

## THE INFLUENCE OF THE PETROLEUM RESIDUA AND CATALYST TYPE ON COPROCESSING

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### Introduction

The goal of coprocessing heavy petroleum crudes and residua with coal is to simultaneously upgrade both materials into higher quality liquid products. Among the benefits of coprocessing is that it offers a bridge between the present petroleum-based technology and the synthetic fuels coal-based technology of the future. Coal and petroleum residua are both low value hydrocarbon resources, which through coprocessing can be transformed into higher quality and higher value synthetic fuels. The nature of the synthetic fuel produced from coprocessing would be quite different from that of conventional coal liquefaction using a coal-derived recycle stream. The highly aromatic coal-derived synthetic fuel would already be combined with ample quantities of highly paraffinic materials, making the product more similar to fuels used today. In addition, the presence of coal-derived synthetic fuel in the coprocessing product would serve as an octane booster. Another advantage of coprocessing is the elimination or minimization of the coal-derived recycle stream used in conventional coal liquefaction technology.

A number of petroleum materials have been surveyed for their ability to solvate coal and to participate in the upgrading process. (1-4) Both bituminous and subbituminous coals have been successfully used in combined processing (5,6). Using catalytic hydrotreatment with small particle size catalysts, coal conversion of greater than 80% have been achieved for both bituminous and subbituminous coals when using petroleum solvents. (5) The interaction between the petroleum solvent and the coal is complex. Synergistic interactions may exist at different concentration levels of coal and petroleum solvent. In this work the interaction between the petroleum solvent and coal at different solvent to coal ratios is examined in terms of product yield and coal conversion. The chemical composition of the petroleum solvent is substantially different from coal-derived solvents. (1) The effect of improvement in the solvent's ability to donate hydrogen through the addition of hydroaromatic compounds on the final product slate has been investigated. Because of the complexity and diversity of the coal-petroleum system, catalyst type may strongly influence one material while not being particularly effective with the other. Examination of the effect of catalyst type on the upgrading of the petroleum residuum and on coprocessing can lead to catalysts that are specifically tailored for enhancement of the coprocessing product slate. In addition, the coprocessing product may be enhanced through a combination of a first stage reaction using a mineral additive and a second stage with a commercial hydrogenation catalyst. This concept is explored in this work.

### Experimental

#### Materials and Feedstocks

The solvents used in this study were heavy petroleum crudes and residua which were supplied by Cities Service Research and Development Company. The specific petroleum materials used were Maya toppler long resid (TLR) and West Texas vacuum short resid (VSR). A bituminous Illinois #6 coal, supplied by Wilsonville Advanced

Coal Liquefaction Research and Development Facility, was used as the coal feedstock. The elemental analyses of these feedstocks are given in Table 1. The catalysts used in these reactions were mineralogical pyrite ground to -200 mesh and powdered presulfided Shell 324 NiMo/Al<sub>2</sub>O<sub>3</sub> that was obtained by grinding 1/16 inch presulfided extrudates. For the hydrogen donor addition experiments, tetralin, 1,2,3,4-tetrahydroquinoline (THQ) and 9,10-dihydrophenanthrene (DHP) were obtained from Aldrich.

### Equipment

The combined processing reactions were conducted in stainless steel micro-reactors which have been described in a previous work (7). The reactor has a volume of 50 cc which was charged with a liquid/solid slurry of 9 g and a hydrogen pressure of 1250 psig at ambient temperature at 100% excess hydrogen for the combined processing reactions. A 6g charge was used for the petroleum upgrading experiments. The pressure of 1250 psig at ambient temperature corresponds to approximately 2950 psig at reaction temperature calculated by means of the ideal gas law and ignoring any solubility of the hydrogen. A recovery of greater than 97% of the original charge was obtained from the coprocessing reactions.

