

STUDIES OF CATALYTIC UPGRADING OF LOW-SEVERITY LIQUEFACTION PRODUCTS FROM LOW-RANK COALS

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Introduction

The optimal liquefaction conditions for low-rank coals appear to be the use of a two stage process, where relatively low temperatures (380^o) are used in the first stage because of the higher reactivity of low-rank coals and the tendency to coke at higher temperatures. This low-severity product can then be subjected to a secondary upgrading process to give a better fuel product. Much of the carboxylate groups of the coal are decarboxylated in the first stage, thus the second stage reaction involving catalytic hydrogenation does not waste much hydrogen on reactions with the evolved carbon dioxide. Transformations of the numerous oxygen functional groups of the low-rank coals occur during both the low-severity and the hydrotreating steps along with the depolymerization and other conversions, and the objective of our studies is to understand these transformations on a quantitative basis and correlate with the other liquefaction parameters, such as yields, changes in molecular weight distributions, and changes in hydroaromatic groups.

This paper is concerned with the catalytic hydrotreatment of a low-severity product obtained from the liquefaction of a Wyodak subbituminous coal in tetralin solvent at 384^oC (1 hour) in carbon monoxide plus hydrogen sulfide. The low-severity product was separated into two fractions, a methylene chloride soluble fraction and methylene chloride insoluble fraction. The results from second stage liquefaction of the methylene chloride soluble fraction under various conditions will be reported here. This fraction comprised the major portion of the low-severity product. The second stage reaction used the same solvent as the first stage. This solvent was chosen because it does not contain oxygen and is a simple system whose products, naphthalene, decalin, methylindan, butyl benzene and dimers, can be easily distinguished in the reaction products. Two reaction temperatures (425^oC and 450^oC) were used in the high severity treatments. Runs for one or two hours were conducted. Hydrogen pressure was another variable during these investigations, although all reactions contained the same amount of the sulfided Co-Moly catalyst.

Experimental

In a typical run, methylene chloride solubles (20 g including tetralin solvent) obtained from the low-severity Myodak liquefaction in tetralin and 0.80 g of sulfided Co-Moly catalyst (AMOCAT) were sealed in a 75 ml tubing bomb. The tubing bomb was evacuated and pressurized with 300 or 400 psi of hydrogen, if needed in the test. The tubing bomb was lowered into a fluidized bed sand bath maintained at the desired temperature (425° or 450°C). The bomb was heated with constant agitation for the desired time (1 or 2 hrs). At the end of the reaction, the tubing bomb was removed from the sand bath, cooled to room temperature and slowly depressurized. The raw product slurry obtained on opening the tubing bomb was transferred to a beaker with methylene chloride and was separated into various product fractions.

The following products were obtained from the product work-ups of the high severity liquefaction product slurry (1):

- 1) methylene chloride insolubles
- 2) pentane insolubles
- 3) low-boiling (less than 160°C/1.4 torr) distillate (mainly solvent, see below)
- 4) high boiling (160-240°C/1.4 torr) distillate (contains some solvent and dimers, see below)
- 5) vacuum bottoms (nondistillable material)

The conversion was calculated as the conversion of the pentane insoluble fraction of the low-severity material to pentane soluble material during the high severity liquefaction, and these data are given in Table 1. Of course this conversion is not the only description of reaction progression of interest. The product yield (coal-derived material) in the distillates is also very important. Also of interest is the retrograde reaction which results in methylene chloride insoluble material.

The product distillate yields were then calculated by subtraction of the solvent (tetralin, naphthalene, and decalin) from the low-boiling distillate yield and adding this to the result obtained by subtraction of the solvent-derived dimers (bitetralin, binaphthyl, naphthyltetralin, etc.) from the high boiling distillate yield. The solvent distillate yields are a combination of the amounts of tetralin, naphthalene, decalin in both distillates plus the solvent-derived dimers in the high boiling distillate.

The volatile products were characterized by GC-FID and GC/FTIR/MS, the nonvolatile products were characterized by photoacoustic FTIR, solid state or solution ¹³C NMR and weight average molecular weight determinations (low angle laser light scattering photometry).

Results and Discussion

Conversions

The data summarized in Table 1 reveal that the degree of conversion is dependent on several factors. The reaction at 425°C for one hour with no hydrogen present gave a conversion of only 30%. Raising the processing temperature to 450° for the same time and with no hydrogen pressure increased the conversion to 84%. Also increasing the contact time from one hour at 425° to two hours (no hydrogen) increased the conversion to 78%. In the tests with 400 psi of hydrogen, the conversions increased to 66% at 425°C for one hour and to 92% at 450° for one hour. The two hour reaction under hydrogen (charged to 300 psi, run one hour, recharge to 300 psi, run another hour) gave 80% conversion. Thus the conversion is directly proportional to the reaction

temperature, the reaction time, and the added hydrogen pressure.

Another interesting feature of the high severity reactions was the solvent conversion, that is tetralin to naphthalene as a result of hydrogen donation to the coal-derived material. The tetralin to naphthalene ratios in the products from high severity treatments were calculated from the GC/FID determinations of the volatile material (low boiling distillate plus a very small amount in the high boiling distillate) and compared with the ratio initially present in the low-severity product. These ratios are also reported in Table 2. The initial tetralin/naphthalene ratio in the low-severity product was 27, indicating the relatively low hydrogen consumption in the low-severity reaction.

The high severity reactions changed the tetralin/naphthalene ratios significantly. The reaction at 425° for one hour without added hydrogen gave a ratio of 3.31. This corresponds to the formation of 3.7 g of naphthalene (24 mmoles) or transfer of 48 mmoles of H₂ from the tetralin to the coal material during the reaction. Increased reaction time further decreased the ratio (to 2.76). Raising the temperature to 450° for one hour, with no hydrogen added, dropped the ratio even more to 2.06, which indicates that more hydrogen is transferred to the coal fragments at higher temperatures and is consistent with the more extensive conversion which was observed at the higher temperature. When molecular hydrogen was added to the reaction mixture (425°, one hour, 400 psi H₂), the ratio of tetralin to naphthalene was somewhat greater (4.16) than that observed when no hydrogen was added (3.31). Longer reaction times with hydrogen present similarly gave higher ratios (2.51) than those reactions with no hydrogen present (2.76), but lower ratios than the one hour reactions. Thus the tetralin/naphthalene ratios for the high-severity ratios are inversely proportional to the reaction temperature and the reaction time and directly proportional to the hydrogen present. These results are in agreement with the conversion percentages, that is the higher the conversion, the more hydrogen was transferred.

Methylene chloride insoluble product

The methylene chloride insoluble material isolated from the reaction products consisted of the added Co-Moly catalyst plus only about 1% of material derived from the starting low-severity material. The insoluble material was studied using photoacoustic FTIR spectroscopy and was found to contain both alkyl and aromatic groups. This material may be the product of retrograde or cross-linking reactions of some of the macromolecules of the low-severity product which occurred during the catalytic high severity reaction. Although it cannot be described exactly as coke, since it has alkyl groups, the retrograde reaction which produces these small amounts may be similar to that described as "coking."

Since the amount of this material is insignificant even in reactions at 450°C with no hydrogen pressure, the soluble low-severity product is not likely to be the source of the coked material obtained during some liquefaction experiments with whole coals. More likely the source is the more aromatic and less soluble part of the coal which continues to donate hydrogens to the more soluble portions until it becomes the coke.

Pentane insoluble product (Methylene chloride soluble)

The decrease in the amount of the pentane insoluble fraction in going from the low-severity material to the high severity product has been discussed above in terms of the conversion of the reaction, which was shown to be highly dependent on the conditions chosen for the high severity reaction. The

question of interest here is how did the structure and properties of the recovered pentane insoluble fraction change in comparison with the pentane insoluble fraction of the starting low-severity material, as a result of the high severity liquefaction carried out under different conditions

The changes in the molecular weights of the coal macromolecules during second stage processing of this methylene chloride soluble fraction from low-severity liquefaction of Wyodak was investigated by static low angle laser light scattering (LALLS) photometry in tetrahydrofuran solvent. This product was nondistillable and nonvolatile. Rayleigh scattering factors were measured for the dilute THF solutions of the pentane insoluble products and corrected by means of the Cabannes factors which were determined for each of the solutions used. The corrected Rayleigh factors gave a linear reciprocal scattering plot (KC/R_{90} versus C) with an r^2 of 0.99. The weight average molecular weight of the pentane insoluble fraction of the starting low-severity material was 5.6×10^6 daltons. The weight average molecular weight of the pentane insoluble material recovered from the high severity treatment in tetralin solvent at 425°C for one hour in the absence of added hydrogen was 6.27×10^6 daltons, a significant increase over that observed for the pentane insoluble fraction of the starting Wyodak low-severity product. An increase in molecular weight was also observed for the pentane insoluble fractions recovered from the high severity treatment of Big Brown lignite in work done earlier (2). There may be two reasons for the increase. First, a selective reaction of the lower molecular weight material during the heating at 425°C would have changed the distribution to a higher molecular weight. Second, the liquefaction reactions may involve some retrograde or polymerization reactions which would increase the molecular weight distribution of this fraction.

The pentane insoluble material recovered from the high severity reaction at 425° for one hour with hydrogen (400 psi) gave a weight average molecular weight of 4.06×10^6 . Again this value is larger than that of the starting pentane insoluble material, indicating either the change in distribution by preferential reaction of lower molecular weight material or retrograde reactions were occurring. The main difference between this material and that isolated from the high severity reaction carried out without hydrogen is that the amount of pentane insoluble material obtained in the presence of hydrogen is much smaller, possibly as a result of minimization of the retrograde reaction by the molecular hydrogen.

Further characterization of the pentane insoluble fractions were carried out using photoacoustic-FTIR and solid state ^{13}C NMR spectroscopy. FTIR spectra of the fractions recovered from the high severity reactions when compared with that of the low-severity fraction showed an increase in the aromatic absorptions at 1600 cm^{-1} . The carbonyl absorptions in these products were insignificant. The increase in aromatics was confirmed by the NMR spectra. The low-severity material showed an aromatic carbon to aliphatic carbon ratio of 1.47. This ratio was 3.25 in the pentane insoluble fraction from the reaction at 425° for one hour in tetralin in the presence of 400 psi of hydrogen. The ratio was even higher in the product of the reaction at 425° for 2 hours in the absence of hydrogen (3.84). These NMR data for the various fractions show that there is a preferential solubilization of the aliphatic material. Two explanations are possible. First, aliphatic material may be cleaved from the aromatic clusters of the coal macromolecules. Second, the more aliphatic members of the distribution of macromolecules may be preferentially degraded during the high-severity liquefaction. The higher ratio for the reaction in the absence of hydrogen as compared with that for the reaction in the presence of hydrogen may be explained in several ways.

First, aromatics may be converted to hydroaromatics in the presence of hydrogen. Second, alkyl radicals formed in the thermal degradations may be converted to alkanes by trapping with molecular hydrogen when present or by reacting with coal structures which result in formation of aromatics in the absence of hydrogen.

Solvent-derived distillate

The low boiling distillates obtained from low-severity treatment of Wyodak in tetralin and the high-severity treatments under various conditions were characterized using GC/MS. The low-severity low boiling distillate consisted mainly of tetralin and naphthalene (T/N ratio = 27) along with small amounts of decalin and methylindan. No significant amounts of solvent-related dimers were found in the low-boiling distillates. The coal derived material in this distillate is discussed separately below.

The high boiling distillate (160-240°C/1.4 torr) consisted of small amounts of tetralin and naphthalene and the dimers (bitetralyl, binaphthyl, naphthyltetralin, naphthyldecalin, etc.) derived from the solvent in addition to the coal-derived material. Some of these dimers were present in the distillate from the methylene chloride soluble fraction of the low-severity material. The amounts of this material formed from the solvent was greatest at the lower (425°C) temperatures when no hydrogen was present and was the least at the high temperatures with or without hydrogen pressure.

Product distillate

A small fraction of the low boiling distillate consisted of coal derived material such as phenols, alkanes and arylalkanes. The volatile material in the high boiling distillate fraction which was derived from the low-severity product was mainly n-alkanes plus the usual variety of 1 to 4-ring aromatics (unsubstituted and alkyl substituted). Substantial amounts of diphenyl ethers and dibenzofuran were found.

The coal-derived product was only 1% of the amount of the low boiling distillate of the methylene chloride soluble fraction of low-severity material but was 2/3 of the high boiling distillate of the low-severity material. The sum amounted to 33% of the mass of the methylene chloride soluble low severity material. As a result of the high severity treatments, the amount of distillable product increased in all cases; the highest yield was obtained for the 450°C reaction with hydrogen, where 81% of the total liquefaction product was the distillate.

Vacuum bottoms

The vacuum bottoms are the undistillable materials left after distillation of the pentane solubles at 1.4 torr. The amounts of the vacuum bottoms obtained from the low-severity product of Wyodak was 0.56 g/batch or 15.6% of the total coal-derived material in the low-severity product. The amounts of vacuum bottoms increased slightly for the high-severity treatment at 425°C with or without added hydrogen. However, raising the reaction temperature to 450°C resulted in decreased amounts of vacuum bottoms.

The vacuum bottoms were characterized using infrared spectroscopy, molecular weight determinations, and proton-decoupled solution ¹³C NMR in deuterated chloroform. Both the infrared spectra and the solution NMR spectra indicate that the vacuum bottoms obtained from the high severity liquefactions are more aromatic than the distillates, but not nearly as aromatic as the pentane insoluble fractions discussed above. The bottoms obtained from the reaction at 450°C with no hydrogen added had an aromatic carbon to aliphatic

carbon ratio of 1.73.

The vacuum bottoms fractions contained some material which sublimed at 0.25 torr and 250^o, but the remainder exhibited large Cabannes factors and large Rayleigh scattering, giving molecular weights of 10⁵ daltons.

Conclusions

The low severity methylene chloride soluble product consists of a high molecular weight pentane insoluble fraction, a high molecular weight vacuum bottoms fraction and one third distillable oils. This material was converted by the high severity conditions into a product consisting of small amounts of a higher molecular weight pentane insoluble fraction, a high molecular weight vacuum bottoms fraction, and an increased amount of a distillable oil product. The relatively small amount of the high molecular weight aromatics in the distillate or volatiles may be a consequence of the absence of very large polycondensed aromatic clusters in the low severity product. When the macromolecules are cleaved they go all the way to small molecular weight species. A similar distribution was observed in the Wyodak ITSL product reported by Moroni (3).

Acknowledgements

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TABLE 1

#	Reaction Conditions	PI	Products (in.gms)		Conversion (%) (PI → PS)	T/N Ratio	
			Prod. Dist.* (%)**	B Total			
1.	Starting Material (L,S)	1.60	1.05 (33.0)	0.56	3.21	--	27.0
2.	425-1-OH ₂	1.10	1.27 (43.0)	0.57	2.94	30.00	3.26
3.	425-2-OH ₂	0.33	1.76 (63.0)	0.73	2.84	78.7	2.76
4.	425-1-400H ₂	0.52	1.27 (50.8)	0.71	2.50	66.40	4.16
5.	425-1+1-300+300	0.31	1.66 (62.64)	0.68	2.65	80.1	2.51
6.	450-1-OH ₂	0.24	1.67 (69.87)	0.48	2.39	84.50	2.06
7.	450-1-400H ₂	0.15	2.23 (81.10)	0.37	2.75	92.0	3.40

* Wt %: does not include low boiling phenolic products (<60°C at 1.4 torr)

** % of total coal-derived products.

PI = Pentane Insolubles

PS = Pentane Solubles

B = Vacuum Bottoms

T/N = Tetralin/Naphthalene

L.S = Low Severity

UPGRADING OF COAL DERIVED OIL BY INTEGRATING
HYDROTREATMENT TO THE PRIMARY LIQUEFACTION STEP

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The Bottrop Coal Liquefaction Project

The coal liquefaction project in the Coal Oil Plant in Bottrop, West-Germany, pursued the following targets:

- Demonstration of the improved Bergius-Pier hydrogenation technology on a technical scale
- Testing and further development of process-related and mechanical components
- Identification of environmental impact
- Development of design data base for a commercial unit and
- Generation of technical and operational know how.

