

**COPROCESSING OF COAL WITH HIGH METAL CONTENT RESIDS**  
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## INTRODUCTION

The energy industry will have to consider alternative sources for the production of liquid fuels in view of the rapid depletion of conventional light oil reserves. Several processes are being developed for upgrading heavy crudes and bottom-of-the-barrel residual oils.<sup>(1,2)</sup> The heavy oils contain large amounts of metals which interfere with catalytic upgrading to clean distillates by acting as catalyst poisons. In the 1970s, several direct liquefaction processes were developed to produce liquid fuels from coal. One of the drawbacks of these processes is the fact that it is necessary to recycle a significant amount of product oil to slurry feed coal. This leads to increased plant complexity and higher production costs. Coprocessing, where coal is liquefied in a once-through mode in a heavy oil slurrying medium, may form a bridge between the existing petroleum-refining technology and the syntuels industry of the future. Besides producing light products from coal as well as from heavy oil, it can accomplish a high degree of demetallation of oil, by rejecting the metals to the solid residue.

The composition of coal-derived recycle solvents is very different from that of heavy oils. The former are highly aromatic and hydroaromatic while the latter are mostly paraffinic and naphthenic. Thus, it should be expected that coal conversion in a heavy oil, in general, would be less than in a coal-derived solvent in the absence of a catalyst. However, it is possible to achieve a high degree of conversion by proper choice of host oil, operating conditions, or by pretreating the host oil before it is used for liquefaction. Yan and Espenscheid have reported that 90% conversion of Illinois No. 6 coal to pyridine-solubles was achieved by liquefying the coal in bottoms from a fluid catalytic cracking unit without using any catalyst<sup>(3)</sup> as this solvent was highly aromatic. Similar high conversions have been reported by researchers using catalysts.<sup>(4-6)</sup> Curtis et al. have reported that petroleum residua are deficient in labile hydrogen; however, if a catalyst is used under hydrogen atmosphere, coprocessing can proceed with fairly high conversions.<sup>(7)</sup> It is possible to increase the liquefying efficacy of a residuum by its prior hydrocracking, or by adding external hydrogen donors.<sup>(8)</sup>

This paper presents the results of thermal (with no added catalyst) coprocessing of Illinois No. 6 (hvBb) coal with Maya (650°F+) ATB residual oil and with whole Boscan crude. The relationship between reaction conditions and coal conversion and product selectivity has been studied. The removal of vanadium during coprocessing has been investigated. The results on heteroatom removal reactions have also been presented as the amount of heteroatoms in petroleum is often correlated with that of metals.<sup>(9)</sup>

## EXPERIMENTAL

Tables 1 and 2 show analyses of Illinois No. 6 coal and the host oils respectively. A few experiments were made using a coal-like char and an activated carbon (NUCHAR). The char was synthesized in this laboratory from cellulose. All liquefaction experiments were conducted using a horizontal 20 ml microreactor. Typically the reactor was loaded with 8-10 g of reactants along with four 2 mm stainless steel balls as a mixing aid. It was pressurized with hydrogen to 6.9 MPa (1000 psig) at ambient temperature. The reactor was then brought to the desired reaction temperature by immersing it in a heated fluidized sand-bath. The reactor was shaken horizontally (five one-inch displacements per second) to ensure adequate mixing. The desired temperature was attained within 3-4 minutes and this was taken as zero time. At the end of the desired reaction time, the reactor was removed from the sand bath and cooled with water. The products were removed by washing the reactor with tetrahydrofuran (THF). Almost all the runs were made in duplicate.

The reaction products were classified as THF-insolubles (also referred to as coke), asphaltenes, and oils based on their solubility behavior. Asphaltenes were defined as product soluble in THF but insoluble in pentane; oils (often called maltenes) were defined as products soluble in pentane. The vanadium content of samples was determined using inductively coupled plasma (ICP).