### Experimental Procedures

A series of experiments were performed using Illinois #6 coal and West Texas VSR in which the solvent to coal ratio was varied from 10:1 to 1:4. The percentage coal present in these reactions ranged from 9.1% to 80%. For comparison, reactions were also performed in which no coal was present and in which no solvent was present. The reaction products were analyzed by a solvent extraction procedure in which the reaction products were sequentially extracted with pentane, benzene, and methylene chloride/methanol. The products obtained were defined as oil, pentane soluble; asphaltenes, pentane insoluble, benzene soluble; preasphaltenes, benzene insoluble, methylene chloride/methanol soluble; and insoluble organic matter (IOM), methylene chloride/methanol insoluble. Analyses performed on the products of the coprocessing reactions were: (1) viscosity at 60°C according to ASTM D-2171 using a Canon-Manning capillary viscometer, (2) specific gravity at 60°F according to ASTM D-70 and ASTM D-287, and (3) Conradson Carbon according to ASTM D-189.

The coprocessing reactions with the addition of hydroaromatic solvents were performed at 425°C, in a N<sub>2</sub> or H<sub>2</sub> atmosphere, for 30 minutes. The charge to the reactor was 3 grams of Illinois #6 coal and 6 grams of total solvent. The solvent was composed of 0.3 g, 1.1 g or 3.0 g of hydroaromatic compound with 5.7 g, 4.9 g or 3.0 g of Maya TLR, respectively. The pressure of H<sub>2</sub> charged to the reactor was 300 psig and of H<sub>2</sub> was 1250 psig.

Mineralogical pyrite and small particle size NiMo/Al<sub>2</sub>O<sub>3</sub>, ground from presulfided 1/16" extrudates were used to determine the effect of catalyst type on the upgrading of West Texas VSR and on coprocessing of Illinois #6 coal with West Texas VSR and Maya TLR. The reactions were performed at 425°C, 30 minutes, with 6 g of petroleum solvent, 3 g of coal and 1 g of catalyst.

The reaction conditions for single stage processing were 60 minutes, 425°C, 1250 psig H<sub>2</sub> charge, and 2 grams of catalyst. The catalysts used were pyrite, NiMo/Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>S which was generated in situ from the reaction of carbon disulfide with hydrogen.

The two stage experiments were performed as two sequential 30 minute reactions at 425°C, 1250 psig H<sub>2</sub> charge, 9 grams of petroleum/coal slurry and 1 gram of catalyst in each stage. The gas weight was determined after the first stage; the reactor was then opened and the second stage catalyst was added. After repressurizing with hydrogen, a second reaction was performed. The total gases were calculated through the addition of the gases produced during each stage. The first stage mineral catalyst was not removed and was present in the second stage reactions. For the calculations of the final amount of reacted FeS<sub>2</sub> remaining, the FeS<sub>2</sub> is assumed to react completely to form FeS.

### Results and Discussion

To tailor the coal-resid system for maximal yields of high quality liquid products, the influence of the petroleum solvent on the products obtained from coprocessing must be known. Addition of additives such as hydrogen donors may enhance the desired product yield. With two complex and diverse materials present, catalyst selection becomes more complex, for a particular catalyst may catalyze reactions of one of the materials much more strongly than the other. Combination of catalyst types may prove feasible to achieve the many diverse reactions needed to achieve high coal conversion and high yields of liquid product simultaneously.

#### The Effect of Solvent to Coal Ratio on Coprocessing

One of the advantages of coprocessing is the elimination or minimization of the coal-derived recycle stream needed in conventional coal liquefaction technology. In conventional liquefaction the solvent to coal ratio usually ranges from 1:1 to 3:1 with the ratio being dependent on the materials used and the operability and range of the mechanical equipment. In coprocessing, a limitation on the solvent to coal ratio will still exist due to physical constraints. In this study, however, we investigated a wide range of solvent to coal ratios to observe the effect of the solvent concentration on the final product distributions obtained. At low solvent to coal ratios, the mass transfer of the hydrogen to the coal may be inhibited. At high solvent to coal ratios, the coal may serve as an extender or enhancer to the petroleum material, by synergistically promoting the upgrading of the petroleum material.

The range of solvent to coal ratios examined was 10:1 to 1:4. The reactions were performed at the coprocessing conditions given in the Experimental section. In these experiments, the reactor liquid plus solid loading was kept constant so that nine (9) grams of petroleum-coal slurry was introduced each time. The amount of catalyst used in each reaction remained constant at one gram. Since both the percentage solvent and coal changed in each reaction, experimental results must be expressed independently of the amounts of petroleum solvent and coal. The hydrogen consumption and coal conversion can be used directly. The amount of material upgraded to oil can also be determined independently of the system by defining it as oil production which is the grams of oil produced (final oil-initial oil) divided by amount of the upgradable material. The upgradable material is composed of maf coal and the nonpentane soluble fraction of the solvent.