The Pilot plant in Bottrop with a capacity of 200 t maf coal/day was erected in order to meet these targets.

The project was initiated in late 1977. After the engineering and construction phase, the plant came on stream in November 1981 and was operated up to May 1987.

The plant was layed out for

300 bar pressure,
475 - 490 °C reaction temperature and
the use of red mud as catalyst.

The project was pursued jointly by RUHRKOHLE AG and VEBA OEL AG. It was from the very beginning supported substantially by the State Government of Northrhine Westfalia and starting from 1984 also by the Government of the Federal Republic of Germany.

The initial process configuration is shown in Fig. 1. In this project phase the program focussed on the primary conversion of coal, using liquid phase hydrogenation reactors. This procedure yielded a raw oil from coal in the boiling range of naphtha and mid distillate, which was highly aromatic and had high contents of oxygen and nitrogen compounds. Secondary upgrading processes were applied in process development units, in order to convert the primary products into marketable fuels, e.g. gasoline, heating oil, kerosene and diesel fuel. Each of the different upgrading routes included severe hydrotreating as first step.

For this reason, the hydrotreating reactors were in 1986 directly linked to the primary conversion system as shown in the simplified flow scheme (Fig. 2). Contrary to the first mode of processing in which the net product fractions - naphtha and middle distillate - were subjected to upgrading processes in separate units, the total vaporised effluent from the liquid phase reactors including the vacuum gasoil fraction is in the integrated alternative fed to the hydrotreating stage, the so called "gasphase reactors". The new configuration makes use of the complete heat content of the LP reactor effluent and supplies re-

action heat from the hydrotreater for the preheating of the fresh coal slurry, improving in this way the complete heat-exchange system thanks to the lower amount of external preheating fuel required. A further advantage of the integrated mode consists of the use of the high pressure of the first step and the secondary upgrading. Only a slightly higher pressure drop over the whole plant - caused by the additional equipment - has to be surmounted in the recycle gas compression.

The fact that the vacuum gasoil fraction from the coal liquids, which is in any case used as slurry oil for the fresh coal, was in the integrated process hydro-treated and hydrogen-enriched caused a large feed-back so the first process step and led to essential improvements in the performance, as described below.

Results

The total operating time of the plant for the coal liquefaction program amounted to more than 28.000 hours. During this time, appr. 166.000 t of coal were converted. Hard coal from the Ruhr Area, such as "Westerholt Coal" or "Prosper Coal", was usually used as feed. However, for comparison with competitive technologies, the program also included a batch of 4.000 t of Illinois No. 6 coal. The process mode with integrated hydrotreating was demonstrated for appr. 2.300 h with a total amount of 18.000 t of processed coal from the Westerholt mine. Fig. 3 compares the yield structures of the two processing modes. Due to the improved quality of the slurry oil, higher oil yields - 57,9 wt-% on maf coal against 50,6 wt-% - were obtained with substantially lower catalyst requirements, lower gas formation and lower amounts of hydrogenation residues.

The effect of integrated hydrotreatment on the sulfur- and nitrogen content of the liquid products is very high (Fig. 4) and leads from a raw oil to the expected refinery feedstock resp. blending component.

In addition, hydrotreatment adds hydrogen to the liquid products, which results in lower densities, aromaticities and higher heating values. The corresponding data for naphtha, middle distillate and vacuum gasoil - used as slurry oil - are listed in the following table:

Tab. 1: Comparison of product qualities

		Naphtha		Middle Distillate		VGO	
		LPH	Int. hydrotr.	LPH	Int. hydrotr.	LPH	Int. hydrotr.
C	(wt-%)	83.1	87.1	86.2	88.4	88.7	88.4
H	(wt-%)	11.8	13.6	9.3	11.9	8.1	11.7
C/H		7.0	6.4	9.3	7.4	11.0	7.6
Aromatic carbon	(wt-%)	29	14	59	21	67	20
Gravity	(kg/m ³)	813	722	979	912	1066	955
Lower heating value	(MJ/KG)	40.2	42.7	39.1	41.3	38.9	40.8

As mentioned above, the new slurry oil quality provided various improvements for the whole process. The hydrotreated vacuum gasoil made it possible to operate the liquid phase hydrogenation section at more moderate conditions. In addition to smaller catalyst requirements, it was possible to reduce the reaction temperature in the liquid phase reactors for 10 - 15 K, which was finally the reason for the lower gas formation and the resulting reduction in the specific overall hydrogen consumption.

While the initial hydraulic conditions in the slurry preparation, the slurry feed system and the preheating section were maintained, the lower density and viscosity of the slurry oil enabled a considerable increase of the coal concentration in the slurry from 40 % to more than 50 %, as well as a raise of the total coal throughput.

As the integrated mode of operation condenses only hydrotreated products instead of the raw materials, the phenol load in the process water stream which is separated from the condensate is reduced to zero. This makes the process water treatment much easier.

A further advantage obtained by the integration of hydrotreatment into the liquefaction process which deserves mentioning is the availability of the reaction heat from the hydrotreater for the whole process. This led to a new concept for the preheating section, shown in principle in Fig. 5. In the original concept, the mixture of slurry and hydrogenation gas is heated in a series of heat exchangers and has to get the required final temperature by passing a gas-fired preheater. This system was very sensitive against deposit and coke formation, especially at the high temperatures prevailing in the preheater tubes. After the integration of the hydrotreating section it was possible, by adding adequate heat-exchanger capacity, to preheat the total amount of slurry together with a small volume of hydrogenation gas - necessary to prevent coking - to an extent that made the use of an additional preheater superfluous. The lacking heat requirement was introduced into the system by overheating the main stream of hydrogenation gas in a separate line by heat exchange and the use of the preheater capacity. With this concept preheater fouling is no problem anymore. To conclude it can be said that the direct connection of the hydrotreating step to liquid phase hydrogenation provided a large improvement for the whole process and yielded products which can be directly fed to refinery streams. The naphtha fraction can be introduced into a refiner/reformer system producing high octane premium-grade motor fuel. The middle distillate fraction may be used as blending component for light heating oil or graded up to diesel fuel by means of ignition accelerators.

Current Use of the Bottrop Plant

The coal liquefaction program in the pilot plant in Bottrop was terminated in May 1987 at a level of technical development and know how which enables the operating companies to design and operate such plants on a commercial scale. The increase in know how which could have been gained from a further continuation of the program would not have justified the financial effort.

However, to keep the technical and operational know how alive and to maintaining the availability the plant for future coal liquefaction requirements, the two companies decided in agreement with the supporting authorities involved to modify the plant for the conversion of vacuum residues from refineries by means of the VEBA-Combi-Cracking process which has the same technological roots as coal liquefaction. The process principle in comparison to that of coal liquefaction is shown in Fig. 6.

The plant capacity for residue conversion amounts to 3.500 bpd of vacuum residue. At a conversion rate of 92 % the productive amounts for:

900 bpd naphtha
2.400 bpd middle distillate and
600 bpd vacuum gasoil

After revamping in the remainder of 1987 the plant was recommissioned in January 1988 with its new feedstock. It is aimed that the future operation will be performed under commercial terms and conditions.

The specific equipment for coal liquefaction is preserved and can at any time be reactivated for coal liquefaction or even coprocessing.

