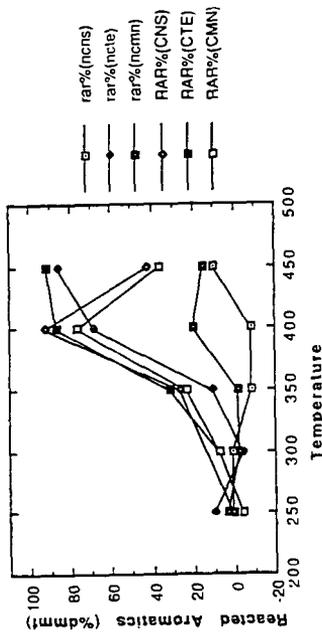


Figure 5. Reacted aromatic carbon as a function of temperature

A Novel Synthesis Route for Liquid Fuels from Coal-derived Syngas

Makarand Gogate, Conrad J. Kulik[#], and Sunggyu Lee
Process Research Center
Department of Chemical Engineering
The University of Akron
Akron, Ohio 44325-3906

[#]Fuel Science Program
Electric Power Research Institute
Palo Alto, California 94303

Keywords: MTG Process, Methanol, Indirect Coal Liquefaction, Synthetic Fuels

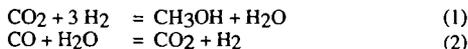
Abstract

Coal-derived syngas can be converted to methanol using Liquid Phase Methanol Synthesis Process. Methanol can be further converted to gasoline using the Mobil Methanol-To-Gasoline (MTG) process. The combination of commercial syngas-to-methanol technology with the MTG Process thus provides a ready synthetic route for liquid hydrocarbon fuels. We have developed a novel process for one-step synthesis of Dimethyl Ether (DME) from syngas. This DME Synthesis improves the reactor productivity and syngas conversion, by as much as 100%, over LPMeOH Process. One-step DME synthesis is thus an ideal front-end for further conversion to gasoline. This substitution is justified not only because DME yields an identical product distribution as methanol, DME is also a true intermediate in the Mobil MTG process. The novel integration scheme has been termed as the Dimethyl Ether-to-Gasoline (DTG) process. The advantages of the UA/EPR1 DTG Process over the conventional Methanol-to-Gasoline Process are in (a) enhanced syngas conversion, (b) superior hydrocarbon yield, (c) superior product selectivity, (d) alleviated heat duties, and (e) integrated energy efficiency. These and other salient features of this novel synthesis route for liquid fuels have been discussed.

Introduction

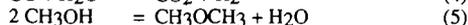
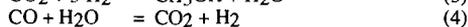
The conversion of syngas to gasoline occurs typically in two stages. Syngas is first converted to methanol over a copper-based hydrogenation catalyst. In the second stage, methanol is converted to gasoline over a ZSM-5 catalyst. These two process steps form the basis for the Mobil Methanol-To-Gasoline (MTG) Process [1-3, 12, 15]. Dimethyl Ether (DME) is a key intermediate chemical species in the second stage. Mobil's MTG process in combination with the commercial syngas to methanol technology thus provide a ready route to synthetic gasoline, i.e., with feedstocks other than petroleum.

The first stage of the MTG process is the synthesis of methanol from syngas. In a typical Liquid Phase Methanol Synthesis (LPMeOHTM) process, the synthesis catalyst (composed of CuO, ZnO, and Al₂O₃) is slurried in an inert hydrocarbon oil [14, 16]. Syngas (H₂, CO, and CO₂) reacts over the active catalyst to produce methanol in-situ. The reaction chemistry for methanol synthesis in the liquid phase from CO-rich syngas has been well-established to be [4-6, 8, 9, 13, 16, 17]:



Syngas-to-methanol conversion technology has recently been modified and improved to synthesize Dimethyl Ether (DME) directly from syngas in a single reactor stage [4-7, 10]. This process augments the per-pass syngas conversion and volumetric reactor productivity as a result of reduced chemical

equilibrium limitation governing the syngas-to-DME conversion. The reaction chemistry for typical single-stage DME synthesis from CO-rich syngas can be written as [7]:



In the Liquid Phase DME Synthesis (LP-DME) process, DME is thus directly produced from syngas, in a single reactor stage. As seen from the reaction sequence, the reaction scheme is a combination of an equilibrium limited reaction (#3, methanol synthesis) and an equilibrium unlimited reaction (#5, DME synthesis, or, methanol dehydration). Reactions #3 and #4 occur over the coprecipitated Cu/ZnO/Al₂O₃ catalyst, while reaction #5 occurs over gamma-alumina. The LP-DME synthesis is thus based on the application of dual catalysis in the liquid phase [10, 11].

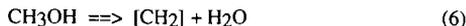
This process can be an effective substitute for the syngas-to-methanol step in the Mobil MTG Process. This substitution is justified based on the following facts (a) DME results in virtually identical hydrocarbon product distribution as methanol and (b) DME is a true intermediate in the Mobil MTG process. The single-stage conversion of syngas to DME (and methanol) thus provides an ideal front-end for further conversion to gasoline.

A novel syngas-to-gasoline process based on this unique integration scheme (Syngas-to-DME and DME-to-Gasoline) has been proven to be superior to the Mobil MTG process. Block diagrams of the conventional Syngas-to-Methanol-to-Gasoline and our novel Syngas-to-DME-to-Gasoline have been shown in Figures 1 and 2. Our novel synthesis process for hydrocarbon fuels has been termed as the UA/EPRI Dimethyl Ether -To- Gasoline (DTG) process. The DTG process merits over the Mobil MTG are in the areas of heat duty, heat of reaction, adiabatic temperature rise, space time and velocity, reactor size, hydrocarbon product yield, and selectivity. These have been conclusively validated in the following sections.

Results and Discussion

1. Heat of Reaction:

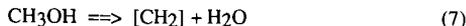
The conversion of methanol to hydrocarbons is an exothermic reaction. Depending on the nature and spectrum of the hydrocarbon product, the heat of reaction will vary. In the simple case when water is the only byproduct, the conversion can be represented stoichiometrically as:



The heat of reaction of methanol conversion to hydrocarbons is a function of the product distribution, or alternately, that of space velocity. Thus, to calculate the heat of reaction of methanol (or, DME) conversion to hydrocarbons, the product distribution spectrum at a fixed space time is necessary. These have been summarized elsewhere [1, 2]. Based on these calculations (at one sample space velocity of 108), the heat of reaction for DME conversion to hydrocarbons (-142 cal/g) was found to be 32% less than that for methanol conversion to hydrocarbons (-211 cal/g). Overall, since methanol dehydration to DME contributes about 25% to the total heat of reaction of the methanol conversion to hydrocarbons, it is expected that the heat of reaction for DME conversion to hydrocarbons at complete conversion would be about 25% lower than that for methanol conversion.

2. Selectivity and Product yield:

The conversion of methanol to water and hydrocarbons is essentially stoichiometric and complete. The stoichiometric representation of the reaction is:



where [CH₂] is the average composition of the hydrocarbon product comprising of paraffins and aromatics. Water is the only co-product. The final stoichiometric composition for methanol conversion then would be [12+2 = 14] atoms of [CH₂] and [2+16 = 18] atoms of [H₂O]. The stoichiometric

product ratio then becomes 14 g to 18 g. This translates to a 44:56 weight ratio basis of the hydrocarbons to water. The selectivity towards hydrocarbons for methanol conversion is then 0.44 g of hydrocarbons / g methanol.