As the percentage of coal increased from 9.1% to 50%, coal conversion increased from 42.6% to 87.2% as presented in Figure 1. At increasingly higher levels of coal, the amount of coal conversion steadily decreased. When no solvent was present, a coal conversion of 33% was obtained. Hydrogen consumption, shown in Figure 2, followed the same trend, giving a maximum at 50% coal loading. The percent oil production achieved at coal percentages of 25% to 50% was constant at

~33% as shown in Figure 3. A similar value of 28% oil production was obtained at 9.1% coal loading. At higher coal loading, the percent oil production decreased rapidly, falling to ~15% at 80 and 100% coal loading.

The complexity of the coprocessing reaction system and the many reactions which occur simultaneously make it difficult to ascertain the reasons for the behavior observed as the solvent to coal ratio was varied. The interrelation-ship among coal conversion, oil production and hydrogen consumption is evident. Hydrogen consumption is directly related to the amount of coal conversion achieved and the amount of oil production observed. The behaviors of coal conversion and oil production as a function of the increased weight percentage of coal in the reactions are more difficult to explain.

Numerous factors may be influencing these behaviors and causing interactive effects. Some of the factors involved may be mass transfer effects, concentration of the coal and solvent blends, compositional effect of the blend of liquefied materials, catalyst poisoning and deactivation and solvolysis of the dissolving coal matrix by the liquid phase present. Since in coprocessing, the molecular composition varies rather dramatically from high solvent to coal ratios to low solvent to coal ratios, solvolysis of the dissolving coal matrix by the liquid present in the reactor may be an important factor in the observed behavior of coal conversion and oil production. The 50% blend of coal to petroleum solvent may provide a good coal dissolving solvent. Mass transfer of  $H_2$  to the dissolving coal matrix is most likely better achieved when a higher proportion of solvent is present. Therefore, the higher yields of oil and of coal conversion achieved at higher solvent to coal ratios compared to the lower ratios may be due to the increased availability of hydrogen to the coal. The decline at high coal loadings may be due to mass transfer limitations on  $H_2$ . In this system, however, it must be remembered that the coal to catalyst ratio increased as the coal loading increased; or stated in another manner, the catalyst loading remained constant as the percent coal in the reaction increased. The decline in coal conversion and oil production may be due to catalyst deactivation and rapid loss of activity in the concentrated coal matrix. As stated earlier, the exact reasons for the behavior observed can not be pinpointed. One possible rationale is that several different mechanisms are occurring and that different mechanisms are dominant at different coal concentrations.

Analyses of some of the physical properties of coprocessing reaction products have been performed and are compared to the original coprocessing solvent, West Texas VSR, and hydrotreated West Texas VSR in Table 2. Products obtained from reactions using a 10:1 solvent to coal ratio and a 2:1 solvent to coal ratio were examined. The physical properties evaluated were viscosity, degrees API gravity, specific gravity and Conradson Carbon. In the hydrotreatment of West Texas VSR the viscosity of the resid at 60° C decreased from 324.8 to 1.07 poise; Conradson Carbon decreased by almost half and °API gravity almost doubled. The viscosities of the materials obtained from coprocessing have much lower viscosities than the original residuum. In the coprocessing reaction with a 10 to 1 solvent to coal ratio the viscosity was reduced to 0.363 poise and the Conradson Carbon was lowered to 13.49. The presence of the coal may be producing synergy in that the viscosity was reduced to less than that of West Texas VSR hydrotreated in the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> but in the absence of coal. Increased coal concentration resulted in an increase in the viscosity to 22.7 poise and an increase in Conradson Carbon to 17.78.