## RESULTS AND DISCUSSION

### COAL CONVERSION AND PRODUCT DISTRIBUTION

Illinois No. 6 coal was liquefied in the Maya ATB at temperatures between 410<sup>o</sup>-450<sup>o</sup>C using various coal-to-solvent ratios. Figure 1 shows the effect of coal concentration on coke yields at 425<sup>o</sup>C. The coke (THF-insolubles) yields comprise unreacted organic matter from the coal along with its inorganic matter and the high molecular weight materials produced during the reaction. At short reaction times (<15 minutes), there was a decrease in the coke yields due to partial dissolution of coal. Part of the coal might have liquefied (breakdown of the macromolecular coal structure) under hydrogen pressure at 425<sup>o</sup>C. Perhaps the dissolution was also due to the extraction of a so-called mobile (trapped) phase from the coal. Some covalent bonds such as C-C, C-O, and C-S bonds which form the linkages in the macromolecular coal structure can be cleaved at 425<sup>o</sup>C to form reactive free radicals. A portion of these free radicals can be quenched with molecular hydrogen at high hydrogen pressures or with the hydrogen transferred from the solvent. As mentioned earlier, heavy oils, relative to recycle solvents, are deficient in hydroaromatic hydrogen - the type of hydrogen which can be easily transferred. Table 3 shows the amount of "transferable" hydrogen present in the Maya ATB, the Boscan ATB and, for the purpose of comparison, from two coal liquids.<sup>(10)</sup> (Note that the table shows the transferable hydrogen from the Boscan ATB, whereas the whole crude was used in the experiments in our study. However the data in Table 3 do provide a valid comparison, as the Boscan crude is very heavy and the difference between the whole crude and the ATB is small.) Table 3 shows that the heavy oils contain very little transferable hydrogen as compared to coal liquids. As a result, it should be expected that coal-derived and resid-derived free radicals would tend to form heavier products such as coke once the transferable hydrogen is consumed.

As shown in Figure 1, the coke yields increased with an increase in the coal concentration in the feed. The higher coke yields are due to the increase in the rates of coking in addition to the higher amounts of THF-insolubles originally present in the feed. The rate of coke formation varied with coal concentration as apparent from the difference in the slopes of the coking curves (at longer reaction times) in Figure 1. Coal concentrations below 25 wt.% showed a negligible increase in the rate of coking over the rate of thermal coking of the Maya ATB alone. However, the rate of coking was significantly higher for 40 wt.% coal concentration. The results can be attributed to the limited supply of transferable hydrogen available in the resid and the higher demand for hydrogen imposed by the high coal concentrations.

It is not possible to calculate the actual coal conversion (to THF-solubles) as the THF-insolubles contain the unconverted coal plus the coke formed from the liquefied coal and also from the resid. However, one can use the "net" coal conversion as an approximate measure of liquefaction. The net coal conversion is a measure of the effective contribution of coal to THF-solubles and can be calculated from the yield of THF-insolubles during coprocessing after subtracting from it the amount of coke formed from the processing of resid alone under identical conditions. Figure 2 shows net coal conversion in the Maya ATB as a function of coal concentration in the coprocessing feed. The net coal conversion showed a maxima relative to the reaction time. At higher reaction times, the net coal conversion decreased due to retrogressive reactions. The decrease was more pronounced for higher coal concentrations. Similar trends were obtained when the Boscan crude was used in place of the Maya ATB. As said earlier, the Boscan crude showed a greater tendency to coke. Figure 3 shows net coal conversion obtained with the Boscan crude. The net coal conversion was slightly lower with the Boscan crude. The effect of coal concentration in the feed on the net coal conversion can be seen from Figures 2 and 3. At long reaction times, net coal conversions with the Maya ATB were higher for higher coal concentrations. This is understandable as a high coal concentration leads to increased hydrogen demand and, if the supply is limited, to increased retrogressive reactions. However, at shorter reaction times with the Maya ATB, net coal conversion for 40 wt.% coal concentration was higher than for 25 wt.% coal concentration. The net conversion for 10 wt.% coal with the Maya ATB was intermediate between those for 25 wt.% and 40 wt.% coal concentrations. Obviously, the data are too scattered to draw a statistically valid inference. Most of the converted coal formed asphaltenes on a net basis and very little oils were generated.

The increased occurrence of retrogressive reactions, when the demand for hydrogen outpaces the limited supply of the transferable hydrogen in the resid, was also apparent when the liquefaction temperature was varied. The effect of temperature on the net coal conversion is illustrated in Figure 4. At high

temperatures, the net coal conversion fell sharply (the yield of coke rose) for reaction times greater than 10 minutes due to high demand for hydrogen. The maximum conversion at 450°C was much lower than that at 410°C and at 425°C.

#### DEMETALLATION OF HEAVY OILS

The coprocessing of coal and heavy oils was accompanied by significant demetallation of the heavy oil. The metals present in the asphaltenes and the oils were transferred to the solids formed during coprocessing. The Maya ATB contained 400 ppm of vanadium. A significant amount of this metal content was rejected along with the coke when the resid was processed by itself; however, the demetallation was significantly higher when the resid was processed along with coal. The results are shown in Figure 5. When the resid was processed without any coal, 65% of the vanadium present in the feed was transferred to the coke, whereas 89% of the vanadium was transferred to the coke when the feed contained 40 wt.% coal. The overall demetallation of the oils (maltenes) was relatively easier than that of the asphaltenes fraction.