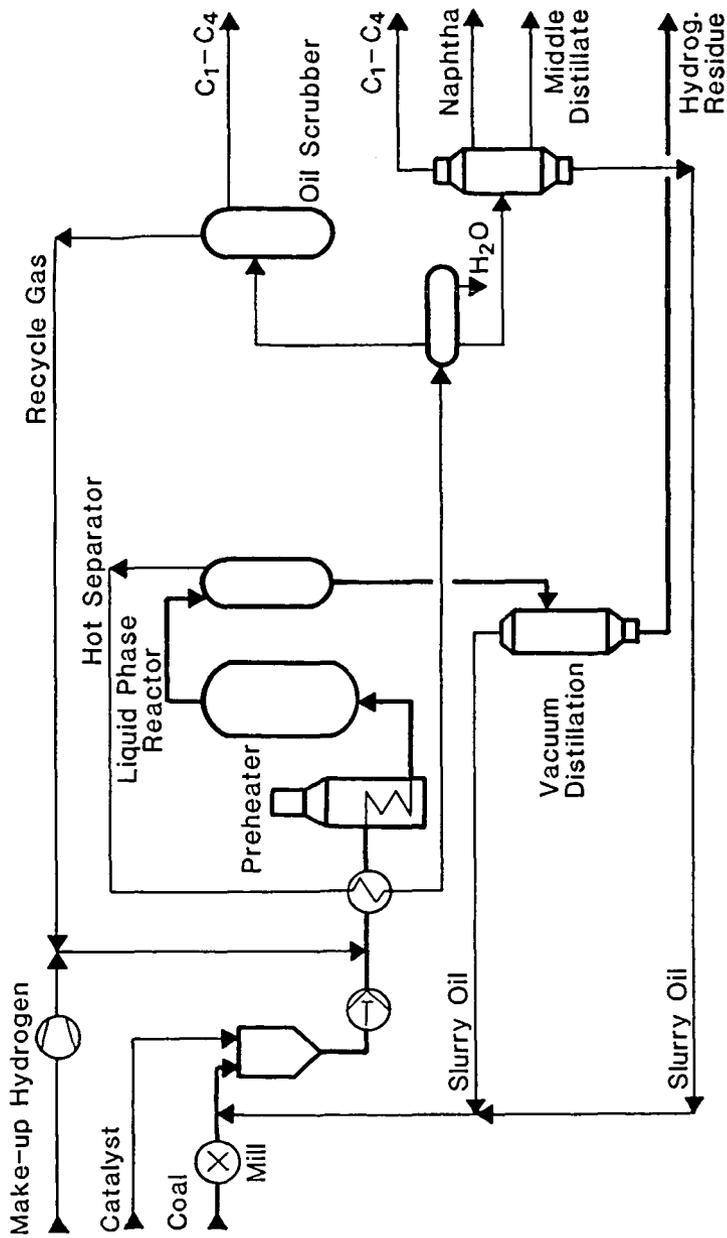


Fig. 1: Liquid Phase Hydrogenation - Initial Process Configuration

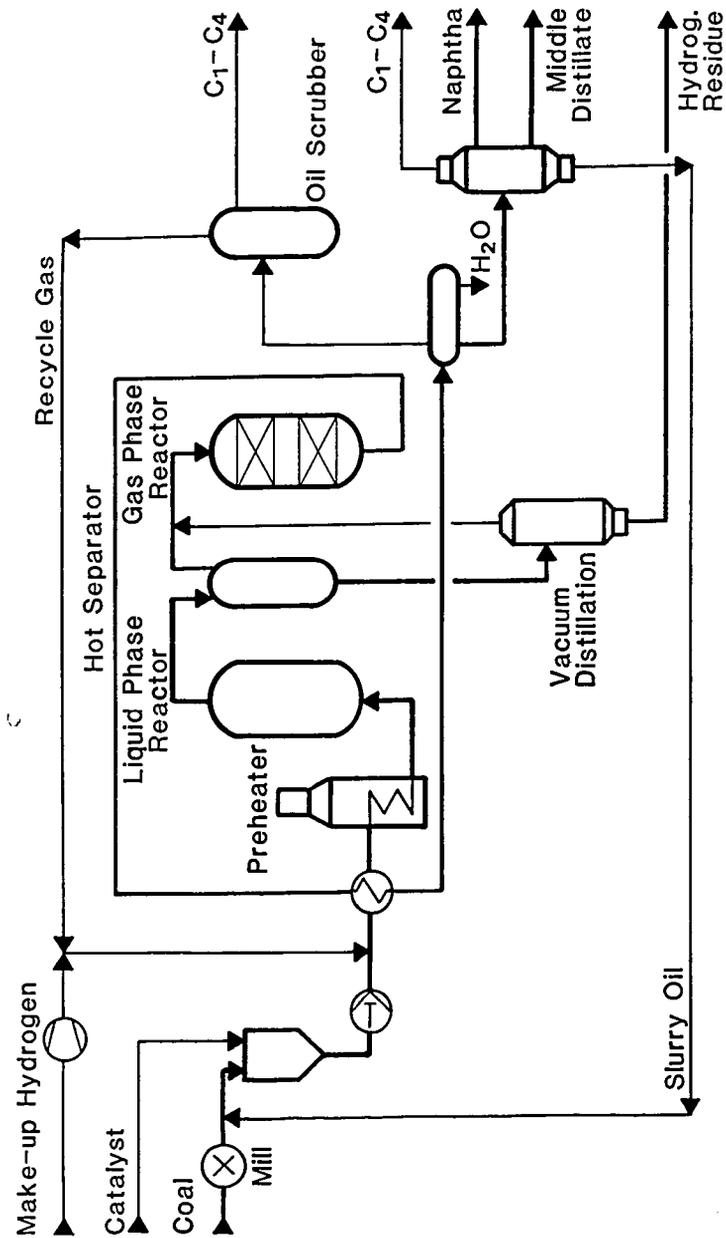


Fig. 2: Liquid Phase Hydrogenation with Integrated Hydrotreatment

Liquid Phase Hydrogenation

Liquid Phase Hydrogenation

with Integrated Hydrotreatment

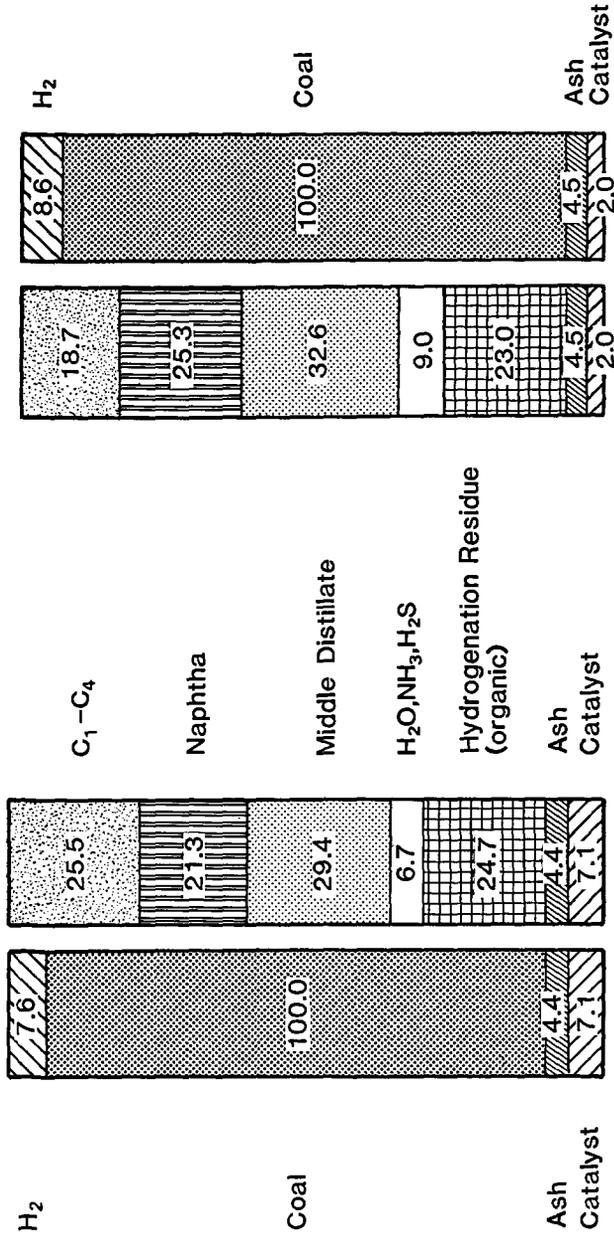


Fig. 3: Comparison of the Yield Structures for the two Process modes

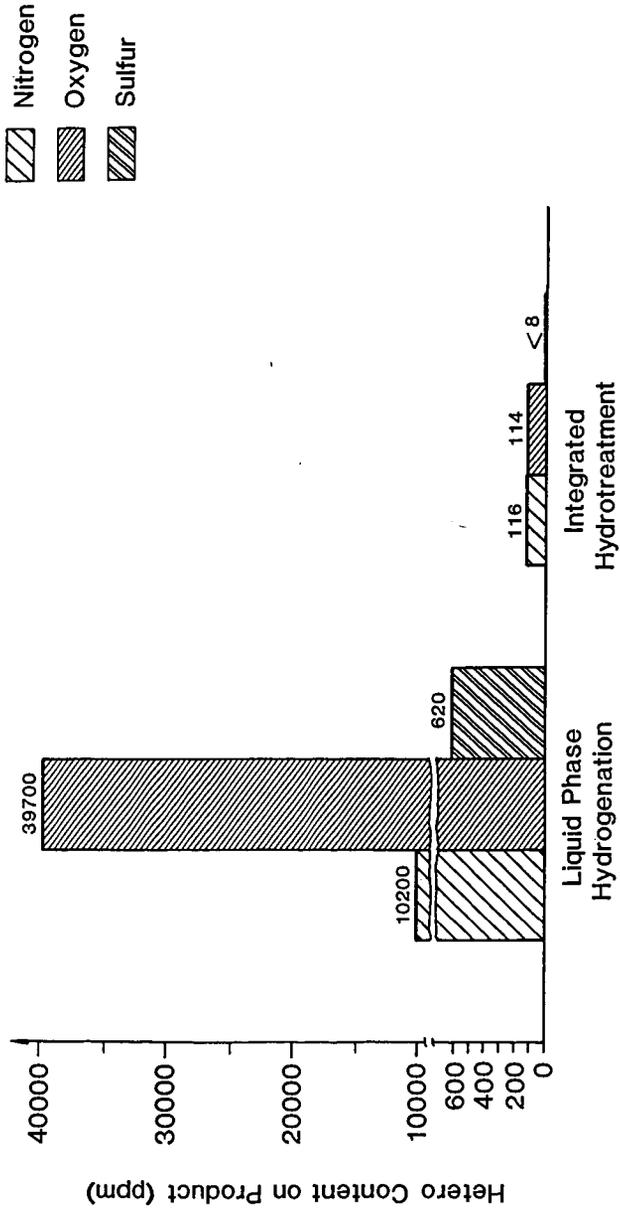
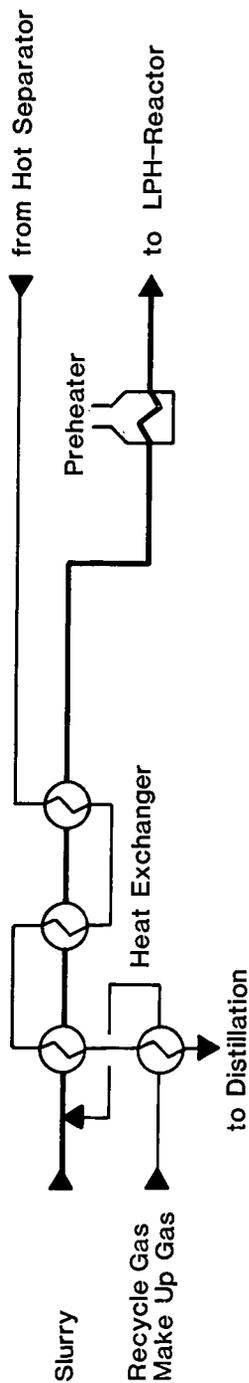
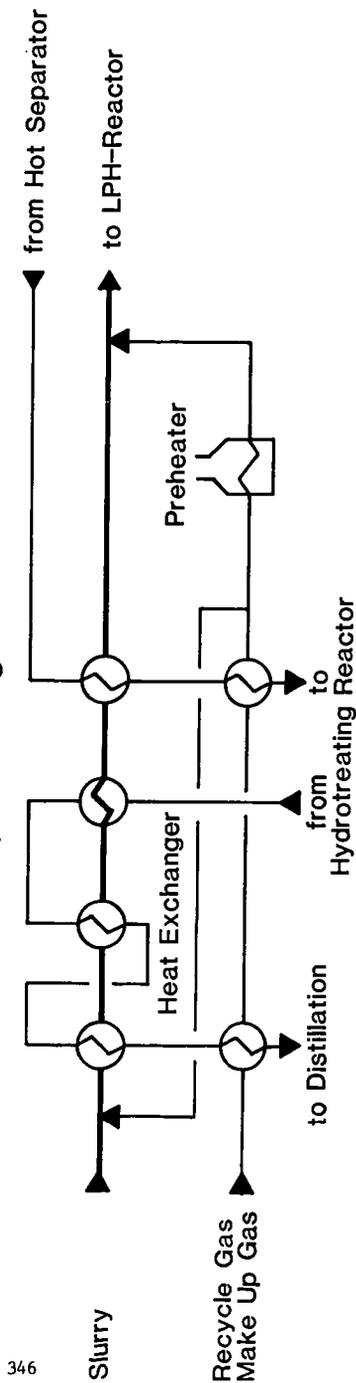


Fig. 4: Hetero Content in Liquid Products

Concept 1: LPH



Concept 2: LPH with Integrated Hydrotreating



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Fig. 5: Preheating Section

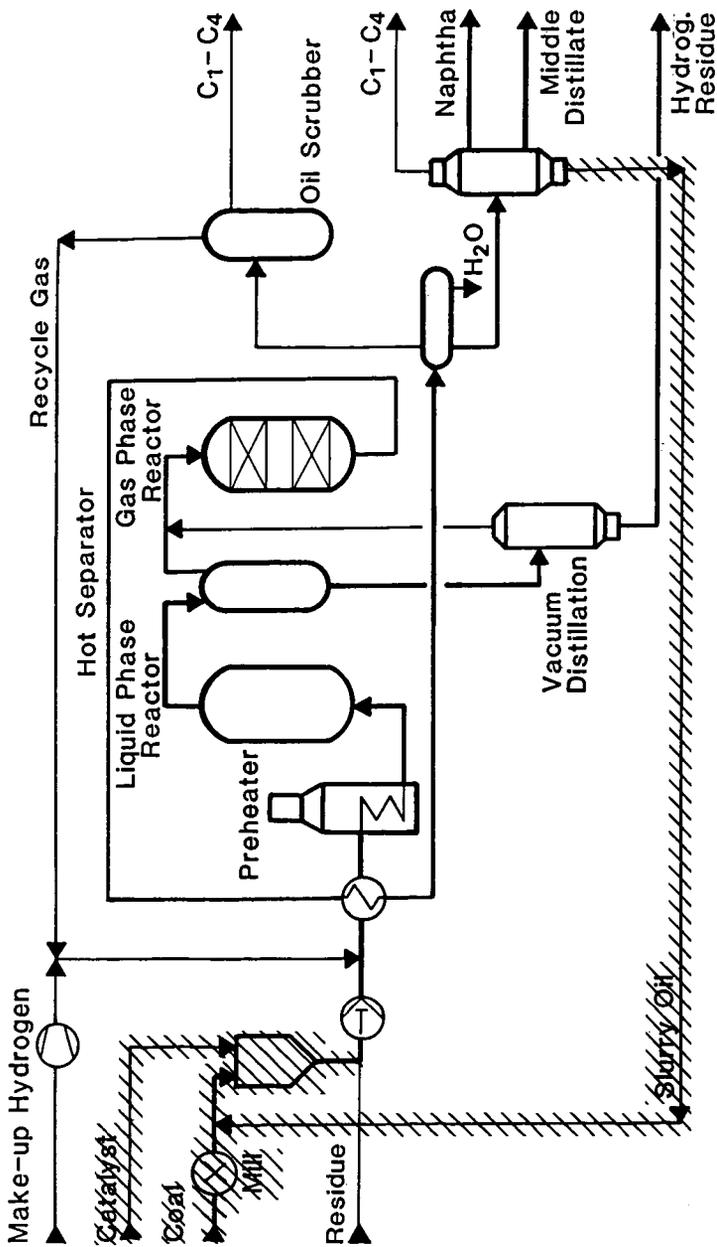


Fig. 6: Coal Liquefaction Plant Bottrop - Residue Conversion Mode

PERFORMANCE OF HYDROUS TITANIUM OXIDE-SUPPORTED CATALYSTS
IN COAL-LIQUIDS UPGRADING

by

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ABSTRACT

Experimental tests were performed in a continuous-flow hydrotreating unit at Pittsburgh Energy Technology Center to evaluate the performance of hydrous titanium oxide-supported (HTO) catalysts as hydrotreating catalysts for use in two-stage coal liquefaction. Catalysts containing either a combination of Co, Ni, and Mo as the active metal components or Pd as the active metal component were tested with representative hydrotreater feed stocks from the Wilsonville Advanced Coal Liquefaction Research and Development Facility. Catalyst performance evaluation was based on desulfurization and denitrogenation activity, the conversion of cyclohexane-insoluble material, and hydrogenation activity during 100-hour reactor runs. Results indicated that the HTO catalysts were comparable to a commercial Ni/Mo-alumina supported catalyst in the areas evaluated.

INTRODUCTION

Personnel from the Pittsburgh Energy Technology Center (PETC) have been collaborating with researchers at Sandia National Laboratories (SNL) to further development of the novel hydrous titanium oxide-supported (HTO) catalysts for use in the hydrotreatment of coal-derived liquids. The HTO materials were originally developed at SNL for use as precursors for ceramic materials¹ and as ion-exchange materials for the decontamination of aqueous nuclear waste streams.² The properties of these materials, including high surface areas and ion exchange capacities, chemical stability, variable Bronsted acidities, and the ability to apply them in thin films, have led to investigations related to their performance as catalysts in a variety of chemical systems.³⁻⁵ They have also been applied to coal-oil coprocessing,⁶ coal hydropyrolysis tars.⁷

The HTO catalysts containing either Co, Ni, and Mo (CoNiMo-HTO) as the active metal components or Pd (HTO-Pd) as the active metal component were tested in a continuous-flow hydrotreater at PETC for possible use as hydrotreating catalysts in the second stage of the integrated Two-Stage Liquefaction process. The PETC has been testing catalysts used in the hydrotreater of the Wilsonville Advanced Coal Liquefaction Research and Development Facility (ACL RDF). Such areas as the effect of catalyst pore size distribution,⁸ the effect of active metals loading,⁹ and the determination of the thermal component of residuum hydrogenation¹⁰ have been studied. The objective of this study was to ascertain if the HTO catalysts could be used to hydrotreat a typical two-stage liquefaction feedstock material containing coal-derived residuum. Catalyst performance

was based on comparison of the desulfurization, denitrogenation, hydrogenation, and cyclohexane-insoluble conversion activities of the HTO catalysts with those of a commercial alumina-supported Ni/Mo-alumina catalyst (Shell 324M) that has been used widely in these types of applications.

Experimental

A typical Two-Stage Liquefaction process¹¹ consists of a thermal liquefaction first stage, followed by a solvent-deashing step, and a subsequent catalytic-hydrotreating stage (Figure 1). The feedstock for the work described herein came from the Wilsonville ACLRD Facility and consisted of a distillate vehicle from the thermal first stage (designated V-178) and the deashed residuum (WSRC) from the solvent-deashing step. These were supplied to PETC from the Wilsonville ACLRD Facility and have been documented elsewhere.^{10,11} Typical analyses of these materials are presented in Table 1. The feedstock used in these experiments consisted of a 1:1 mixture of V-178 and WSRC. The hydrous titanium oxide-supported catalysts were prepared from an HTO-Na material by ion exchange of the Na with Co, Mo, Ni, and Pd from aqueous solutions of their salts. The HTO-Na was prepared by hydrolyzing the product of a reaction between tetraisopropyl titanate and a methanol solution of NaOH. Detailed preparation procedures have been described elsewhere.³⁻⁵

The HTO catalysts remain in the form of a low-tap-density powder (0.3 g/cm³) through the ion exchange step used to load the active metals. For this application, the ion-exchanged powders were pressed into discs, which were subsequently crushed and screened to -10/+20 mesh to minimize diffusion effects in comparing the HTO catalysts with the Ni/Mo-alumina catalysts. The latter were obtained as 1/32-inch extrudates. The as-prepared HTO catalysts are calcined prior to use to remove the volatiles (15 to 25 wt %), which consist primarily of water along with small amounts of alcohols. This calcination can be done either in the reactor or in an external furnace before the catalysts are loaded into the reactor. A density change accompanies calcination of the hydrous titanium oxide-supported catalyst, so that bed shrinkage during calcination in a system that utilizes constant catalyst volumes must be compensated for in loading the catalyst bed. In either case the material was calcined in a nitrogen atmosphere using a temperature of 100°C to remove the bulk of the volatiles and a final one-hour soak at 375°C for the CoNiMo-HTO catalysts and at 300°C for the HTO-Pd catalysts.

Sulfiding of the CoNiMo-HTO catalyst was done in the reactor with a hydrogen gas stream containing 10 vol% hydrogen sulfide for five hours at 390°C. The Ni/Mo-alumina catalyst was activated by heating in the same manner. The HTO-Pd catalyst did not require sulfiding prior to use.

Compositions and some physical properties of the catalysts used in this work are presented in Table 2. Two HTO-Pd catalysts are listed because there was a significant difference in the way the materials were prepared. The difference involved the acidification step used to increase the Bronsted acidity of the support; phosphoric acid was used in the preparation of HTO-Pd1, but sulfuric acid was used in the preparation of HTO-Pd2. The use of different acids resulted in variations in surface area, as well as the expected compositional changes.

Two experiments of 100-hour duration using the CoNiMo-HTO catalyst and two experiments of 100- and 700-hour duration using the Ni/Mo-alumina

catalyst were completed. The reaction conditions (temperature, pressure, and volume hourly space velocity) were kept the same for both catalyst systems and are presented in Table 3. The reaction conditions used with the HTO-Pd catalysts were the same as those given in Table 3 with the following exceptions. The run using the HTO-Pd1 catalyst was intended to be a 100-hour run but was terminated at 42 hours owing to a power failure. The duration of the run with the HTO-Pd2 was 100 hours; however, the run temperature was held at 320°C for at least 24 hours, and the temperature was then raised to 370°C and finally to 390°C during the course of the run.