#### Effect of Hydrogen Donor Addition on Coprocessing

Recent studies have shown the importance of hydrogen donors and transfer agents in the dissolution of coal (8-11). The role and importance of hydrogen transfer in

coprocessing are investigated herein by studying the effect of the addition of hydrogen donor compounds such as tetralin, 1,2,3,4-tetrahydroquinoline (THQ) and 9,10-dihydrophenanthrene (DHP) to the petroleum solvent used in coprocessing. In these coprocessing reactions, the coprocessing solvent was Maya TLR and the coal was Illinois #6. Three levels of donable hydrogen have been studied, 0.15%, 0.55% and 1.5% in N<sub>2</sub> and H<sub>2</sub> atmospheres. The effect of these additions on oil production and coal conversion obtained from coprocessing reactions is presented in Table 3. In the coprocessing reactions in which tetralin was added, both coal conversion and oil production increased when comparing N<sub>2</sub> to H<sub>2</sub> atmospheres for equivalent donable hydrogen addition. However, at the 0.15% tetralin addition level in the H<sub>2</sub> atmosphere, the product slate was very similar to that obtained in H<sub>2</sub> using only Maya TLR. The effect of a H<sub>2</sub> atmosphere on coal conversion was dramatic, increasing coal conversion from 19.6% in N<sub>2</sub> to 58.9% in H<sub>2</sub> at the lowest donor hydrogen addition level. When 1.5% donable hydrogen was present in the tetralin Maya/TLR system, coal conversion in N<sub>2</sub> was 62.1% which was essentially equivalent to the coal conversion obtained with 0.15% donable hydrogen in a H<sub>2</sub> atmosphere. In these reactions, it appears that the form that the hydrogen is in, whether molecular hydrogen or donable hydrogen from hydroaromatic compounds, is not critical. The necessary criterion for coal conversion to be achieved is for the hydrogen to be present in a form which can be utilized by the coal. The use of a H<sub>2</sub> atmosphere to the tetralin/Maya TLR system with 1.5% donable hydrogen further aided in coal conversion, indicating that a hydrogen deficiency existed in the N<sub>2</sub> atmosphere even when a significant amount of tetralin was present.

As in the tetralin system, the effect of the H<sub>2</sub> compared to the N<sub>2</sub> atmosphere on the THQ/Maya TLR system was dramatic. At 0.15% donable hydrogen, coal conversion increased from 23.2% in N<sub>2</sub> to 58.0% in H<sub>2</sub>. In contrast, coal conversion in the THQ/Maya TLR system at the highest donable hydrogen level was insensitive to atmosphere. In N<sub>2</sub>, 89.0% coal conversion was observed while in H<sub>2</sub>, 90.4%, was seen. The amount of pentane soluble materials produced was the same in N<sub>2</sub> regardless of the amount of donable hydrogen. In H<sub>2</sub>, only a small increase in pentane solubles was observed by increasing the amount of donable hydrogen from 0.15% to 1.5%.

Oil production increased in the 1.5% donable hydrogen tetralin system compared to the 0.15% tetralin system. A possible reason for the increased oil production is the availability of more hydrogen to the dissolving coal matrix resulting in an increased amount of hydrogenation occurring and the production of hydrogenated products soluble in pentane. The change in solvent composition due to the presence of the hydroaromatic may also be partially responsible for the observed change in percent oil production. Further elucidation of the role of hydrogen donor compounds in coprocessing was sought by comparing the effect of DHP on the product slate to that of tetralin and THQ. The choice of DHP was based upon its comparable ability to convert coal as THQ (12) and upon the fact that it is a hydrocarbon without any of the detrimental characteristics generally associated with nitrogen containing hydroaromatics. When compared at a 0.55% donable hydrogen level, DHP converted more coal to soluble material than THQ and yielded a higher percent oil production than did tetralin.

Comparing the low levels of donable hydrogen using tetralin and THQ showed remarkably similar product distributions in both H<sub>2</sub> and N<sub>2</sub> atmospheres. A contrast is observed, however, when comparing these two at the highest donor level. In THQ, a markedly lower amount of pentane soluble material was produced than in tetralin. The percent oil production in the 1.5% donable hydrogen system in N<sub>2</sub> was -30.7% in THQ and 15.9% in tetralin; likewise, in H<sub>2</sub> the values were 4.0% in THQ and 25.0% in tetralin. The product slate obtained from THQ contained many more asphaltenes than that from tetralin.