The Boscan crude contained 1100 ppm of vanadium. The results on demetallation of the Boscan crude are shown in Figure 6. The results are similar to those on the Maya ATB. Although the Boscan crude contained much more vanadium, the amount of vanadium removed with coke was similar to that from the Maya ATB on a percentage basis. With a feed containing 25 wt.% coal and 75 wt.% Boscan crude, 84% of the total vanadium was rejected to coke.

In order to understand the mechanism of demetallation in coprocessing, a few samples of the feedstock, THF-solubles, THF-insolubles, pentane-solubles, and pentane-insolubles were analyzed using X-ray absorption fine structure (EXAFS) spectroscopy using facilities at Stanford University. X-ray absorption near-edge spectra (XANES) of all the samples were very similar and matched that of a vanadyl porphyrin (tetraphenylporphyrin) standard. Although these results are insufficient to identify precisely the type of vanadium compounds present, it can be concluded that the removal of vanadium along with the solids formed is not due to any change in the nature of bonding of vanadium. Vanadium remains chiefly in organometallic complexes very similar to the original porphyrins. This is contrary to that found in catalytic hydrodemetallation where vanadium on adsorption on a catalyst is converted to an inorganic form.<sup>(11)</sup> The samples studied here were obtained on noncatalytic coprocessing at 425°C and at 1000 psi (measured at ambient temperature) hydrogen pressure. It is possible, of course, to have different behavior under more severe conditions or when a hydrogenation catalyst is present.

There are several potential pathways by which the demetallation might have occurred. The metal-containing components might have been adsorbed on the surface of coke. It is also possible that such compounds might have been trapped in the coke matrix during its formation. The third possibility is that the metal components became chemical constituents of the coke. If either of the latter two routes is valid, then the extent of demetallation would depend upon the amount of coke produced during the reaction. If the demetallation occurs through adsorption, the extent of demetallation would not only depend upon the amount of coke produced but could also depend upon the amount of unconverted coal present in the system. Several experiments were made to shed light on the mechanism of demetallation using chars made from cellulose and also using activated carbon in place of coal.

Cellulose when heated to high temperatures (330°C-475°C) in an inert atmosphere yields chars whose elemental analysis and infrared spectra resemble those of coal.<sup>(12)</sup> Chars can be liquefied similar to coal. When a feed containing 90 wt.% Maya ATB and 10 wt.% of a char made from cellulose at 415°C-425°C and under 5.2 MPa nitrogen pressure was coprocessed at 425°C, 80% of the vanadium content was rejected along with coke after one hour reaction time. Under similar conditions, 69% of the vanadium was removed using 10 wt.% coal. It was further observed that the liquefaction and the demetallation behavior of char and its IR spectrum were dependent upon the conditions under which it was synthesized. It can be concluded that the demetallation is dependent upon the chemical nature of the liquefying substance. Since the char did not contain inorganics, the inorganic matter in coal is not responsible for the observed demetallation. Activated carbon in place of coal was equally effective in removing metals. There was no decrease in the yields of THF-insolubles at any reaction time indicating that as expected, the activated carbon, unlike coal, did not liquefy. The net amount of coke produced was higher relative to the processing of the Maya ATB alone. Thus, it is not clear if the demetallation observed with the activated carbon was due to the adsorption of the metal compounds on the activated carbon or it was due to the coke formed during the reaction.

Although the mechanism of demetallation is not clear from this series of experiments, it is possible to make some observations. It is unlikely that demetallation occurs due to the trapping of metal-containing compounds in the coke matrix as it forms, since only a small amount of coke formed can cause large amount of demetallation. In the early stages of coprocessing, when the yield of coke decreases due to the liquefaction of coal, the demetallation is seen to proceed at a rapid rate. This indicates that the demetallation is dependent not on the amount of coke present in the system (which includes the unreacted coal and the coke formed) but rather on the amount of coke formed during the reaction. Thus, physical adsorption of metal-containing compounds on coal is not likely the main mechanism of demetallation. Yan has studied the use of inorganic solids to demetallate heavy oils.<sup>(13)</sup> The extent of demetallation was found to be strongly dependent upon the processing temperature. At 700°F (371°C), metal removal was very small. The demetallation increased rapidly as the temperature was increased to 800°F (427°C). The amount of demetallation was independent of the surface area of the solids at higher temperatures. In a recent paper, Audeh and Yan reported that very low levels of demetallation are observed when an adsorbent such as silica gel is used in place of coal under the conditions of low coking.<sup>(14)</sup> This again indicates that adsorption is not the main mechanism of demetallation although it may be a contributing factor.