RESULTS AND DISCUSSION

The average run results of tests using the CoNiMo-HTO and Ni/Mo-alumina catalysts are presented in Table 4. There were sufficient variations in the slurry feed rate of the continuous-flow unit to cause the volume hourly space velocity to vary, thus precluding a detailed comparison of the catalyst activities. In examining the data in Table 4, it is apparent that there are significant differences in the results of the two CoNiMo-HTO 100-hour runs. This may be because two different batches of catalyst were used, but it is more likely due to variations in the space velocity during the runs. Differences of the same magnitude are observed when comparing the 100-hour Ni/Mo-alumina run with the first 100 hours of the 700-hour Ni/Mo-alumina run. Since these runs did not use different batches of catalyst, the variations in the results are probably due to a variable space velocity. The differences between the average results of the first 100 hours of the 700-hour Ni/Mo-alumina run and those of the final 500 hours of the 700-hour run are due to catalyst deactivation. These differences are not as great as those seen when comparing the initial 100 hours of both Ni/Mo-alumina runs. However, there appear to be trends in the data that allow for a qualitative comparison of the HTO and Ni/Mo-alumina catalyst systems using the average activities calculated over the duration of the runs specified in Table 4.

The CoNiMo-HTO catalyst appears to be similar in overall activity to the Ni/Mo-alumina system (Shell 324M). Hydrogenation activity, as measured by the change in the hydrogen-to-carbon atomic ratio (H/C) of the product as compared to the feed, was on the order of 10% for each catalyst. The range of conversions of cyclohexane-insoluble material to cyclohexane-soluble material and the desulfurization activity of the two catalytic materials also appear to be comparable. The denitrogenation activity of the CoNiMo-HTO catalyst was somewhat lower than that of the Ni/Mo-alumina catalyst based on the 100-hour tests. However, when the level of denitrogenation of the CoNiMo-HTO is compared to the "lined-out" activity of the Ni/Mo-alumina catalyst at 700 hours, both catalysts seem to have similar activities. The activity of the Shell 324 Ni/Mo-alumina catalyst is known to "line out" after approximately 200 hours under the conditions used in these runs. Long-term runs, i.e., 700 hours, with the CoNiMo-HTO catalyst are needed before a more definitive comparison can be made.

One would expect that a noble metal such as palladium would be an ineffective catalyst under the conditions described herein owing to sulfur and nitrogen poisoning. However, batch tests indicated that the HTO support seems to provide some protection to the Pd against sulfur poisoning and that the degree of protection increased with increasing temperature. The Pd catalyst, HTO-Pd1, used in the initial test, which was done under

conditions in Table 3, deactivated early in the run. Table 5 shows that the most sensitive indicator of this was the change in H/C atomic ratio of the product with respect to the feed. Conversions of cyclohexane- and pentane-insoluble materials also decreased somewhat while the desulfurization activity appeared to remain relatively constant. The run was prematurely ended at 42 hr owing to a power failure.

The second test of a HTO-Pd catalysts used a material that was considerably different both in composition and in surface area (Table 2). Batch testing indicated that the palladium hydrous titanium oxide-supported catalyst was active at lower temperatures, and consequently, the operation of the continuous-flow unit was altered with respect to reaction temperature as described previously where the temperature was increased stepwise from 320°C to 390°C throughout the course of the 100-hour run. All other experimental conditions were the same as those given in Table 3. At the time this paper was written, the only analytical results available for this run were the H/C ratios given in Table 6. As can be seen, the HTO-Pd2 experienced a decrease in hydrogenation activity during the first 19 hours at 320°C. Increasing the run temperature restored the activity to that observed during the initial 7 hours of the run, and the hydrogenation activity appeared to be increasing during the final 24 hours of the run at 390°C.

CONCLUSIONS AND RECOMMENDATIONS

The experimental results indicate that HTO-supported catalysts such as CoNiMo-HTO are capable of achieving catalytic activities similar to those of a Ni/Mo-alumina catalyst (Shell 324M), which is considered to be as good as any commercial catalyst for this particular application. A HTO-Pd catalyst also showed considerable promise for this application. Both HTO-supported materials must be subjected to further research before definitive comparisons can be made with other catalyst systems.

Previous testing of the Ni/Mo-alumina system has shown that only moderate increases in catalytic activities can be achieved by manipulating the average pore size distribution and pore structure of the alumina support. Since no attempt has been made as yet to modify or optimize the physical properties of HTO supports, there may be potential for significant improvements in these materials.

ACKNOWLEDGMENTS

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DISCLAIMER

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

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Table 1. Representative Analysis of Feed Materials

	RESIDUUM (WSRC)	VEHICLE (V-178)
Elemental Analysis, wt%		
Carbon	88.6	88.3
Hydrogen	6.8	9.8
Nitrogen	1.3	0.4
Sulfur	0.6	0.3
Moisture, wt%	0.1	0.1
Ash, wt%	0.3	< 0.01
Specific Gravity, 60°F/60°F	1.19	1.01
Solvent Analysis, wt%		
Toluene insolubles	12.1	< 0.02
Asphaltenes*	47.8	4.9
Oils** (by difference)	40.1	94.9

* Toluene soluble, pentane insoluble

** Toluene soluble, pentane soluble

Table 2. Physical Properties and Composition of Catalysts After Calcining

	Shell 324M	CoNiMo- HTO	HTO-Pd1	HTO-Pd2
BET surface area, m ² /g	161	245	116	320
Pore Volume, cm ³ /g	0.427	0.310	*	*
Average Pore Diameter, Å	106	39	*	*
Cobalt, wt%	-	0.9	-	-
Nickel, wt%	2.5	1.1	-	-
Molybdenum, wt%	13.0	10.6	-	-
Palladium, wt%	-	-	5.4	7.5
Phosphate, wt%	-	-	17.5	-
Sulfate, wt%	-	-	-	4.5

* Not determined

Table 3. Reaction Conditions for Shell 324M NiMo and CoNiMo-HTO Runs

Pressure	2000 psig
Temperature	390°C
Catalyst charge	80 cm ³
Target hourly space velocity	0.6 cm ³ resid /cm ³ cat
Hydrogen gas feed rate	8 scfh
Slurry feed rate	114 g/hr
Feedstock	WSRC/V178 weight ratio = 1/1

Table 4. Results of Reactor Runs using CoNiMo-HTO and Shell 324M Catalysts

CATALYST	CoNiMo-HTO	CoNiMo-HTO	Ni/Mo-alumina		
			Shell 324M	Shell 324M	Shell 324M
Test duration, hr	100*	100	100	(100)**	200-700
Variation of space velocity	0.49-0.65	0.59-0.74	0.46-0.84	0.57-0.60	0.56-0.63
Percent change in H/C atomic ratio	10	7	9	10	9
Conversions, wt%					
cyclohexane	73	57	71	58	54
Desulfurization, wt%	85	76	85	71	52
Denitrogenation, wt%	22	20	40	23	16

* The catalyst was contacted with kerosene at room temperature prior to this test, and a carbon residue was left on a portion of the catalyst. This was not planned and did not seem to affect catalyst performance.

** First 100 hours of the 700-hour test

Table 5. Hydrotreating Results Using HTO-PdI Catalyst

Time, hr	10	22	35
Percent change in H/C atomic ratio	12	11	3
Conversions, wt%			
cyclohexane	77	78	68
pentane	60	58	56
Desulfurization, wt%	75	75	75

Table 6. Hydrogenation Activity of HTO-Pd2

Operating Conditions		Change in Atomic H/C ratio, percent
temp., °C	time, hr	
320	7	7
320	10	4
320	19	2
320	23	3
	27 temp. change	
370	35	4
370	36	3
370	45	5
	50 temp. change	
390	63	8
390	67	7
390	73	8
390	85	8
390	91	9
390	98	8

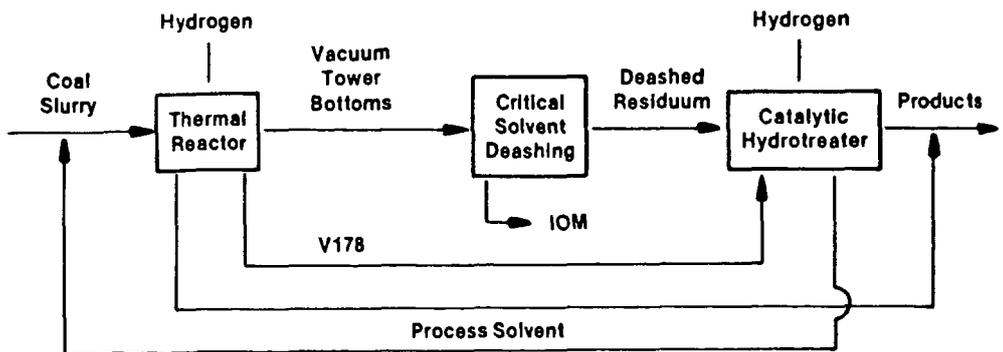


Figure 1. Typical Two-Stage Liquefaction Process

HEAVY OIL UPGRADING USING HALIDE CATALYSTS
IN A BUBBLING MICROAUTOCLAVE

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ABSTRACT

Athabasca bitumen has been treated with halide catalysts under a continuous flow of H_2 in a 15 mL microautoclave. The H_2 was bubbled through the liquid using a microporous steel grid. $ZnCl_2$, $CuCl$ and $ZnCl_2/CuCl$ mixtures, with and without tetralin, were used as catalysts. The experimental conditions were: 13.8 MPa operating pressure, 1 LSTP/min as H_2 flowrate, 425-450°C and 30 min as reaction temperature and time respectively. $ZnCl_2$ has been found effective for converting asphaltenes into maltenes while lowering the coke formation with respect to the uncatalyzed reaction. The addition of tetralin to the reaction mixture minimized coke and gas formation.

INTRODUCTION

Bitumen and heavy oil upgrading has been the subject of many investigations since the early thirties (1). Present industrial technologies such as delayed coking or fluid coking result in the formation of large amounts of coke (up to 22% of the feed) (2). This decreases the yield of valuable liquid products. Whereas coke derived from petroleum in general may find a variety of uses, the high sulphur content of the coke produced from Canadian oil sands bitumen such as Athabasca bitumen, precludes its use (3).

Hydrocracking of Athabasca bitumen has proven to yield 10-15% higher liquid distillate product than conventional coking processes (4). Catalysts are required for effective removal of sulphur and nitrogen and to improve liquid yields. Coke is also formed during hydrocracking, although

significantly less than in coking. However, this creates operational problems such as reactor fouling and catalyst poisoning. Coke formation increases with temperature (5,6) and decreases with hydrogen partial pressure (5). Addition of coal and coal-based catalysts has been claimed to reduce coke formation (7).

Coke formation from oil sands bitumen is believed to be related to its high asphaltene content (2). Dickie and Yen (8) have studied structures of asphaltenes from various sources and postulated that asphaltene aggregates are made of planar sheets of condensed aromatic rings, saturated carbon chains and a loose net of naphthenic rings. Therefore, polynuclear aromatic hydrocarbons may be considered as possible constituents of asphaltene and catalysts which are effective in hydrocracking polynuclear aromatic compounds should also be effective in asphaltene hydrocracking.

Molten halide salts have been found to be excellent catalysts in the hydrocracking of the polynuclear (9,10) and alkyl substituted polynuclear aromatic hydrocarbons (11). Zieike et al. (9) have shown the superiority of molten $ZnCl_2$ catalysts over conventional hydrocracking catalysts for pyrene, coal and coal extract and subsequently carried out continuous hydroliquefaction of subbituminous coal in molten $ZnCl_2$ (12).

Herrmann et al. (13) carried out a comparative study of Fe, $ZnCl_2$ and $ZnCl_2$ -promoted Fe catalysts for hydrocracking of Athabasca bitumen. They found $ZnCl_2$ to be the most active, to produce less hydrocarbon gas and significantly less sulphur in the liquid product. Nomura et al. (2) studied hydrocracking of Athabasca asphaltene over molten $ZnCl_2$ -KCl-NaCl mixtures with and without an additive of some transition metal chlorides and found a mixture of $ZnCl_2$ -KCl-NaCl₅ to give higher asphaltene conversion (60% pentane soluble) and small amounts of coke (3.7% benzene insoluble). Based on this information we decided to carry out systematic experiments to investigate the hydrocracking of Athabasca bitumen with molten $ZnCl_2$, CuCl and their mixtures with and without tetralin. This latter hydrogen donor compound was added to rapidly transfer H and then prevent coke formation by recondensation of the hydrocracked radicals.

FEEDSTOCK AND REAGENTS

Athabasca bitumen produced by hot water process from mined oil sands of the McMurray stratigraphic unit by Suncor Inc. and obtained from the Alberta Research Council was used as the feedstock. Table 1 summarizes the relevant properties of the bitumen.

All the reagents used were of ACS reagent grade. Tetralin and $ZnCl_2$ were purchased from Aldrich Chemicals, Milwaukee, WI.; $CuCl$ was purchased from Anachemia Ltd., Montreal and hydrogen was purchased from Liquid Carbonic Inc., Montreal.

EQUIPMENT

Traditionally laboratory scale hydrocracking experiments have been carried out in stirred autoclaves (13) and rocking autoclaves (2). However, the fluidodynamic conditions in these traditional autoclaves are considerably different from those of an industrial hydrocracker because industrial hydrocrackers operate under continuous flow conditions.

To simulate industrial conditions as closely as possible we used a bubbling microautoclave system of our own design. A schematic diagram of the experimental setup is shown in Fig. 1. It consists of a 15 mL bubbling microautoclave, water cooled condenser, gas collection assembly, molten salt heating bath, cooling water bath, connecting tubings, and instrumentation. The bubbling microautoclave is the heart of the experimental setup and is equipped with a microporous steel grid, through which gas can be dispersed.

The gas collection assembly was specially designed to collect all the gases. It consists of two 75 L tanks, capable of withstanding pressures up to 20 psig. The contents can be mixed thoroughly by means of two built-in stirrers. In addition a pump can transfer the contents from one tank to another and vice versa thereby facilitating intermixing the contents of both.

EXPERIMENTAL PROCEDURE

The microautoclave was filled with about 7 g of bitumen for the non-catalytic experiments plus desired amounts of catalysts for the catalytic experiments. ZnCl_2 and CuCl were oven dried at 100°C for about 3 h prior to use to eliminate any moisture. The microautoclave was then completely sealed. Hydrogen was then bubbled through the microporous grid and the system pressure was raised to the desired pressure (13.8 MPa). The hydrogen flowrate (1 LSTP/min) was established by a pre-calibrated mass flow meter (Brooks Instruments, Model 5850). The microautoclave was then plunged into the preheated molten salt bath heater and the previously evacuated gas collection assembly was started. The temperature of the microautoclave contents was monitored constantly by an electronic temperature indicator (Analogic, Model AN2572). It usually took about 5-7 min to reach the desired reaction temperature (425°C - 450°C). Experiments were carried out for 30 min after reaching the reaction temperature. The microautoclave temperature was carefully controlled as follows: when it exceeded the desired reaction temperature by 2°C , the autoclave was partially withdrawn momentarily from the molten salt bath to reduce the temperature to the reaction temperature. In this manner it was possible to stay within $\pm 3^\circ\text{C}$ of the desired temperature.

At the end of the experiment, the microautoclave is quickly immersed into the cooling water bath while the hydrogen is continued. When room temperature is reached (25°C), which takes about 1-2 min, the gas flow is stopped. The gas remaining in the system is then evacuated into the gas collection assembly.

ANALYTIC PROCEDURE

The gases were well mixed in the gas collection assembly for about 1 h, then analyzed by a gas chromatograph (Hewlett Packard, Model 5890) equipped with a Porapak Q and a Molecular Sieve column in series.

The microautoclave was weighed before and after the experiment and the difference gave the quantity of gas formed plus any entrainment. Usually entrainment was negligible as the condenser was purposely oversized and was filled with metal springs. Most of the gases were thus condensed and returned to the microautoclave.