For the conversion of DME to hydrocarbons and water, the stoichiometric representation of the reaction is:



where $[\text{CH}_2.\text{CH}_2]$ is the average composition of the hydrocarbon product. The final stoichiometric composition for DME conversion would then be $[12+2+12+2 = 28 \text{ atoms}]$ of hydrocarbons and $[2+16 = 18 \text{ atoms}]$ of water. This stoichiometric ratio then becomes 28 g to 18 g. This translates to a product ratio of 60.8 : 39.2 weight basis ratio of hydrocarbons to water. The selectivity towards hydrocarbons is then 0.61 g hydrocarbons/ g DME. The reactor productivity would then be 0.61 g/unit volume of the reactor, when compared 0.44 g for methanol case, this is 38% higher for the DME conversion.

3. Space Velocity and Reactor Size:

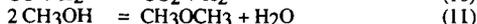
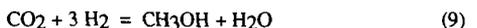
The conversion of methanol and DME to hydrocarbons is a function of space velocity (or, space time in the reactor). The reaction paths for methanol and DME conversion [2] bring out this fact in greater detail. A substantially more space time (or, contact time) is needed for complete and stoichiometric conversion of methanol to hydrocarbons when compared to that needed for DME conversion to hydrocarbons. The relative difference between the space times for these two cases is estimated at 1 magnitude of space time (1/ [g reactant/g cat. h]). Based on the reaction paths given in [1], it is estimated that for identical space time, the DTG reactor size can be about 25% lower than of the MTG reactor, for complete and stoichiometric conversion. Conversely, for identical MTG and DTG reactor size, the DTG reactor will be 25% more productive (i.e., reactor productivity per unit volume) than the MTG reactor.

4. Overall Comparison and Analysis:

Sections (1-3) have elucidated the rationale and the philosophy behind operating the novel Syngas-to-DME-to-Gasoline process, as against the conventional Syngas-to-Methanol-to-Gasoline process. The conclusive advantages of this novel synthesis route (DTG) have been summarized as follows. These advantages have also been summarized in Table I.

[1] One-step conversion of syngas to DME improves the per-pass syngas conversion and reactor productivity over syngas to methanol. The comparison of our experimental results are as follows. At 250 °C, 70 atm, 1-liter slurry reactor, per-pass syngas conversion to methanol is 53%. At nominally identical operating conditions, per-pass syngas conversion to DME is at 74%. Starting with 1 gmol of syngas, this translates to about 0.47 gmol of recycle / gmol of syngas for syngas to methanol case. The recycle load is reduced to only 0.26 gmol / gmol of syngas for the syngas to DME case. The recycle load is thus reduced by about 46%.

[2] The conversion of syngas to methanol uses copper-based $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst. This catalyst is susceptible to deactivation by crystal growth in the liquid phase rich in methanol and water. However, the conversion of syngas to DME uses a dual catalyst system based on a combination of $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst and gamma-alumina catalyst. This conversion offers a favorable scenario for crystal growth of copper catalyst because of two reasons. First, the liquid phase is lean in methanol because of in-situ conversion to DME over gamma-alumina. Second, water produced by both methanol synthesis (CO_2 hydrogenation) and DME synthesis (methanol dehydration) constantly is shifted by the forward water gas shift reaction. This is perhaps the most significant merit of the one-step conversion of syngas to DME, a fact well-proven by the research at the University of Akron. The reaction chemistry of syngas to DME conversion is as follows, starting with CO-rich or the so-called unbalanced syngas:



[3] The one-step conversion of syngas to DME improves the volumetric reactor productivity by as much as 100%, over that of syngas to methanol conversion. This is because of conversion of syngas to DME is not nearly limited by chemical equilibrium as syngas to methanol. This fact has been well-proven by the research at the University of Akron. For example, at 250 °C at 70 atm, starting with 1 gmol of unbalanced syngas, methanol yield is about 0.14 gmol, or, 0.14 gmol (CH₃) equivalent. At identical conditions, the yield of DME is about 0.12 gmol, or, 0.24 gmol of (CH₃) equivalent. This corresponds to an increase of about 72% in the reactor productivity, at identical conditions.