These results are in agreement with those observed in coal liquefaction where hydroaromatics having a nitrogen functionality readily dissolve coal. The reasons for their effectiveness resulted from their ability to penetrate and swell coal and their ability to transfer hydrogen. These good features of the nitrogen containing compounds were, however, overridden by their propensity to form adducts with themselves and with coal-derived materials. This adduct formation has been extensively studied by Cronauer (13). The adduct formation is readily apparent in the increased levels of asphaltenes observed during the coprocessing reaction containing THQ.

#### Effect of Catalyst Type on Coprocessing

The effect of catalyst type on the coprocessing of heavy crudes and residua with coal has been investigated using a mineralogical pyrite and a small particle size NiMo on  $\gamma$ - $Al_2O_3$ . Both of these catalysts were used to study their effect on upgrading residua and on the product slate from coprocessing. In the resid upgrading experiments, West Texas VSR was used; in the coprocessing reactions both West Texas VSR and Maya TLR were used. In Table 4, upgrading reactions of West Texas VSR are compared among the thermal reaction, the reaction containing pyrite and the reaction with small particle size NiMo/ $Al_2O_3$  catalyst. The original solubility distribution obtained prior to reaction is given as a reference. Compared to the original West Texas VSR, the thermal reaction produced gases and IOM, lost oil, and increased slightly the amount of asphaltenes present. When pyrite was added as a catalyst, the asphaltenes were virtually eliminated from the residuum, producing primarily pentane soluble oil. Small amounts of gases, preasphaltenes and IOM were also produced. In contrast, the presence of a small particle size NiMo/ $Al_2O_3$  catalyst did not change the oil fraction but did reduce the asphaltene fraction by ~80% producing gas, preasphaltenes and IOM in almost equal amounts.

The effect of pyrite and NiMo/ $Al_2O_3$  addition on the products obtained from coprocessing are presented in Table 5. Four different reactions are compared with West Texas VSR: (1) thermal reaction (2) two reactions with pyrite and (3) reaction using small particle size NiMo/ $Al_2O_3$ . The conditions for all the reactions were the same; both pyrite and NiMo/ $Al_2O_3$  were introduced at the same gram level. The pyrite reaction produced the most coal conversion, 87.6%, compared to 79.3% for the NiMo/ $Al_2O_3$  and 55.0% for the thermal reaction. In terms of pentane soluble oils, the amount produced by the pyrite reaction fell between that obtained by the thermal reaction and by the commercial catalyst. Due to the effect observed on the residuum alone, pretreatment of the solvent with pyrite and hydrogen prior to using as a coprocessing solvent was thought to be possibly beneficial in improving the entire product slate. However, comparison of the product slate using the hydrotreated West Texas VSR to that obtained using the original showed little improvement that could be attributed to hydrotreatment. One possible explanation for this behavior is that the primary effect of the pyrite is in the upgrading of the residuum asphaltenes to pentane solubles and that the reaction producing pentane solubles from coal is not substantially affected by the presence of pyrite. Thus, the majority of the pentane solubles produced from the coprocessing reaction using the original West Texas VSR was produced most probably from the residuum and not from coal. In the hydrogen pretreatment case, most of the upgrading of the residuum had occurred prior to the coprocessing reaction leaving little material from the residuum for further upgrading. Consequently, little change in the product slate was observed between the original and hydrotreated material. When pyrite was used in coprocessing experiments using Maya TLR, similar results were obtained.

### Single Stage and Two Stage Coprocessing Reactions

Two stage processing using sequential and possibly different catalysts in the first and second stages may produce a more favorable product slate from coprocessing as well as a more efficient use of hydrogen. Two sets of experiments were performed to investigate the effects of two stage processing and sequential catalytic treatment on coprocessing. One was a series of one hour reactions in which pyrite, NiMo/Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>S were used individually as catalysts and in combination. These results are given in Table 6. In the second set two stage experiments were run for a total of one hour but after the first half hour the gases were vented, a new catalyst was added, and fresh hydrogen was charged. The catalyst charge at the end of both reactions was 2 grams.