The microautoclave was then cleaned thoroughly with dichloromethane. Dichloromethane insoluble products were filtered, dried in an oven at 100°C and weighed. When catalysts were used, the dichloromethane insoluble material was washed with hot water in an ultrasonic bath. $ZnCl_2/CuCl$ remaining in the dichloromethane insoluble material (except those chemically combined) were thus removed. The solvent was then evaporated in a rotary evaporator (Buchi, Rotavapor RE121). n-Pentane in 1:50 ratio was then added and the mixture placed in an ultrasonic bath for 15 min. It was left for 24 h before n-pentane insolubles, termed as asphaltenes were filtered. The asphaltenes were then dried in a vacuum dessicator, weighed and collected. n-Pentane was evaporated from the filtrate in the rotary evaporator and the remaining yellowish material, termed as maltenes, was collected.

RESULTS

The experimental conditions and product analysis in terms of coke (dichloromethane insolubles), asphaltene (pentane insolubles), maltenes (pentane solubles) and gas are summarized in Table 2. The following observations are made.

The amount of coke and gas increase, in general, with reaction temperature (see expts. 1,5,8 for the non-catalytic and expts. 2,6,9 for the catalytic runs). Both the asphaltene and the maltene fractions appear to decrease with temperature for the range studied (see expts. 1,5,8).

Addition of $ZnCl_2$ decreases the asphaltene, coke and gas fractions whereas it increases the maltene fraction with respect to the uncatalyzed reaction. The asphaltene fraction decreases whereas the maltene fraction increases with increased $ZnCl_2$ as can be seen from expts. 1-4,5-7, and 8-11. The gas fraction initially decreases with respect to the uncatalyzed reaction but increases with additional $ZnCl_2$. Although there is some scatter in the data the coke content also appears to decrease somewhat with $ZnCl_2$.

Addition of tetralin results in decreased gas and coke fractions as can be seen by comparing expts. 1, 12-14. The asphaltene fraction also decreases somewhat whereas the maltene fraction increases. CuCl also has some catalytic activity towards heavy oil cracking, but its reactivity is lower than that of ZnCl₂. Addition of CuCl to ZnCl₂ lowers the coke content of the product, but decreases the reactivity towards asphaltene cracking as can be seen by comparing expts. 7, 17 and 18.

Some observations on the performance of the bubbling microautoclave with respect to conventional stirred autoclaves are worth mentioning. Our results were compared with those of Herrmann et al. (13), carried out under somewhat similar conditions with Athabasca bitumen. A substantial difference in the quantity of gas formed was noted. In the present case it ranged from 15 to 23 wt % for runs carried out at 440°C and 450°C. In the case of Herrmann et al. (13) it was about 6 wt %. This is probably an indication of improved cracking in the microautoclave. We attribute this to a homogeneous distribution of temperatures and gas throughout the fluidized system and to the absence of hot spots on the walls.

CONCLUSIONS

Athabasca bitumen has been hydrocracked in a bubbling microautoclave with molten halide catalysts. ZnCl₂ has been found to be an effective catalyst for the conversion of asphaltenes into maltenes and gases. Since ZnCl₂ is in the liquid state under hydrocracking conditions it may be used as a homogeneous catalyst for the hydrocracking of bitumen and heavy oils. The addition of tetralin reduces gas and coke formation but a substantial amount is required to significantly reduce coke.

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Table 1

Select properties of Athabasca bitumen

API gravity	10.1	Density	0.999 g/mL
Viscosity, 25°C	42000 cP	Ash	0.48 wt %
Carbon	83.77 wt %	Hydrogen	10.51 wt %
Nitrogen	0.37 wt %	Sulphur	4.75 wt %
Oxygen	0.88 wt %	Vanadium	200 ppm wt
Nickel	75.5 ppm wt	Asphaltene	16.1 wt %
Pitch (524°C+Fraction)	53.7 %	Coke	0.57 wt %
		Maltene	83.33 wt %

Table 2

Summary of the experimental conditions and product analyses

<u>Expt. #</u>	<u>Temp.</u> °C	<u>Catalyst</u> %	<u>Cat.</u> <u>Conc.</u> wt %	<u>Coke</u> wt %	<u>Asphaltene</u> wt %	<u>Maltene</u> wt %	<u>Gas</u> wt %
1	450	-	-	8.4	8.6	60.1	22.9
2	450	ZnCl ₂	1.5	5.5	8.2	66.0	20.2
3	450	ZnCl ₂	10	6.3	4.4	67.7	21.6
4	450	ZnCl ₂	25	2.8	2.4	72.3	22.5
5	440	-	-	4.8	10.4	66.7	18.1
6	440	ZnCl ₂	1.5	3.8	8.3	69.9	18.0
7	440	ZnCl ₂	10	4.1	3.2	72.1	20.6
8	425	-	-	3.6	11.7	67.0	17.7
9	425	ZnCl ₂	1.5	3.2	9.1	74.7	12.9
10	425	ZnCl ₂	10	4.0	4.7	78.9	12.4
11	425	ZnCl ₂	25	1.6	4.0	77.7	16.7
12	450	Tetralin	25	4.6	6.5	68.1	20.8
13	450	Tetralin	50	3.8	5.2	73.9	17.1
14	450	Tetralin	100	2.7	5.4	76.5	15.4
15	440	CuCl	1.5	6.7	7.2	67.9	18.2
16	440	CuCl	10	5.9	6.3	69.8	18.0
17	440	ZnCl ₂ +	10				
		CuCl	1.5	3.6	6.1	70.0	20.3
18	440	ZnCl ₂ +	10				
		CuCl	4.5	3.4	5.2	72.4	19.0

* values are wt % of feed.

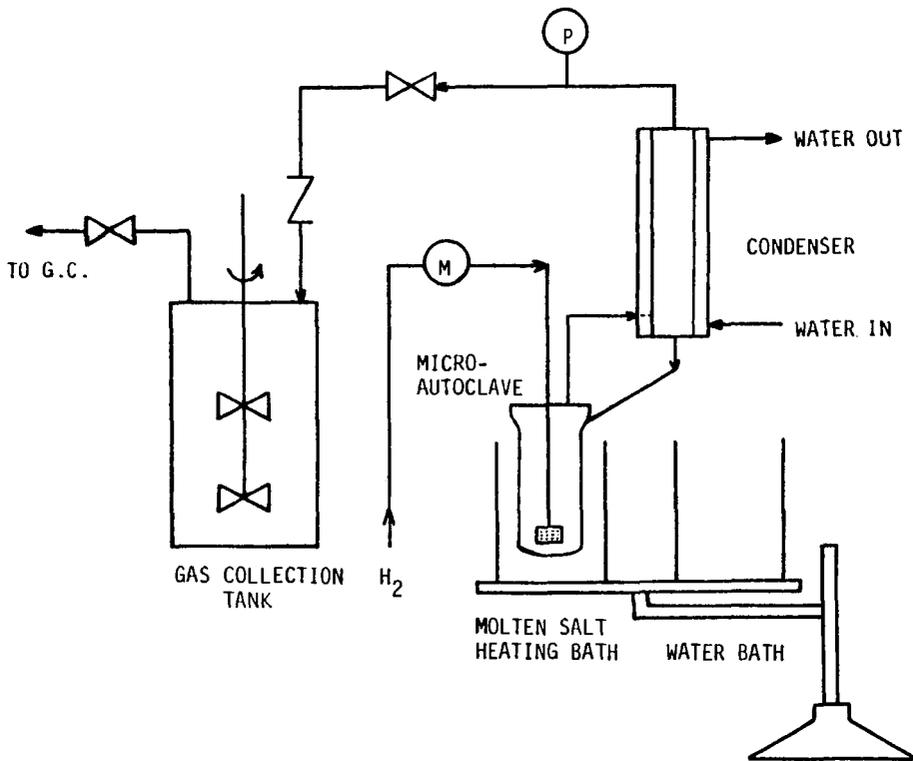


Figure 1. Schematic diagram of bubbling microautoclave.

PROCESS OPTIONS FOR EXTINCTION RECYCLE CONVERSION OF HEAVY OILS IN
CATALYTIC TWO STAGE LIQUEFACTION

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ABSTRACT

Hydrocarbon Research, Inc. (HRI) is developing a Catalytic Two-Stage Liquefaction (CTSL) Process which converts coal to distillate liquid products. A particularly attractive feature of the process that has been demonstrated recently using two bituminous coal feedstocks (Illinois No. 6 and Ohio No. 5/6 coals) is the capability to achieve extinction conversion of heavy oil products (heavy vacuum distillate and soluble residuum oil) through integration of coal cleaning, product solids separation, and selective recycle. Yields of distillate oils of up to five barrels per M.A.F. ton of coal have been achieved. Elimination of heavy oils of boiling points above 700-750°F greatly simplifies downstream processing requirements. Several process configuration options and the resulting yield distributions are discussed.

INTRODUCTION

Hydrocarbon Research, Inc.'s (HRI) Catalytic Two-Stage Liquefaction (CTSL) Process features two close-coupled catalytic ebullated-bed reactor stages in series, with the first stage at a lower temperature than the second stage, so as to optimize the hydrogenation/conversion functions of the two stages. The process has been under development, sponsored by the U. S. Department of Energy (DOE), since 1982. This paper summarizes the status of the program and discusses the results of the most recent operations in HRI's continuously operated bench-scale unit which demonstrated extended operations with virtually complete elimination of residual oil and/or heavy vacuum gas oils from the net products of the operation. Upgrading studies by Chevron⁽¹⁾ have correlated upgrading costs directly with product oil end points and emphasized the need to eliminate the heavy vacuum gas oil products. Recently completed economic studies by HRI have shown a product cost benefit for the extinction mode of operation.⁽²⁾ Such modes of operation were demonstrated for Illinois No. 6 and Ohio No. 5/6 bituminous coals.

PROCESS DESCRIPTION

The key feature which distinguishes the CTSL Process from other single- or two-stage liquefaction processes is the use of a relatively low temperature (<800°F) in the first-stage reactor which contains an effective hydrogenation catalyst. In this stage, coal is largely converted at a controlled rate by dissolution in the recycle solvent, allowing catalytic hydrogenation reactions, necessary to maintain solvent hydrogen-transfer capability and stabilize the liquefaction products, to keep pace with the rate of coal conversion. The second stage operates at more severe conditions, but not as severe as required in a single-stage mode such as in the H-Coal® Process, and it completes the job of coal conversion with the additional conversion of high boiling primary liquefaction products to high quality distillates. Overall, the CTSL Process obtains higher yields of better quality distillate products than obtained in competing technologies.

BENCH UNIT DESCRIPTION

Process development studies have been conducted in HRI's continuously operating two-stage Bench Unit, schematically shown in Figure 1. The operation is sustained with the net feed of only coal and hydrogen, with recycled solvent recovered from the contemporary gross products leaving the reaction system, by the distillation and filtration means indicated in Figure 1. The immediate recovery and recycle of solvent is a true prototype of full scale operations and facilitates the interpretation of the operating results, by avoiding the problems of batch and once-through experimental modes. There is an on-line sampling system for the slurry leaving the first stage, so that the effectiveness of each of the two stages can be assessed.

An important factor in process performance is the nature of the solvent that is recycled. Figure 1 includes a schematic summary of the modes of adjusting solvent composition. First, slurry product from the reaction system is distilled at atmospheric pressure to eliminate from the solvent pool middle distillate oils for which there is little incentive to submit to further processing by recycling to the liquefaction reactors. The atmospheric bottoms slurry can be recycled directly or further modified for recycle, either by a solids removal method, here pressure filtration although alternative methods are feasible, or by vacuum distillation which provides heavy vacuum distillate for incorporation in the recycle solvent pool. In the bottoms extinction demonstration operation summarized in this report, the atmospheric still was operated with a stripping gas to give a middle distillate endpoint (atmospheric still overhead going to product pool) and solvent pool IBP such that the solvent pool was virtually completely eliminated by undergoing further secondary reactions in the liquefaction reactors.

Bench unit scale of operations during the development program has been approximately 50 pounds per day. Scale up of the results from reactor systems of this size to plant scale has proven satisfactory for the H-Oil® and H-Coal® Processes, which employ the ebullated-bed reactor system used in the CTSL Process. The bench unit operations use a single charge of catalyst which is used in an extended operation, up to thirty days in some cases, without augmentation. This is in

contrast with anticipated application to plant scale where, because of the convenience of the ebullated-bed system, a portion of the catalyst is to be replaced on a daily basis, so as to maintain a constant catalytic performance, while holding the reactors at a fixed temperature. Again, the interpretation of the bench scale results in projection of the amount of catalyst replacement required on a plant scale has proven to be satisfactory. The catalyst used in the operation described in this report is a commercially available hydrodesulfurization catalyst, one of several which have performed equally well.

DEMONSTRATION RUN PARAMETERS

The bottoms extinction operations showed that a sustained operation could maintain a product distribution eliminating the highest boiling constituents from the product pool. This mode requires that all such materials leaving the reactor be recycled to the reactor system. A portion of these high boiling oils are mixed with product solids (unreacted coal and ash), in the filter cake for these operations, and for inclusion in the solvent recycle pool these oils must be separated from the solids. For these experiments the filter cake was washed with low-boiling aromatic solvent, and the extracted oils were returned to the solvent pool after distilling off the solvent. Since this solvent washing operation had some handling and processing inefficiencies, some of the solvent range material was not available for recycle and was rejected as a net product of the operation. The bottoms extinction objective is limited only by the engineering problems of the recovery for recycle of solvent range material.

To reduce the scale and cost of the solvent/solids separation operations it is desirable to process feed of relatively low ash content. To this end for the demonstration operation, the available mine-washed coal was further cleaned by heavy-media washing which reduced the ash content by approximately half. Table 1 gives, for Illinois coal, the analyses for the as-received mine-washed coal and the heavy-media washed coal used in the demonstration run. Table 2 gives these analyses for the Ohio coal. The CTSL results with heavy media washed coal are not appreciably different from those using mine-washed coal, as shown in Table 3 which compares the CTSL results for the two types of feed in process development operations using the same operating conditions. The principal difference in the results is 3% higher coal conversion with the heavy-media washed feed, with the increased conversion appearing as light and middle distillate product. This higher coal conversion is ascribed to the removal, along with the ash, of a portion of the most difficult to convert portion of the coal. The bottoms extinction mode is as feasible for the mine-washed feed as for the heavy-media-washed feed. The selection between these alternatives is an economic-engineering judgment involving the costs of product solids separation and the feasibility of alternative uses for the high ash reject from the heavy-media washing operation.

The vacuum gas oil extinction mode of operation consisted principally of unfiltered atmospheric still bottoms along with sufficient vacuum gas oil, obtained by vacuum distillation of the balance of the atmospheric still bottoms, to achieve extinction of the vacuum gas oil components. Here, too, the atmospheric still was operated with stripping gas to give a solvent pool IBP such that the vacuum gas oil

component would be eliminated. Because of the reduction of the proportion of residual oil in the recycled solvent pool there would be a net production of residual oil from the operation, which would be withdrawn from the process as a vacuum bottoms slurry in combination with the unreacted coal and ash.

With the normal catalyst activity decline, operating conditions were adjusted so as to maintain the bottoms or gas oil extinction objectives. To this end, the temperatures of the two stages were increased progressively during the runs. Figure 2 summarizes the reactor temperature changes during the bottoms extinction demonstration run using Illinois No. 6 coal. Here, between the seventh day and the twenty-fifth day of the run, during which the bottoms extinction objectives of the run were attained (see below), the first-stage temperature was increased by 15°F and the second-stage temperature was increased by 20°F. Nominally, in a plant scale operation with daily replacement of catalyst, any level of performance obtained during the run could be maintained using the temperatures holding at that stage of the run and an appropriate rate of catalyst replacement that would maintain the catalyst activity holding for the particular stage of the operation. Also, during the run there was a progressive adjustment in the cut point between the atmospheric overhead withdrawn as product and the solvent recycle component being extincted, as summarized in Figure 3. This cut point was increased by about 80°F over the interval of the run during which the extinction objective was maintained. Nominally, such an adjustment of the cut point is not necessary to maintain the extinction objective, but without this adjustment in cut point greater changes in reactor temperatures would have been necessary in maintaining the extinction objective at a constant distillate product end point.