[4] The conversion of methanol to gasoline is highly exothermic with a heat of reaction of 398 cal/g of methanol converted. For this reason, the conversion is usually split in two parts, for exothermic heat management. In the first, methanol is converted to an equilibrium mixture of DME, water (and unconverted methanol). In the second, this mixture of methanol, DME, and water is converted to gasoline. The first step contributes to about 25% of the total exothermic heat of reaction. The conversion of DME to gasoline is thus about 25% less exothermic, with a heat of reaction of about 300 cal/g of DME converted.

[5] . As elucidated in point [4], the conversion of methanol to gasoline requires the conversion of methanol to methanol, DME, and water first, to manage the exothermic heat of reaction. The one-step conversion of syngas-to-DME followed by DME conversion to gasoline thus obviates the need for a separate methanol dehydration reactor. This contributes to significant savings in capital and operating cost.

[6] The adiabatic temperature rise in the conversion of methanol to gasoline is estimated at about 650 °C, while that for the conversion of DME to gasoline is only at about 475 °C.

[7] In methanol to gasoline conversion, equilibrium mixture of DME, water, and methanol is usually fed to the gasoline synthesis reactor. The ZSM-5 based zeolite catalyst is extremely sensitive to water in the feed (water is a catalyst poison). For this reason, water is removed from the feed. In the conversion of DME to gasoline, very little to no water is fed to the gasoline synthesis reactor, because the single-step syngas-to-DME conversion produces DME with extremely high selectivity (>99%). Catalyst life cycle in the gasoline synthesis reactor is favorable in the direct conversion of DME-to-gasoline because of (a) lower concentrations of water in the reactor and (b) about 25% reduced exothermicity of the reaction.

[8] The stoichiometric conversion of methanol to gasoline produces 44 % (w/w) to 56 % (w/w) mixture of hydrocarbons to water. For example, 1 g of methanol yields 0.44 g hydrocarbons [CH₂] and 0.56 g water, at complete and stoichiometric conversion. On the contrary, 1 g DME yields 0.61 g hydrocarbons [CH₂] and only 0.39 g water. The yield of gasoline hydrocarbons for DME conversion is thus 38 % higher than that for methanol conversion. The yield of water is concomitantly 30 % lower for the DME conversion case.

[9] Hydrocarbon product distribution is directly related to the space time for both methanol and DME conversion. For methanol conversion, the reactor space time is estimated to be 20% higher than that for DME conversion, to achieve a stable hydrocarbon product distribution. Intuitively also, this can be immediately validated considering that reaction path of methanol conversion to hydrocarbons involves DME as the intermediate. At identical space time, the DTG reactor size can be 25% lower than the conventional MTG reactor.

[10] Finally, there are important differences between two cases of syngas-to-DME-to-gasoline process, where syngas is derived from coal or from natural gas. Syngas derived from coal is CO-rich (or, unbalanced), while that derived from natural gas is H₂-rich (or, stoichiometric). These differences are in the areas of:

- (a) recycle load (about 0.34 gmol / gmol for coal vs 0.52 for NG case).
- (b) CO₂ rejection is mandatory in coal-based syngas. CO addition is necessary for NG.
- (c) overall [CH₂] productivity is about 30% higher for coal-based syngas.
- (d) overall, coal-based syngas process is more attractive. However, the availability and price of coal in comparison to NG remains a primary concern.

Conclusions

Process comparison and analysis of Syngas-to-Methanol-to-Gasoline and Syngas-to-DME-to-Gasoline conclusively proves that synthesis of gasoline via direct DME route has definitive process advantages over the synthesis via methanol route. These process merits are in the areas of higher gasoline yield, higher syngas conversion, good adaptability to coal-based syngas, and integrated energy efficiency. Further experimental investigation to establish these merits is currently underway at the University of Akron.