The single stage one hour reactions showed similar results to that observed previously. The coprocessing reaction using pyrite catalyst again produced the highest coal conversion; however, the conversions observed from Shell 324 NiMo/Al<sub>2</sub>O<sub>3</sub> were also both above 80%. The percent oil production observed is given below for the reactions containing the different catalyst

NiMo/Al<sub>2</sub>O<sub>3</sub> > Pyrite + NiMo/Al<sub>2</sub>O<sub>3</sub> > Pyrite > H<sub>2</sub>S > Thermal 1)

The small particle size NiMo/Al<sub>2</sub>O<sub>3</sub> is by far the most effective catalyst in producing pentane soluble oil.

To test the hypothesis that H<sub>2</sub>S was the catalytic agent rather FeS<sub>2</sub> in the reactions using the pyrite catalyst, CS<sub>2</sub> which readily reacts with H<sub>2</sub> to form H<sub>2</sub>S was added to the reaction. The amount of CS<sub>2</sub> added was equivalent to that needed to produce the same amount of H<sub>2</sub>S as would be generated from FeS<sub>2</sub>. Under these conditions, the product slate obtained did not vary significantly from the thermal reaction. This result suggests then that the important catalyst in the reactions using pyrite is the pyrite itself or its reduced form, not the evolved H<sub>2</sub>S.

In two stage processing, four sets of experiments were performed: thermal for the first stage and thermal for the second stage; pyrite in both stages; then pyrite in the first stage with NiMo/Al<sub>2</sub>O<sub>3</sub> in the second stage and NiMo/Al<sub>2</sub>O<sub>3</sub> in both stages. The highest amount of coal conversion achieved, 92.2%, occurred in the experiments using pyrite in both stages. The pyrite/NiMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>/NiMo/Al<sub>2</sub>O<sub>3</sub> reactions also produced high coal conversions, 85.9% and 84.1%, respectively. The oil production from the two stage coprocessing showed the same order as did the single stage experiments. The reaction with NiMo/Al<sub>2</sub>O<sub>3</sub> in both stages produced the most oil while the combination of pyrite/NiMo/Al<sub>2</sub>O<sub>3</sub> was second.

### Summary and Conclusions

In coprocessing, the solvent to coal ratio has a definite influence on the product distribution, oil production and coal conversion. The highest coal conversion occurred at a 50% coal concentration level and maximal oil production was achieved at 30 to 50% coal concentration. When reacted in a hydrogen atmosphere, the addition of hydrogen donor compounds to the coprocessing solvent definitely influenced the products from coprocessing. At equivalent donable hydrogen levels, DHP produced the highest coal conversion and oil production. At and above the 0.55% donable hydrogen level, THQ was very effective in converting coal but was detrimental to oil production. In general, the hydrogen donor compounds without heteroatoms appear to be more effective in producing oil than the nitrogen containing hydroaromatics.

The catalyst type is important in coprocessing since different catalysts influence different reactions in the two materials. Pyrite affected the upgrading of the residium by promoting the conversion of petroleum asphaltenes into oil. In coprocessing, the notable effect of pyrite was the reduction of the IOM levels and consequent increase in coal conversion. Compared to the thermal reaction, pyrite was effective in increasing the oil production in coprocessing. The small particle size NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, however, was still more effective in hydrogenating the dissolving coal matrix and producing pentane soluble oil. In two stage processing, the combination of pyrite in the first stage and NiMo/Al<sub>2</sub>O<sub>3</sub> in the second produced a much improved product slate compared to thermal processing. The highest oil production and coal conversion were, however, still achieved by using NiMo/Al<sub>2</sub>O<sub>3</sub> in both stages.

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Table 1  
Analysis of Petroleum Solvents

Starting Materials	Oil	Asphaltenes	C	H	N	S	O by difference	Ash
Illinois #6 Coal			68.4	4.4	1.4	3.2	12.0	10.6
Maya TLR	79.5	20.5	85.3	10.8	0.51	4.19		0.082
West Texas VSR	86.2	13.8	86.1	10.4	0.44	3.33		0.012

Table 2  
Physical Properties Comparison

Material Tested	Viscosity 60°C, poise	°API	Specific Gravity, 60°C	Conradson Carbon
West Texas VSR	324.8	7.9	1.015	16.4
Product from 10:1 West Texas VSR to Coal Coproprocessing Reaction	0.363	13.39	0.9766	13.49
Product from 2:1 West Texas VSR to Coal Coproprocessing Reaction	22.7	7.1	1.021	17.78
Hydrotreated West Texas VSR	1.07	15.9	0.96	9.34