Demetallation through chemical reactions is a probable occurrence. It is known that the cokes produced from petroleum resids or coal liquids are anisotropic in nature.<sup>(15)</sup> The transformation of isotropic resid into anisotropic coke occurs via an intermediate anisotropic nematic liquid-crystal phase. The nematic liquid crystals consist of lamellar constituent molecules stacked parallel to each other. The coking process involves continuous polymerization of the constituent molecules of the liquid-crystal phase eventually forming a solid semicoke. The intermediate phase between the starting isotropic liquid and the solid semicoke is called mesophase. Large molecules containing planar regions tend to form mesophase. The asphaltenic molecules present in resids can form mesophase very easily. It has been reported that metals tend to concentrate in mesophase.<sup>(16)</sup> The organometallic structures found in petroleum are planar or have planar regions and hence are probably capable of forming mesophase. It is reasonable to expect that such structures would participate in the polymerization process leading to the formation of coke. It should be pointed out that such condensation need not involve any change in the nature of vanadium bonding. The formation of mesophase is initiated when the concentration of mesophase precursors reaches a threshold level. The enhanced demetallation in the presence of coal is perhaps due to the introduction of components (such as coal-derived asphaltenes) which participate in the process. Recent report that addition of deashed SRC (which is a liquid at the coprocessing temperatures) can demetallate heavy oils<sup>(10)</sup> support this hypothesis. Another cause for the enhanced demetallation may be the interaction between mesophase and solid surfaces. Solid coal particles may increase the amount of mesophase formed.<sup>(17)</sup> It has been observed in this laboratory, using a high-pressure and high-temperature microscope, that the presence of solids aids in the crystallization of mesophase under typical coprocessing conditions. The solid surface may act as a depository for condensed products.

#### HETEROATOM REMOVAL

Illinois No. 6 coal contained 2.98 wt.% sulfur and 0.67 wt.% nitrogen, while the Maya ATB contained 4.6 wt.% sulfur and 0.48 wt.% nitrogen. The amount of heteroatoms in the THF-solubles decreased on coprocessing. Treating 10:90 and 25:75 coal-to-resid feeds for one hour at 425°C removed 40-50% of the sulfur present in the resid to the coke and the product gas. A 35% sulfur removal was observed processing the Maya ATB alone under the same conditions. Similar observations were made on nitrogen removal. 55% of the nitrogen present in the feed was removed when 25:75 coal-to-resid ratio was used compared to 8% removal observed when the Maya ATB was processed alone. The results can be attributed to the association between heteroatoms and metals.

#### CONCLUSIONS

Illinois No. 6 bituminous coal was coprocessed with Maya ATB (650°F+) and with whole Boscan crude under thermal, non-catalytic conditions. Retrogressive reactions hinder production of THF-solubles when the demand for hydrogen increases as when the temperature is high or when the feed contains a high concentration of coal. Coprocessing results in a significant level of demetallation and heteroatom removal as these compounds are removed with the product coke. It is thus possible to achieve over 85% removal of vanadium. Very high levels of demetallation can also be achieved using char or activated carbon in place of coal.

## ACKNOWLEDGEMENTS

This work was supported by a grant from the U.S. Department of Energy (DE-FC-22 85PC80009). We are grateful to Pittsburgh Energy Technology Center for assistance in the experimental work.

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**TABLE 1**  
**ANALYSES OF ILLINOIS NO. 6 COAL**

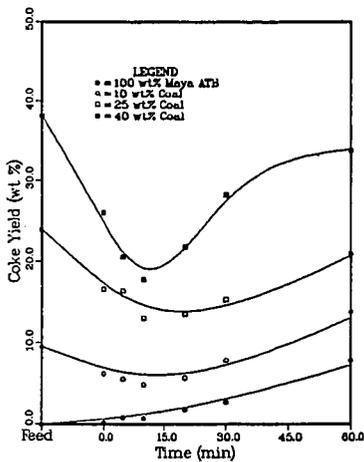
<u>PROXIMATE ANALYSIS (wt.%)</u>		<u>ULTIMATE ANALYSIS (wt.%)</u>	
Moisture	4.24	Hydrogen	5.04
Volatile Matter	36.93	Carbon	67.18
Fixed Carbon	48.18	Nitrogen	0.89
Ash	10.56	Sulfur	2.98
		Oxygen	13.26
		Ash	10.56