A comparison of the process options investigated highlighting the cut point differences is presented in Table 4.

OPERATING RESULTS WITH ILLINOIS COAL

The operating results for the demonstration operation in the bottoms extinction mode with Illinois coal are summarized in Table 5. The results are the average values for the seventh through twenty-fifth days of the run during which bottoms extinction objectives were maintained. Recycle solvent inventory corrections based on actual analysis were included. Figures 4 through 8 summarize day-by-day some details of the product distribution during the run, illustrating the degree to which minimum bottoms yields were maintained. Over this interval of the run, during which the endpoint of the atmospheric overhead product averaged 750°F, the yield of C₄-750°F distillate product averaged 77.2 W % of M.A.F. coal (corresponding to 5 barrels/ton of M.A.F. coal), with 1.0 W % yield of heavier distillates boiling to 975°F, and 2.7 W % yield of residual oil. Table 5 also summarizes the results of a comparable conventional CTSL operation with the heavy-media washed coal in which the 650-750°F boiling range material was included in the solvent recycle.^(3,4) The change in the composition of the solvent recycle lowered the yield of 750°F+ oils plus residuum from 19.6 W % of M.A.F. coal to 3.6 W %. Some of this change is due to the higher reactor temperatures used in the extinction mode operation, but other experimental work has shown that less than one-half of the difference is associated with the change in temperatures.

Figure 4 shows that the yield of C₄-End Point (about 750°F) product scattered around the average value during the seventh through twenty-fifth days of the run. Figure 5 displays a similar pattern for the 975°F⁺ residual oil yield, and Figure 6 for the yield of heavy distillate to 975°F retained in the solvent recycle pool. Figure 7 shows an increase in coal conversion of about 1.5 W % over this interval of the run. Figure 8 shows an increase in C₁-C₃ hydrocarbon gas yield of about 2.5 W %.

OPERATING RESULTS WITH OHIO COAL

The operating results for the demonstration operations with Ohio No. 5/6 bituminous coal in the bottoms extinction mode and in the gas oil extinction mode are summarized in Table 6. These two types of operation were demonstrated in a single run, in which the bottoms extinction mode was used for the first ten days, and the vacuum gas oil extinction mode for the balance of the operations up to twenty-two days. The stage temperatures were progressively increased during these operations, similarly to the pattern used for the Illinois coal operations, with the reactor temperatures being increased by about 20°F over the interval of the run during which the extinction objectives were attained.

The bottoms extinction operation with Ohio coal maintained a 975°F⁺ residual oil yield of 1.8 W % of M.A.F. coal. However, the yield of 750-975°F gas oil was somewhat higher, averaging 8.5 W %. Since there was virtually complete elimination of the 750-975°F fraction in the subsequent vacuum gas oil extinction operation, there is probably no barrier to equivalent extinction in the bottoms extinction mode. The shortfall in performance in this specific operation was probably due to too low a cut point between the atmospheric still overhead product and solvent recycle pool, at 700°F. It is probable that with this cut point raised by 25-50°F, there would have been essentially complete extinction of the 750°F⁺ materials, with a total yield of C₄-750°F distillate product of about 77 W % of M.A.F. coal. This is similar to the yield in this mode of operation with Illinois coal. Beyond this consideration of the heavy gas oil extinction, the greatest difference from the Illinois coal results is about 2 W % higher yield of unconverted coal for the Ohio coal.

The vacuum gas oil extinction operation with Ohio coal gave a yield of 750-975°F gas oil of 0.2 W % of M.A.F. coal. For this operation, the yield of 975°F⁺ residual oil was 14.1 W %, which would be taken off as a vacuum bottoms slurry along with the unreacted coal and ash. Such a slurry would have a composition of 61% residual oil, 21% unconverted coal, and 18% ash, and could be pumped for internal use as fuel or as raw material for hydrogen manufacture. The yield of C₄-750°F distillate was 65.1 W % of M.A.F. coal for this operation.

RESULTS AND CONCLUSIONS

- Heavy oil extinction recycle has been demonstrated for vacuum gas oil and vacuum gas plus residual oil for bituminous coals.
- Up to five barrels of distillate liquid product per ton of moisture ash free coal feed was produced. These yields are the highest demonstrated continuously for a direct liquefaction process.
- Increased liquid yields and reduced process separation costs were achieved through deep cleaning of bituminous feed coals.
- The distillate yields from Ohio coal are equivalent to those from Illinois coal at similar extinction recycle operating conditions.

ACKNOWLEDGEMENT

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TABLE 1

ILLINOIS COAL FEED ANALYSIS

SOURCE: ILLINOIS No. 6, BURNING STAR No. 2 MINE

	<u>MINE-WASHED</u>	<u>HEAVY MEDIA CLEANED</u>
<u>PROXIMATE, W % DRY</u>		
Fixed Carbon	51.5	54.1
Volatile Matter	38.2	40.4
Ash	10.3	5.5
<u>ULTIMATE, W % DRY</u>		
Carbon	70.4	73.9
Hydrogen	4.5	4.9
Nitrogen	1.4	1.5
Sulfur	3.6	2.8
Ash	10.6	5.8
Oxygen (Difference)	9.5	12.1
<u>PETROGRAPHIC, V %</u>		
Total Reactives	88.2	91.5
Total Inerts	11.8	8.5
Fusinite	1.9	0.3

TABLE 2

OHIO COAL FEED ANALYSIS

SOURCE: OHIO No. 5/6, CRAVAT COAL COMPANY

	<u>MINE-WASHED</u>	<u>HEAVY MEDIA CLEANED</u>
<u>PROXIMATE, W % DRY</u>		
Fixed Carbon	56.1	50.6
Volatile Matter	43.9	43.4
Ash	8.5	4.0
<u>ULTIMATE, W % DRY</u>		
Carbon	73.1	77.5
Hydrogen	4.8	5.0
Nitrogen	1.5	1.6
Sulfur	2.9	2.1
Ash	8.5	4.0
Oxygen (Difference)	9.2	9.8
<u>PETROGRAPHIC, V %</u>		
Total Reactives	88.0	90.4
Total Inerts	10.8	7.8
Fusinite	1.1	1.8

TABLE 3

**OPERATING RESULTS BENCH UNIT CTSL OPERATIONS WITH
MINE-WASHED AND HEAVY MEDIA WASHED ILLINOIS COAL**

	WASHED	
	Mine	Heavy-Media
COAL PREPARATION		
ASH IN COAL FEED, W %	10.55	5.33
RUN	18	19
DAYS ON STREAM, Average	8	9
<u>Reactor Temperatures, °F</u>		
First Stage, Average	750	750
Second Stage, Average	810	810
End Point of Atmospheric Overhead Product, °F	670	664
<u>PRODUCT DISTRIBUTION, W % OF M.A.F. COAL</u>		
C ₁ -C ₃ in Gases	5.9	6.2
C ₄ -390°F Naphtha	17.2	19.0
390-650°F Distillates	32.9	35.7
650-975°F Distillates	19.2	18.5
975°F+ Residual Oil	8.3	8.3
Unconverted Coal	7.0	4.0
Water	11.7	11.7
H ₂ S, NH ₃ , CO _x	5.0	4.3
Total (100 + H ₂ Reacted)	107.2	107.7
Total C ₄ -975°F	69.2	73.2
Distillate Yield Bbls/Ton	4.2	4.7

TABLE 4

COMPARISON OF PROCESS OPTIONS EVALUATED

	Product		Clean Coal	Solids Rejection	W % Distillate	Distillate End Point
	Vacuum Gas-Oil	Residual Oil				
<u>Illinois No. 6 Coal Runs</u>						
I-10/11 - Demonstration	Yes	Yes	No	VSB	60	975°F
I-13 - Process Variable	No	No	No	DS		
I-27 - Demonstration	No	No	Yes	DS	77	750°F
<u>Ohio No. 5/6 Coal Runs</u>						
O-1 - Demonstration	No	No	Yes	DS	70	700°F
	No	Yes	Yes	VSB	65	700°F

VSB = Vacuum Still Bottoms
DS = Dry Solids

**EXPERIMENTAL RESULTS OF CONVENTIONAL AND EXTINCTION
MODES OF CTSL BENCH UNIT OPERATIONS WITH ILLINOIS COAL**

TABLE 5

MODE	CONVENTIONAL	EXTINCTION
RUN	19	27
DAYS ON STREAM, Average	14	16
<u>Reactor Temperatures, °F</u>		
First Stage, Average	750	761
Second Stage, Average	810	817
End Point of Atmospheric Overhead Product, °F	656	749
<u>PRODUCT DISTRIBUTION, W % OF M.A.F. COAL</u>		
C ₁ -C ₃ Hydrocarbons	6.8	8.3
C ₄ -390°F Naphtha	18.9	20.3
390-650°F Distillates	32.4	37.5
650-750°F Distillates	9.1	19.5
C ₄ -750°F Distillates	60.4	77.3
750-975°F Distillates	11.0	1.0
975°F ⁺ Residual Oil	9.5	2.7
Unconverted Coal	3.8	3.3
Water	11.2	10.8
H ₂ S, NH ₃ , CO _x	4.6	4.2
Total (100 + H ₂ Reacted)	107.3	107.6

**EXPERIMENTAL RESULTS OF BOTTOMS AND VACUUM GAS OIL
EXTINCTION CTSL BENCH UNIT OPERATIONS WITH OHIO COAL**

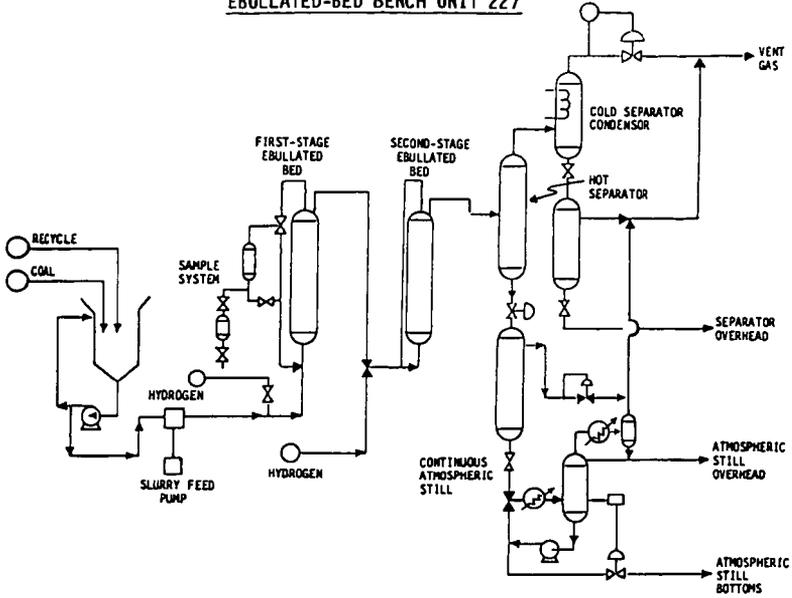
TABLE 6

MODE	BOTTOMS EXTINCTION	VACUUM GAS OIL EXTINCTION
RUN	0-2	0-2
DAYS ON STREAM, Average	7	18
<u>Reactor Temperatures, °F</u>		
First Stage, Average	753	764
Second Stage, Average	806	819
End Point of Atmospheric Overhead Product, °F	702	697
End Point of Vacuum Gas Oil Product, °F	---	975
<u>PRODUCT DISTRIBUTION, W % OF M.A.F. COAL</u>		
C ₁ -C ₃ in Gases	7.9	10.1
C ₄ -390°F Naphtha	19.1	18.8
390-650°F Distillates	36.8	38.1
650-975°F Distillates	14.6	8.1
C ₄ -750°F Distillates	70.5	65.1
750-975°F Gas Oil	8.5	0.3
975°F ⁺ Residual Oil	1.8	14.1
Unconverted Coal	5.2	4.8
Water	10.0	9.0
H ₂ S, NH ₃ , CO _x	3.5	3.4
Total (100 + H ₂ Reacted)	107.4	106.7
Distillate Yield, Bbls/Ton	4.3	4.0