Table 3  
Effect of Hydrogen Donor Addition on Coprocessing

	Oil Production, %		Coal Conversion, %	
	H <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub>
Maya TLR	11.8	-11.6	60.0	24.1
0.15% Donable Hydrogen Added				
Tetralin	11.2	- 9.2	58.9	19.6
THQ	6.7	-12.3	58.0	23.2
0.55% Donable Hydrogen Added				
Tetralin	10.5	0.7	58.8	39.3
THQ	2.5	-11.4	75.4	52.7
9,10-DHP	17.5	4.6	81.0	58.8
1.5% Donable Hydrogen Added				
Tetralin	25.0	15.9	81.0	62.1
THQ	4.0	-30.7	90.4	89.0

Table 4  
Effect of Catalyst on Upgrading of West Texas VSR

	West Texas VSR Original	West Texas VSR	West Texas VSR	West Texas VSR
Catalyst	NA	None	Pyrite	NiMo/Al <sub>2</sub> O <sub>3</sub>
Coal	NA	None	None	None
Gas	0.0	3.5	1.9	3.9
Oil	86.2	79.1	95.3	86.6
Asphaltenes	13.8	15.0	0.6	3.1
Preasphaltenes	0.0	0.1	1.2	2.8
IOM	0.0	2.3	1.0	3.6
H <sub>2</sub> Consumption, %	NA*	4.9	15.4	31.9

\*NA: not applicable

Reaction Time: 30 minutes

Table 5  
Effect of Catalyst on the Coprocessing Reactions

Catalyst	West Texas	West Texas	Hydrotreated*	West Texas
	VSR Original	VSR	West Texas	VSR
	None	Pyrite	Pyrite	NiMo/Al <sub>2</sub> O <sub>3</sub>
Gas	4.2	3.3	3.0	4.3
Oil	58.6	67.1	68.3	72.9
Asphaltenes	15.2	19.6	16.6	13.4
Preasphaltenes	8.2	6.2	6.6	3.0
IOM	13.8	3.8	5.5	6.4
Coal Conversion, %	55.5	87.6	82.3	79.3
H <sub>2</sub> Consumption, %	24.2	37.9	30.0	52.9
Oil Production, %	-2.1	18.8	2.25	33.1

\*The solvent was hydrotreated in the presence of pyrite.

Catalyst	Maya TLR	Maya TLR	Maya TLR
	None	Pyrite	NiMo/Al <sub>2</sub> O <sub>3</sub>
Gas	4.3	3.3	4.7
Oil	60.1	64.6	69.7
Asphaltenes	14.7	19.1	16.4
Preasphaltenes	8.5	7.1	2.2
IOM	12.4	5.9	7.1
Coal Conversion, %	60.0	81.0	77.0
H <sub>2</sub> Consumption, %	18.9	40.1	55.6
Oil Production, %	11.7	21.5	32.9

Table 6  
Single Stage Coprocessing Using West Texas VSR

Catalyst	Thermal	~0.32g CS <sub>2</sub>	Pyrite	NiMo/Al <sub>2</sub> O <sub>3</sub>	Pyrite & NiMo/Al <sub>2</sub> O <sub>3</sub>
Coal Conversion, %	58.2	57.4	89.2	85.0	83.7
Hydrogen Consumption, %	30.4	33.3	57.1	72.5	66.5
Oil Production, %	-8.3	-6.9	23.9	54.3	39.3

Two Stage Coprocessing Using West Texas VSR

First Stage Catalyst	None	Pyrite	Pyrite	NiMo/Al <sub>2</sub> O <sub>3</sub>
Second Stage	None	Pyrite	NiMo/Al <sub>2</sub> O <sub>3</sub>	NiMo/Al <sub>2</sub> O <sub>3</sub>
Coal Conversion, %	64.3	92.2	85.9	84.1
Hydrogen Consumption, %	14.5	27.5	35.6	41.1
Oil Production, %	-0.4	26.8	43.0	58.5