**TABLE 2**  
**ANALYSIS OF MAYA (650°F+) ATB RESID AND BOSCAN CRUDE**

	<u>MAYA ATB</u>	<u>BOSCAN CRUDE</u>
Gravity (°API)	8.8	10.0
H/C Atomic Ratio	1.52	1.55
S (wt.%)	4.60	5.30
N (wt.%)	0.48	0.60
V (ppm)	400	1100
Ni (ppm)	78	100

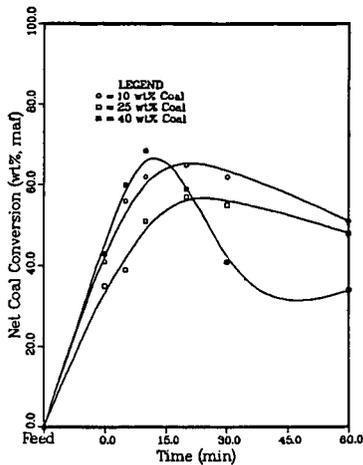
**TABLE 3**  
**TRANSFERABLE HYDROGEN IN RESIDS AND COAL LIQUIDS(10)**

	TRANSFERABLE HYDROGEN	
	(mmol/g)	(% of total H)
Maya (650°F+)	2.1	4
Boscan (650°F+)	1.9	4
Wilsonville VTB	3.7	11
Wilsonville ITSL Solvent	7.5	16



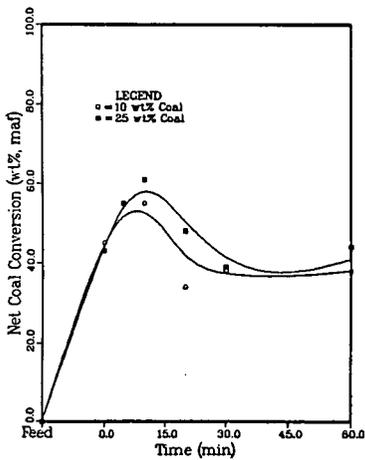
EFFECT OF COAL CONCENTRATION ON COKE YIELDS FROM MAYA ATB AT 425 C

Figure 1



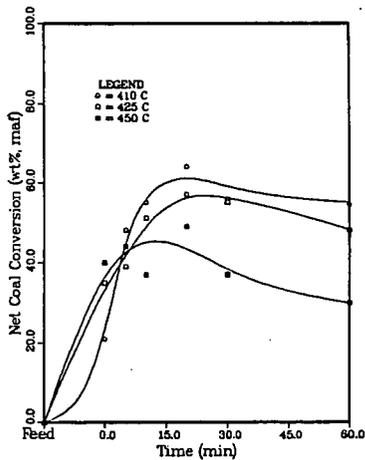
EFFECT OF COAL CONCENTRATION ON COAL CONVERSION IN MAYA ATB AT 425 C

Figure 2



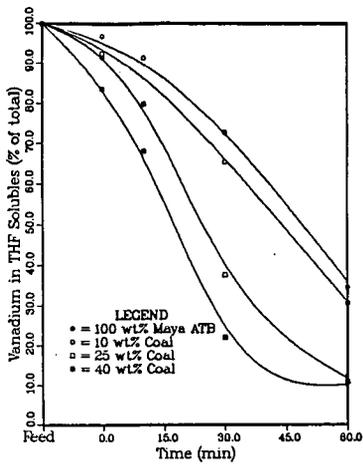
EFFECT OF COAL CONCENTRATION ON COAL CONVERSION IN BOSCAN CRUDE AT 425 C

Figure 3



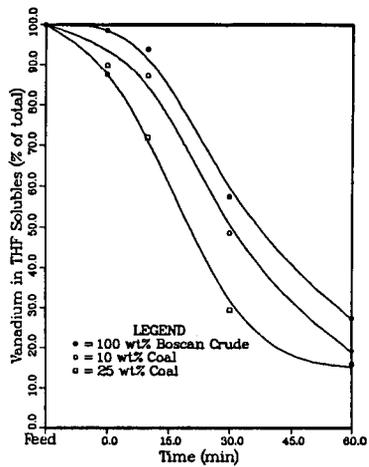
EFFECT OF TEMPERATURE ON NET COAL CONVERSION IN MAYA ATB AND 25 WT% COAL

Figure 4



EFFECT OF COAL CONCENTRATION ON REMOVAL OF VANADIUM FROM MAYA ATB AT 425 C

Figure 5



EFFECT OF COAL CONCENTRATION ON REMOVAL OF VANADIUM FROM BOSCAN CRUDE AT 425 C

Figure 6