Note: C₄975°F Yield, 79% equal to 5:1 Bbls/Ton

FIGURE 1

EBULLATED-BED BENCH UNIT 227



BENCH UNIT - RECYCLE PROCEDURES

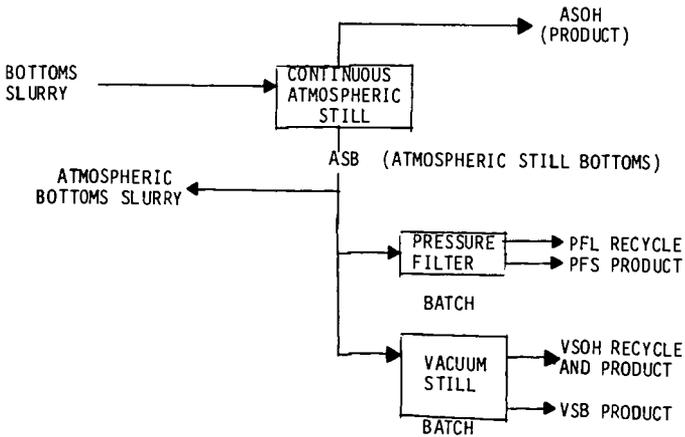


FIGURE 2

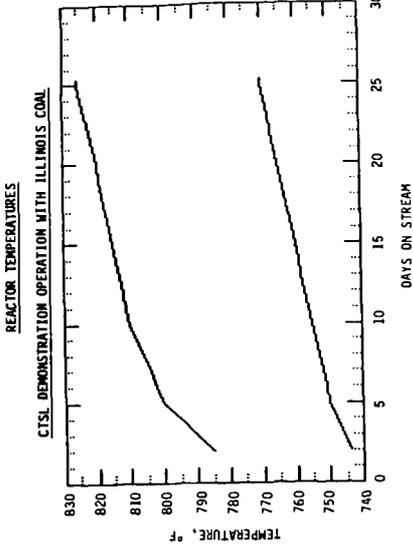


FIGURE 3

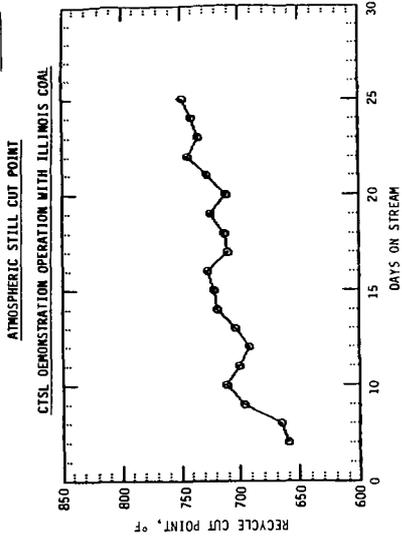


FIGURE 4

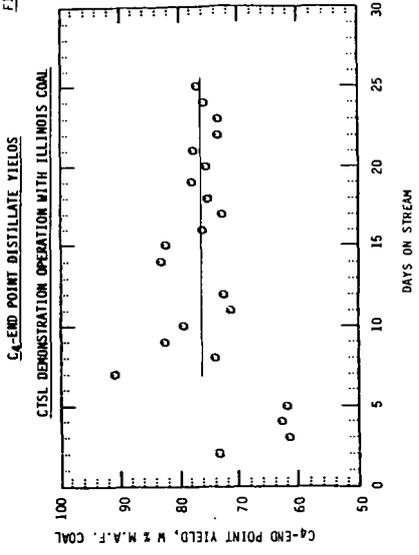


FIGURE 5

975°F YIELD

CITSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

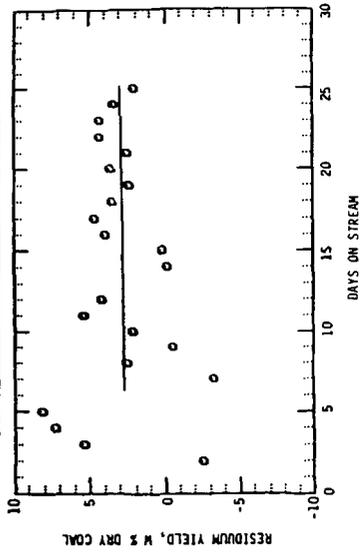


FIGURE 6

END POINT PLUS DISILLATE YIELD

CITSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

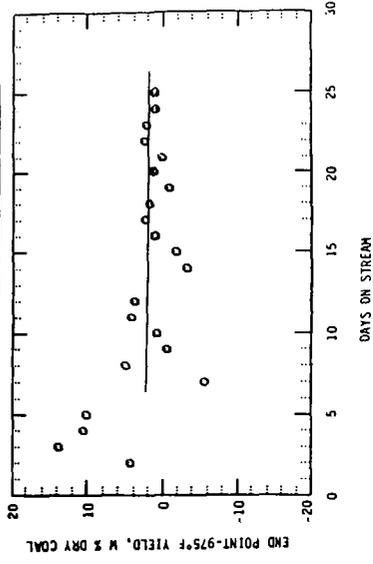


FIGURE 7

COAL CONVERSION

CITSL DEMONSTRATION OPERATION WITH ILLINOIS COAL

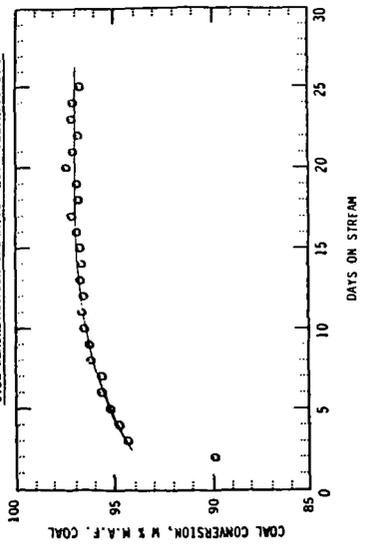
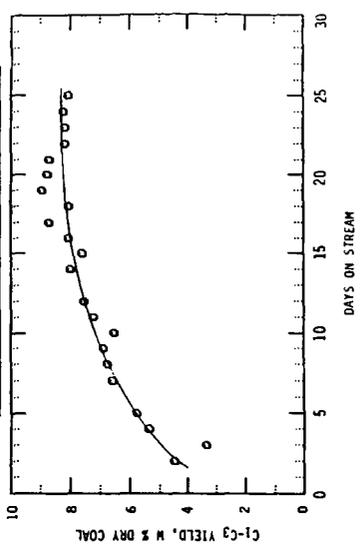


FIGURE 8

C₁-C₃ YIELDS

CITSL DEMONSTRATION OPERATION WITH ILLINOIS COAL



ACTIVITY AND SELECTIVITY OF MOLYBDENUM
CATALYSTS IN COAL LIQUEFACTION REACTIONS

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During coal liquefaction, coal fragments forming a liquid product with reduced heteroatom content. Coal can be considered to be a large network of polynuclear aromatic species connected by heteroatoms and alkyl bridging structures. Predominant heteroatoms contained in coal are sulfur, oxygen, and nitrogen. Predominant alkyl bridges are methylene and ethylene structures. The purpose of this work is to evaluate how effectively three different molybdenum catalysts promote reactions involving heteroatom removal and cleavage of alkyl bridge structures. The reactions studied include: hydrogenation (HYD), hydrodeoxygenation (HDO), hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrocracking (HYC).

Both model and coal liquefaction reactions were performed to test the activity and selectivity of three different molybdenum catalysts. The three catalysts used were molybdenum naphthenate, molybdenum supported on gamma alumina ($\text{Mo}/\text{Al}_2\text{O}_3$) and precipitated, poorly crystalline molybdenum disulfide (MoS_2). The model compounds, chosen to mimic coal structure, on which the effectiveness of the catalysts for the model reactions was tested were: 1-methylnaphthalene, representing aromatic hydrocarbons, for hydrogenation; 1-naphthol, representing oxygen containing compounds, for deoxygenation; benzothiophene, representing sulfur containing compounds, for desulfurization; indole, representing nitrogen containing compounds, for denitrogenation; and bibenzyl, representing alkyl bridging structures, for hydrocracking. Catalytic reactions of combinations of reactants were performed to simulate a complex coal matrix. Thermal and catalytic coal liquefaction reactions were performed using Illinois No. 6 coal with anthracene as a solvent. The efficacy of the catalysts was determined by comparing the product and compound class fractions obtained from the liquefaction reactions.

Molybdenum Catalysts. All the catalysts used in this study have the element Mo (molybdenum) as the active metal component complexed with sulfur in a MoS_x form. Mo naphthenate is a thermally decomposable, hydrocarbon-soluble organometallic compound which was dispersed directly in the reaction mixtures. The catalytic species was generated in situ. Bearden et al. (1) postulates that at elevated temperatures and pressures inherent to coal liquefaction the metal naphthenate is converted to the active form by thermal decomposition. The active form is postulated to be MoS_2 (2,3) which is formed during pretreatment with H_2S or sulfur present in the feedstock. The Mo naphthenate used in this study was obtained from Shepherd Chemical consisting of ~6% Mo. The active form of the catalyst was generated in situ by introduction of excess sulfur to the reaction mixtures.

The $\text{Mo}/\text{Al}_2\text{O}_3$ used in this study was Amocat 1B obtained from Amoco. The active form was generated by presulfiding. The surface area of this material was 212 m^2/g .

Precipitated MoS_2 was prepared by the method of Chianelli and Dines (4) by precipitating MoS_2 from an ethyl acetate solution of MoCl_4 and Li_2S followed by annealing in H_2S . Precipitated MoS_2 exhibits a poorly crystalline "rag" structure (5), consisting of several stacked and highly disordered S-Mo-S layers. The layers have unusual flexibility in terms of number of dimension of the stacks and increased ability to intercalate organic species (5-7). Despite its poorly crystalline structure, precipitated MoS_2 exhibits an X-ray diffraction pattern similar to that of highly crystalline hexagonal MoS_2 (7). The synthesis of precipitated MoS_2 was confirmed by X-ray diffraction in this work. The surface area of precipitated MoS_2 was 42 m^2/g .

Experimental

Model Reactions. Model reactions were performed in horizontally mounted stainless steel tubing bomb reactors of ~20 ml volume. The model compounds and solvent, hexadecane, were obtained from Aldrich. All compounds of less than 99% purity were recrystallized before use. Model compound reactions were performed at 380°C with 1250 psig H₂ (cold) for 25 minutes and were agitated at rates greater than 800 cpm. For the individual reactions, the reactants were charged at 2 wt% in n-hexadecane; for the reactions with combined reactants, each component was introduced at 1 wt% giving 5 wt% reactant solutions. The reaction products were analyzed using a Varian 3700 FID chromatograph with a DB-5 fused silica capillary column. Para-xylene was used as internal standard. Catalyst, if used, was added in the individual reactant experiments at 1500 ppm Mo/g of reactor charge and in the combined reactions at 3500 ppm Mo/g of reactor charge. Elemental sulfur was added only to those reactions involving Mo naphthenate at a ratio of 2.5 to 1 sulfur to Mo by weight. Thermal reactions with excess sulfur were also performed to determine the independent effects of sulfur on reactant activity. Sulfur was added in the thermal reactions at a sulfur to Mo ratio of 2.5 to 1, calculated by assuming Mo would have been present at a loading of 1500 ppm/g reactor charge for the individual reactions.

Coal Liquefaction Reactions. Coal liquefaction reactions were performed thermally and catalytically with all three molybdenum catalysts in ~50 ml stainless steel horizontal reactors. The reactor charge was 0.5g coal with 0.5g anthracene as solvent and 1250 psig H₂ (cold). Reactions were performed at 425°C for 30 minutes at an agitation rate of 850 rpm. The catalyst loading was 3500 ppm Mo/reactor charge; 0.01g of sulfur was used for the Mo naphthenate reactions.

The liquid and solid products were separated by sequential washing with methylene chloride-methanol (9:1 v/v) solution (MCM) and tetrahydrofuran (THF). The separation produced three fractions: MCM solubles (MCMS), MCM insolubles-THF solubles (THFS) and THF insolubles or ash-free insoluble organic matter (IOM). The MCMS fraction was further fractionated by the chromatographic method of Boduszynski (8) into compound class fractions: hydrocarbons (HC), nitrogen heterocycles (NH), hydroxyl aromatics (HA) and polyfunctional compounds (PC). The HC fraction was further analyzed for anthracene and its hydrogenation products using the same GC analysis procedure as the model systems.

Results and Discussion

A sequence of reactions was performed with each model which included thermal reactions, thermal reactions with excess sulfur, and catalytic reactions using Mo naphthenate, Mo/Al₂O₃, and precipitated MoS₂. The product distributions achieved from the model reactions were summarized using several defined terms. The terms are: (1) percent hydrogenation which is the number of moles of hydrogen required to achieve the obtained product distribution as a percentage of the moles of hydrogen required for the most hydrogenated product; (2) percent hydrogenolysis which is the summation of the mole percent of components resulting from carbon-carbon and carbon-heteroatom bond cleavage; (3) percent desulfurization which is the summation of the mole percents of components not containing sulfur; (4) percent hydrodeoxygenation which is the summation of the mole percents of components not containing oxygen; (5) percent hydrodenitrogenation which is the summation of the mole percents of components from which nitrogen has been removed; and (6) percent hydrocracking which is the summation of the mole percents of components resulting from the breakage of an alkyl bridge structure.

Hydrogenation of 1-Methylnaphthalene. Hydrogenation of 1-methylnaphthalene proceeds through two pathways, both culminating in the production of decalin. 1-methylnaphthalene can either be hydrogenated to methyltetralins (tetrahydromethylnaphthalenes) followed by demethylation to naphthalene and

further hydrogenation, or demethylated initially forming naphthalene and its hydrogenation products, tetralin and decalin (9-11).

Under thermal and thermal with sulfur conditions, essentially no hydrogenation of 1-methylnaphthalene occurred as presented in Table 1. Under catalytic conditions, Mo naphthenate produced the highest conversion of 1-methylnaphthalene among the three Mo catalysts, yielding major products of 5-methyltetralin and 1-methyltetralin. Conversion to hydrogenated naphthalenes was not observed with any of the Mo catalysts, although small quantities of naphthalene were produced. Very little hydrogenolysis of the methyl group was observed, indicating that these Mo catalysts were not selective for cleavage of the carbon-carbon bond.

Table 1
Activity and Selectivity of Mo Catalysts in Model Compound Systems

	Thermal	Thermal with Sulfur	Mo Naphthenate	Mo/Al ₂ O ₃	P-MoS ₂ *
<u>1-Methyl-Naphthalene</u>					
Hydrogenation, %	0.7±0.3	0.8±0.6	31.3±0.8	13.5±0.6	7.6±0.5
Hydrogenolysis, %	0.4±0.1	0.5±0.1	1.6±0.4	0	0
<u>1-Naphthol</u>					
Hydrogenation, %	28.5±4.0	10.6±2.7	53.1±0.6	41.0±0.3	46.1±0.6
Deoxygenation, %	38.5±1.7	17.4±3.3	100.0	100.0	100.0
<u>Benzothiophene</u>					
Hydrogenation, %	1.3±0	1.1±0.1	51.9±0.5	51.0±0.2	51.1±0.1
Hydrodesulfurization,0	1.4±0.1	1.2±0.1	100.0	100.0	100.0
<u>Indole</u>					
Hydrogenation, %	1.6±0.5	1.1±0.2	35.6±4.3	22.6±0.1	8.2±1.6
Hydrodenitrogenation, %	0	0	18.6±4.7	11.9±0.1	2.0±0.8
Hydrogenolysis, %	1.7±1.0	0.5±0.2	69.6±5.4	38.2±0.5	10.4±5.0
<u>Bibenzyl</u>					
Hydrogenation, %	2.7±0.1	1.7±0.1	2.3±0.2	1.9±0.3	1.8±0.01
Hydrocracking, %	4.8±0.3	2.7±0.1	3.8±0.3	3.2±0.1	3.2±0.1

*P-MoS₂ = precipitated MoS₂

Hydrodeoxygenation of 1-Naphthol. Two reaction pathways for the hydrodeoxygenation of 1-naphthol are available, one in which 1-naphthol is hydrodeoxygenated and then hydrogenated to tetralin and decalin and one in which 1-naphthol is hydrogenated without removal of oxygen forming 5,6,7,8-tetrahydro-1-naphthol and 1-tetralone (12).

Significant thermal hydrogenation of 1-naphthol which followed both reaction pathways was observed. When sulfur was added, a marked inhibition of naphthol hydrogenation activity was obtained (Table 1), although the reaction still proceeded through both reaction pathways. In the catalytic reactions (Table 1), considerably more hydrogenation of 1-naphthol was observed. However, the catalytic hydrogenation proceeded through only one reaction pathway, the one involving immediate removal of the hydroxyl group with the major product being tetralin. All three Mo catalysts completely deoxygenated 1-naphthol; however, differences were observed in their ability to hydrogenate the deoxygenated 1-naphthol. Mo naphthenate was most active for hydrogenating 1-naphthol, followed

by precipitated MoS_2 and then $\text{Mo/Al}_2\text{O}_3$.

Hydrodesulfurization of Benzothiophene. The reaction pathway for benzothiophene involves first hydrogenation to the dihydro form, then ring cleavage at the carbon-sulfur bond and finally hydrodesulfurization releasing H_2S (10,11,13,14).

Sulfur had no effect on thermal reactions of benzothiophene which was only slightly reactive without a catalyst present (Table 1). The thermal reactions formed the products, dihydrobenzothiophene and ethylbenzene, in small quantities. In the catalytic reactions, complete desulfurization was achieved with all of the Mo catalysts, producing primarily ethylbenzene and a minor product of ethylcyclohexane in all cases. Similar results have been observed over $\text{CoMo/Al}_2\text{O}_3$ catalysts (13). The hydrogenation activity of all of the catalysts was also nearly equivalent (Table 1).

Hydrodenitrogenation of Indole. The reaction pathway for indole hydrodenitrogenation proceeds by hydrogenation of the five-membered ring, followed by ring cleavage, removal of NH_3 and then hydrogenation to a six-membered ring alkane (15).

Thermal reactions of indole showed nearly 6% conversion primarily to dihydroindole. The addition of sulfur to thermal indole reaction had little or no effect on indole reactivity. The catalytic reactions yielded substantially more hydrogenation and hydrodenitrogenation of indole (Table 1). Mo naphthenate proved the most selective for denitrogenation of indole, with the major products being o-ethylaniline and ethylcyclohexane, with minor products of dihydroindole and ethylbenzene. Neither complete denitrogenation nor hydrogenation was achieved with any of the catalysts. The ranking for denitrogenation selectivity among the three catalysts was Mo naphthenate > $\text{Mo/Al}_2\text{O}_3$ > P-MoS_2 .