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Table I

Syngas-to-Methanol-to-Gasoline Vs. Syngas-to-DME-to-Gasoline

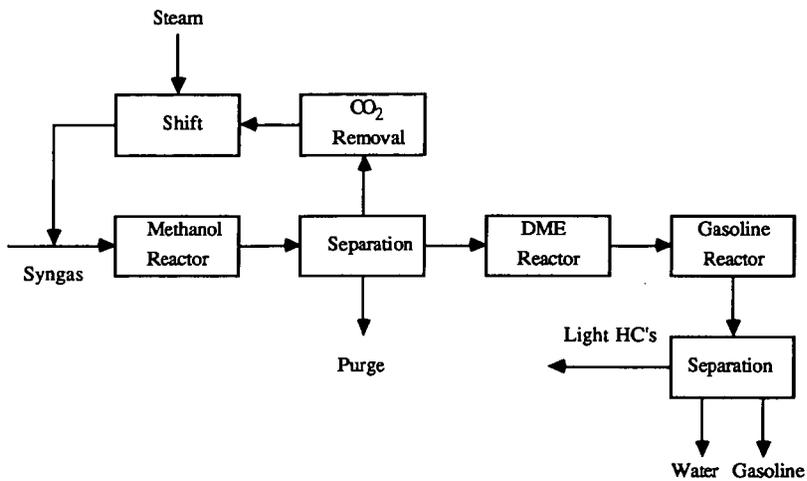
	MTG	DTG
Syngas-to-Methanol Vs. Syngas-to-DME		
1) productivity, g product [#]	10.9	11.8
2) hydrogen conversion, %	72.4	87.7
3) CO conversion, %	38.2	62.3
4) syngas conversion, %	53.0	73.4
5) recycle, gmol / gmol feed syngas	0.47	0.27
6) heat of reaction, cal (exothermic)	8008	13745
7) catalyst life	good	better

[#]On basis of experimental data, 2.68 mol (= 50 g) syngas feed, 250 °C, 70 atm, 1-Lit Autoclave.

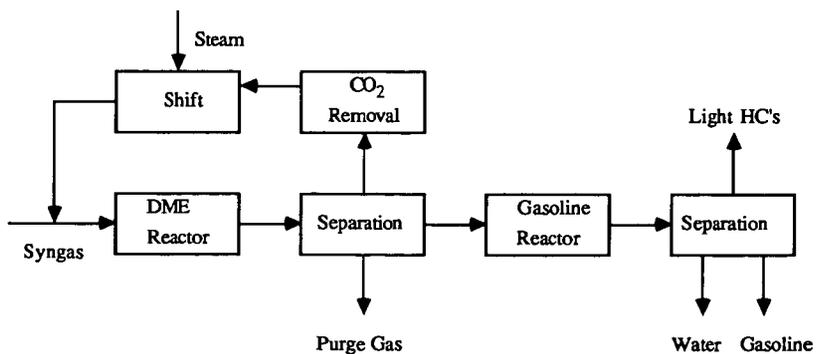
Methanol-to-Gasoline Vs. DME-to-Gasoline

8) productivity, g [CH ₂] [#]	4.79	7.46
9) conversion, %	100	100
10) heat of reaction, cal / g (exothermic)	398	300
11) adiabatic temperature rise, °C	600	475
12) reactor size at identical WHSV	1.25	1
13) catalyst life	poor	better
14) methanol dehydration reactor	necessary	not nec.
15) water concentration in the reactor	high	low
16) overall water production, g [H ₂ O]	6.16	5.15
17) [CH ₂] selectivity, g / g converted	0.44	0.61
18) [H ₂ O] selectivity, g / g converted	0.56	0.39
19) Overall hydrogen consumption, g [CH ₂] / g	3.42	4.31

[#]On basis of complete and stoichiometric conversion, 375 °C, 1 atm, feed item (1).



**Figure 1. Syngas-to-Methanol-to-Gasoline-Methanol Condensation
-Low Pressure Gasoline Reactor.**



**Figure 2. Syngas-to-DME-to-Gasoline-DME Condensation
-Low Pressure Gasoline Reactor.**