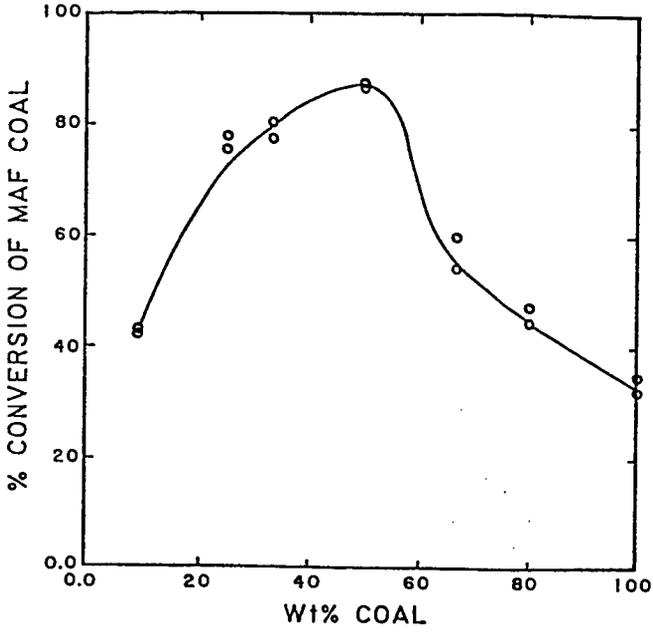


Figure 1. Coal Conversion as a Function of Coal Concentration

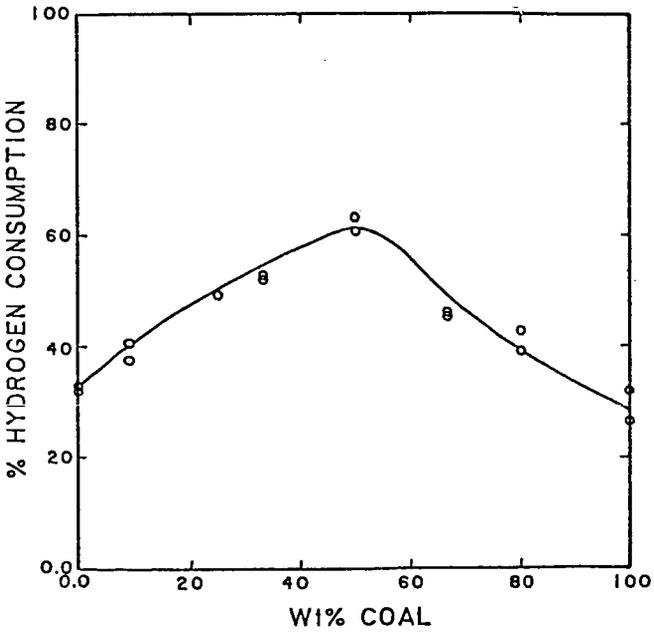


Figure 2. Hydrogen Consumption as a Function of Coal Concentration

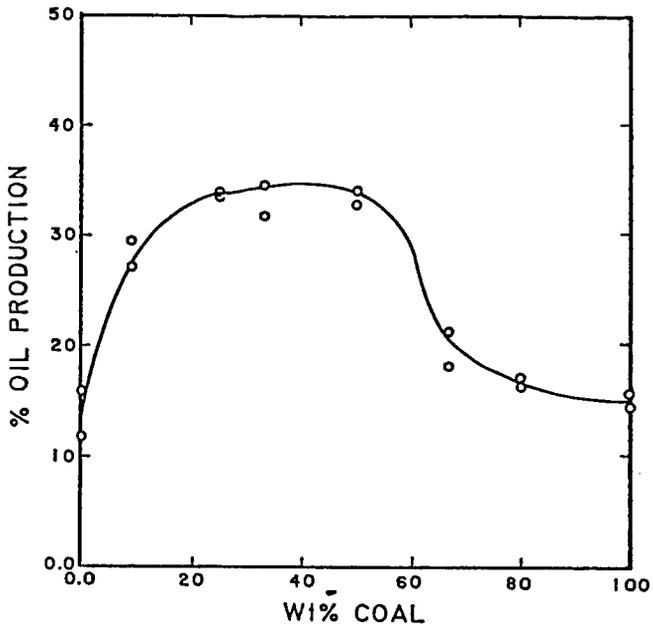


Figure 3. Oil Production as a Function of Coal Concentration