Hydrocracking of Bibenzyl. The reaction pathway for the hydrocracking of the ethylene bridge in bibenzyl can either proceed by cleaving the carbon-carbon bond of the bridge structure forming toluene or by cleaving the bond between the aromatic ring carbon and the ethylene bridge, forming ethylbenzene and benzene. Under proper conditions, these hydrocracked products can be further hydrogenated (16).

Hydrocracking of bibenzyl only occurred to a small degree both thermally and catalytically. For all cases, percent hydrocracking was ~3% (Table 1). Products observed in most cases were minor amounts of ethylbenzene, ethylcyclohexane, toluene and benzene.

Combined Reactant Reactions. Reactions were performed thermally and catalytically with solutions composed of 1 wt% of all five model compounds in order to simulate the interaction among the different functionalities in a coal liquefaction system. Combined thermal reactions resulted in an increase of indole conversion to indoline and a decrease in the reactivity of 1-naphthol compared to the individual reactions.

Catalytic reactions performed with Mo naphthenate revealed the same trend as the thermal reactions but to a much greater degree. Complete conversion of indole was observed as well as complete deoxygenation of 1-naphthol; however, significant inhibition of the hydrogenation products of 1-naphthol was observed. Also, a decrease in hydrogenation of 1-methylnaphthalene and in bibenzyl hydrocracking was observed compared to the individual reactions. Since increased catalyst loading was used for the combined reactions, individual reactions with indole were performed with increased Mo loading of 3500 ppm Mo per g of reactor charge to ascertain the effect of increased catalyst loading compared to additional reactants. The same trends were observed as stated above, with small increases in inhibitive effects.

Reactions performed on combined solutions with $\text{Mo/Al}_2\text{O}_3$ exhibited different trends. The inhibitive effects noted with Mo naphthenate were reversed with $\text{Mo/Al}_2\text{O}_3$. Increases were achieved in the hydrogenation products of 1-methylnaphthalene and 1-naphthol, with the same corresponding conversion of indole

as observed with the Mo naphthenate reactions.

Reactions performed with precipitated MoS₂ on the combined solutions yielded results similar to that of Mo naphthenate, but to a lesser degree. Hydrogenation of 1-methylnaphthalene and 1-naphthol products was inhibited as was hydrocracking of bibenzyl. An amplification of indole conversion was also observed.

Coal Liquefaction Reactions. A series of coal liquefaction reactions was performed to assess the activity and selectivity of the three Mo catalysts for the conversion of Illinois No. 6 coal to soluble products. Final assessments of selectivity and activity were based upon the production of the different solubility fractions and compound classes described in the Experimental section. Hydrogenated products of the solvent, anthracene, were also analyzed to assess the percentage of hydrogenation achieved during the reaction.

Thermal reactions of Illinois No. 6 coal yielded a coal conversion of 62%. The product distributions of gas, MCMS, THFS, and IOM, given in Table 2, indicate low thermal gas production and appreciable IOM after reaction. Much higher coal conversion was produced during the catalytic reactions as shown in Table 2. Mo naphthenate achieved 92% coal conversion; Mo/Al₂O₃ yielded 90%, and precipitated MoS₂ converted much less at 79%.

Production of THFS ranged from 22% thermally to 31% with Mo/Al₂O₃. The production of THFS was generally related to an increase or decrease in the amount of the MCMS fraction. The lowest production of THFS was generated by Mo naphthenate at 17% which was accompanied by the highest production of MCMS, 48%. The largest production of THFS was obtained with Mo/Al₂O₃, which also exhibited a relatively high MCMS fraction, 40%. Mo/Al₂O₃ was not as effective as Mo naphthenate in converting THFS to MCMS. Precipitated MoS₂ produced low THFS at 21% and a MCMS of 37% which was comparable to Mo/Al₂O₃ but was not as effective for overall coal conversion.

Table 2
Product Distribution from Coal Liquefaction Reaction

Product Fraction	Weight Percent			
	Thermal	Mo Naphthenate	Mo/Al ₂ O ₃	P-MoS ₂
Gas	8.7±3.3	28.2±4.3	19.6±1.7	20.2±0.9
MCMS				
HC	11.5±1.8	24.0±1.0	16.6±0.1	15.0±0.7
NH	3.9±1.2	4.6±1.4	6.1±0.1	5.0±0.1
HA	8.1±2.0	8.8±0.2	9.7±0.5	10.8±2.3
PC	8.4±0.5	9.5±0.6	7.5±0.4	6.3±1.4
THFS	21.6±5.2	16.5±0.9	30.9±0.3	21.4±2.8
IOM	37.8±3.8	8.4±3.8	9.6±1.9	21.3±0.3
Coal Conversion, %	62.2±3.8	91.6±3.8	90.4±1.9	78.7±0.3

Comparisons of the compound class separations given in Table 2 indicate that Mo naphthenate produced the largest percentage of hydrocarbons (HC) at 24%. The other catalysts yielded less, 17% with Mo/Al₂O₃ and 15% with precipitated MoS₂. The nitrogen heterocycles (NH) were 4% thermally and in the presence of a catalyst

increased only slightly to 6%. The same trend was observed with hydroxyl aromatics (HA) with thermal production at 8% and increasing to 11% with the precipitated MoS₂ catalyst. The increase in the NH and HA fractions in the catalytic reactions was due to increased coal conversion and MCMS production, yielding more nitrogen heterocycles and hydroxyl aromatics soluble and analyzable.

The relative differences in the NH and HA fractions of the catalytic reaction can be seen more easily by examining the average results on a MCMS basis as given in Table 3. A general trend could be seen for Mo naphthenate and Mo/Al₂O₃, where the catalysts produced the NH and HA fractions on a proportionate basis, although the former produced less overall of the two fractions. P-MoS₂ produced a different distribution with the HA fraction produced being disproportionately higher than that of the other catalysts and the NH fraction being lower than Mo/Al₂O₃ but not as low as Mo naphthenate. These compound class distributions indicated that precipitated MoS₂ was more selective for denitrogenation than for deoxygenation.

Table 3
Compound Class Fractions from Coal Liquefaction
Reactions on a MCMS Basis

Compound Classes, Wt% on MCMS Basis	Mo			
	Thermal	Naphthenate	Mo/Al ₂ O ₃	P-MoS ₂
HC	36.1±4.0	51.3±1.7	41.7±0.2	40.4±0.2
NH	12.2±2.6	9.8±3.2	15.1±0.1	13.5±0.4
HA	25.3±3.5	18.7±0.3	24.3±1.3	29.1±4.9
PC	26.4±3.0	20.2±1.1	18.9±0.5	17.0±4.6

Polyfunctional compound (PC) decreased smoothly from thermal conditions at 26% to catalytic with precipitated MoS₂ at 17% on a MCMS basis. These results are best interpreted in terms of the HC fraction. The increase of HC to 51% for Mo naphthenate was a result of the reduction of all the other classes, NH, HA and PC. Mo/Al₂O₃ followed the same patterns but only produced ~42% HC. Precipitated MoS₂ yielded 40% HC which was produced more from denitrogenation than from deoxygenation.

In terms of the greatest selectivity for hydrocarbon production, hydrodeoxygenation and coal conversion to soluble products, the catalysts can be ranked as Mo naphthenate > Mo/Al₂O₃ > P-MoS₂. However, for hydrodenitrogenation selectivity of greatest impact was Mo naphthenate > P-MoS₂ > Mo/Al₂O₃.

Anthracene Hydrogenation. Anthracene hydrogenation during coal liquefaction ranged from 33% under thermal conditions up to 41% for Mo naphthenate reactions (Table 4). Reaction products resulting from anthracene hydrogenation included dihydroanthracene (DHA), hexahydroanthracene (HHA) and octahydroanthracene (OHA). Some cracking of anthracene was observed, from 4 to 6 mole percent, with the cracked products being in the boiling point range for naphthalene and its derivatives. Reactions with Mo/Al₂O₃ produced the highest level of cracking. The percent hydrogenation of the solvent remained within a deviation of 3 mole percent for all catalysts with only slight variations in product distributions.

Table 4
Anthracene Hydrogenation in Thermal and Catalytic
Coal Liquefaction Reactions

<u>Reaction</u>	<u>Hydrogenation, %</u>
Thermal	33.0±0.7
Mo Naphthenate	41.1±2.7
Mo/Al ₂ O ₃	36.1±2.3
P-MoS ₂	40.1±1.2

Summary

The oil-soluble Mo naphthenate was the most effective catalyst for reactions involving hydrogenation, deoxygenation and denitrogenation. Effective hydrocracking was not achieved with any of the catalysts involved. Roughly equal activity for desulfurization was observed for each Mo catalyst. Reactions containing model compounds representative of the five reactions studied, experienced interactive effects which included hydrogenation and hydrocracking inhibition and increased reactivity of nitrogen compounds in the presence of Mo naphthenate and precipitated MoS₂. These inhibitive effects were reversed to promotional effects in the presence of Mo/Al₂O₃.

Mo naphthenate was also the most effective catalyst for overall coal conversion and the production of MCMS fraction and hydrocarbons. This catalyst also proved most effective for denitrogenation and deoxygenation. Mo/Al₂O₃, while exhibiting comparable coal conversion as Mo naphthenate, produced less MCMS and hydrocarbons. Precipitated MoS₂ showed the least propensity for coal conversion, but did exhibit somewhat better selectivity for denitrogenation than did Mo/Al₂O₃. The anthracene hydrogenated thermally and catalytically forming hydroaromatic species. Hydrocracking of anthracene was observed in all reactions, with those using Mo/Al₂O₃ producing the most.

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ORIGINS AND REACTIONS OF ALKYL AND ALKANES IN DIRECT COAL LIQUEFACTION

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INTRODUCTION

Recent analytical methods have attempted to unveil the nature of the aliphatic part of the molecules present in coal structures, and, with some approximation, they were successful in determining the origins and the size distribution of the alkyl chains and of the linear hydrocarbons. The abundant presence of alkyl groups have been observed among the products of thermal and donor solvent dissolution reactions of various coals. While the analytical determination of alkyls presence in the products of coal conversion and the speculation of their original status in the coal matrix have been extensively studied, their roles in the various reactions occurring in coal liquefaction have not received adequate attention by the research community. In particular, the high severity of operation used in the experimental research works for so many years and, regrettably, even in present research works, has precluded the determination of the role of each of the reactive components existing in the coal structure or formed in various stages of coal liquefaction. In addition, there is a scarcity of information on the role of each of the reactive species and their effect on the reactivity of the other components of coal and coal liquids.

It is commonly accepted that beneficial results are obtained in coal liquefaction by the programmed or staged temperature approach(1), and, currently, this experimental mode has become popular with many researchers.

For a more fundamental approach in coal liquefaction there is an opportunity to study the reactions occurring at the low temperature ranges, say 250-380°C, for each of the reactive components, or each group of components present in coal or formed in the initial stages of liquefaction, which can be related to the most significant beneficial effects observed in the staged temperature experiments.

By increasing the reaction temperature to above 380-400°C, the researcher must be aware that he or she is approaching the threshold separating the predominance of hydrogenation reactions of aromatic compounds at the lower temperatures from those of dehydrogenation of hydroaromatic compounds which occurs at the higher temperatures.

This paper, presently in the form of a communication to be complemented by the oral presentation and expanded for publication in Energy and Fuels, intends to present some of the reactions involving alkyl groups as well as formation of alkanes, which might have important roles in coal liquefaction. The paper has the additional objective to stimulate the research community to undertake a more systematic research approach in liquefaction which ought to separate the many reactions occurring at the lower temperature range from the subsequent reactions occurring at the higher temperatures. The latter are profoundly affected by the way the former are carried out.

INITIAL STAGES OF COAL LIQUEFACTION

In coal liquefaction experiments, in which coal is slurried in a solvent and heated up to promote coal dissolution, reactions are observed to start at 250-280°C with evolution of mainly CO₂, particularly evident in low-rank coals. A large conversion of CO₂ to methane has been observed when the reaction off-gas is in the presence of hydrogen pressure and hydrogenation catalysts, and by increasing the reaction temperature from 300° to 380°C. This undesirable reaction consumes hydrogen and creates obvious confusion if one desires to determine accurately the methane derived from the cleavage of methyl groups from the coal structure, at the same or subsequent higher temperatures. Up to date most researchers in coal liquefaction have neglected this occurrence, and, for that matter, to provide full material balances. At the same temperature range in which CO₂ converts to methane, there are other reactions involving the isomerization of alkylphenols. These reactions occur in the presence of gamma-alumina, and perhaps of clays present in the coal mineral matter, such as montmorillonites and illites. By increasing the reaction temperature above 350°C, alkylphenols isomerize to the more thermally stable meta-position. The thermal removal of the hydroxyl groups from meta-alkylphenols is much harder than from the ortho-alkylphenols.

The importance of removing the hydroxyl groups has been emphasized by this author in a previous paper(2), because of the substantial benefits it provides in both liquefaction stage and in the subsequent upgrading stage. An example cited in that paper was the cleavage of the oxygen bridge in diphenyl ether, very often used as model compound reaction related to coal liquefaction according to recent literature, in which the oxygen bridge is cleaved at lower severity if an alkyl group is present in one of the ring, and, in particular, if it is located in ortho-position to the oxygen.

This seems to be in agreement with the fact that oxygen moieties have been removed with ease at much lower severity of experimental conditions in coal liquefaction than from oxygen-containing model compounds commonly used by researchers in this field. This fact would confirm that alkyl groups and, for that matter, other groups which are present in the ring structure of coals, are playing an important role in the initial stages of coal liquefaction. But, given the preponderance of oxygen moieties and the hydrogenation environment required, the predominant feature in coal liquefaction is the dominance of phenolic chemistry.

SUBSEQUENT LIQUEFACTION STAGES

At higher severity of operations, the phenolic chemistry is still dominant in coal liquefaction, because of the conversion of phenol-precursors to phenols. In the 400-450°C temperature range, transalkylation reactions occur as polyalkylated phenols are able to donate alkyl groups to the non- or less-alkylated phenols, in the presence of clay catalysts(3). At hydrolysis temperature range of 600-1000°C, oxygen in the aromatic rings and hydroxyl groups of phenols were found to strongly enhance the methane yield(4), decarbonylation being the key initial step.

At one point in coal liquefaction perhaps the active oxygen moieties will be practically removed, and other functional groups will probably emerge as

the critical reactive species. However, little is known of the reactions involving alkylated cyclic compounds containing nitrogen and sulfur in the ring. It is believed that the chemistry of alkyl polycyclic aromatics, or hydroaromatics, ought to have a more influential role in the upgrading and refining steps. The selection of the proper catalyst and the experimental conditions in these steps appear to affect the reactions involving alkyl groups, such as, isomerization, transalkylation and "paring" reactions(5).

CONCLUSIVE REMARKS

The abundance of various oxygen moieties and alkyl groups in coals, revealed by current sophisticated analytical devices, signifies that they are a critical part of coal reactivity and consequently are having a major effect on the initial stages of coal liquefaction and very likely in the upgrading and refining steps.

Little is known about the homogeneous chemical reactions which, during liquefaction, bring about the reaction of either the removal of each of these groups, or condensation reactions, that is, coupling for the phenols and cyclization for large alkyl groups. Even less known is the effect of one group on the other, and the combined effect on other critical reactions in coal liquefaction.

This communication lists some of the reactions known from unrelated past works which, it is felt, could be profitably pursued in future coal liquefaction research. An amplified version of this communication will be covered during the oral presentation, and a more detailed and complete set of data will be published in Energy and Fuels.

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