

The Roles and Importance of Hydrogen  
Donation and Catalysis in Coprocessing

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The roles and relative importance of hydrogen donation and catalysis in producing an upgraded product slate from coprocessing are explored. These effects are examined in two types of systems: the upgrading of residuum and the coprocessing of coal with residuum. In these experiments, the reactions were performed both thermally and catalytically in the presence and absence of tetralin (TET) to elucidate possible synergetic interactions between the catalyst and TET for increased coal conversion and an improved product slate.

Catalytic coprocessing which has been extensively reviewed by Monnier (1) generally produces an improved product slate and a higher degree of upgrading than does thermal coprocessing. Previous work performed by Curtis et al. (2,3) has shown the necessity of having highly accessible catalysts for coprocessing. Catalyst accessibility affects both the amount of coal conversion and the degree of upgrading of liquefied coal to soluble products and of petroleum asphaltene to pentane solubles. In this work, two highly accessible catalysts are investigated: an oil soluble catalyst, Mo naphthenate, and a presulfided commercial NiMo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalyst which was ground to -200 mesh to increase its accessibility and, hence, its activity. Mo naphthenate is a metal salt of an organic acid that is thought to be converted to an active catalyst under typical coprocessing conditions of high temperature and hydrogen atmosphere with a partial pressure of hydrogen sulfide. The active species is believed to be a noncolloidal metal sulfide (4,5).

The effect of hydrogen donor compounds on the products obtained from coprocessing has been examined by Curtis et al. (6). They concluded that hydrogen must be available for upgrading reactions to occur in coprocessing and that the hydrogen can be present either as molecular H<sub>2</sub> or donable hydrogen. The type of donor present affected the product slate; tetrahydroquinoline promoted coal conversion while tetralin and dihydrophenanthrene promoted the production of lighter products. When reacted in either a H<sub>2</sub> or N<sub>2</sub> atmosphere, concentrations of donable hydrogen at the 0.5 wt% level or higher were required to substantially affect coal conversion.

The objective of the current work is to investigate the effect of hydrogen donor addition in conjunction with catalytic hydrotreatment on the products obtained from upgrading residuum and coprocessing coal with petroleum residuum. The reaction products are evaluated in terms of solubility fractions, coal conversion to solubles in the solvent extraction scheme used and oil production. Oil production is defined as the amount of pentane solubles after reaction minus the initial pentane solubles divided by the upgradeable materials which are the pentane insoluble materials from maf coal and the residuum. In addition, the amount of hydrogen transferred to the products via gas-phase molecular hydrogen and donation by hydrogen donors is examined. The efficacy of donable hydrogen in promoting coal conversion and producing a high quality product slate is evaluated in thermal and catalytic coprocessing.

## Experimental

Upgrading and Coprocessing Reactions. Upgrading and coprocessing reactions were conducted in 50 ml stainless steel reactors, charged with 1250 psig H<sub>2</sub> cold (giving ~3000 psi at reaction temperature), 3g mf coal and 6g solvent. In the catalytic experiments, the catalyst charge was 1g of presulfided Shell 324 NiMo/Al<sub>2</sub>O<sub>3</sub> (0.044g Mo/g mf coal) ground to -200 mesh from 1/16" inch extrudates or, when using Mo naphthenate, the charge was 0.002g Mo/g mf coal. Reaction conditions were 30 minutes at 400°C for the thermal reactions and at 400° and 425°C for the NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo naphthenate reactions. The reactors were agitated at 700 cpm with 2 steel balls as agitation aids. Maya topped long resid (TLR) was used in the upgrading reactions and as the solvent in the coprocessing reactions. For coprocessing, Western Kentucky 9/14 bituminous coal was used. In the reactions using TET, one weight percent donable hydrogen was introduced; the TET composed about one-third of the solvent. Each upgrading or coprocessing reaction was, at least, duplicated and some were triplicated or quadruplicated. The activity of the NiMo/Al<sub>2</sub>O<sub>3</sub> was tested by reacting naphthalene in H<sub>2</sub> at 300°C. Naphthalene (NAPH) was nearly totally hydrogenated forming TET and decalin (DEC), producing the expected amount (7). The activity of the Mo naphthenate was also tested using naphthalene hydrogenation.

Product Analysis. The liquid products obtained from the upgrading and coprocessing reactions were analyzed using solvent extraction. The product fractions obtained were PS - pentane soluble; BS - benzene soluble, pentane insoluble; MCMS - methylene chloride/methanol soluble benzene soluble; THFS - tetrahydrofuran (THF) soluble, methylene chloride/methanol insoluble; IOM - insoluble organic matter, insoluble in THF. In the coprocessing reactions, coal conversion was calculated on the basis of the amount of material converted to soluble products and was corrected for the amount of IOM formed in the upgrading reactions with equivalent reaction conditions. The weight of the gas after reaction was measured and the hydrogen consumption was determined using PVT methods. The hydrogen consumption was calculated for each reaction.

The PS and BS fractions of the reaction products were analyzed by temperature programmed gas chromatography using a Varian Model 3700 equipped with a FID and a 60 m DB-5 J and W fused silica capillary column. The PS and BS fractions were analyzed for TET, DEC and NAPH to determine the amount of hydrogen transferred by TET to coal and the petroleum solvent. An internal standard, p-xylene, was used. Dihydronaphthalenes were not detected at detectability levels of  $2.4 \times 10^{-11}$ g.

Solvent extraction analysis of Maya TLR showed that the residuum before reaction was composed of 77.6% PS and 22.4% BS. TET, NAPH, and DEC were not observed in the chromatograms of the extracted residuum at the detectability levels of  $2.4 \times 10^{-11}$ g. Western Kentucky 9/14 coal was nearly insoluble at room temperature with less than 3% MCMS and 1% THFS being present.

## Discussion of Results

Upgrading of Residuum. The results from the thermal and catalytic upgrading reactions performed in the presence and absence of tetralin are given in Table 1. After Maya TLR was thermally upgraded in H<sub>2</sub>, the product solubility fractions obtained deviated only slightly from the unreacted residuum. The major change observed was the decrease of the BS fraction and the formation of lighter and heavier fractions. Hydrogen consumption during the reaction was 17.7 mmole of H<sub>2</sub> per 6 g charge of residuum. No TET, NAPH, or DEC was observed in the upgraded residuum. When TET was added at the one percent donable hydrogen level, the product analysis was similar to that without TET except that the IOM was greater

and the oil fraction was slightly less (Table 1). Both hydrogenation and dehydrogenation reactions involving TET were observed in the reaction system:



The dehydrogenation reaction was predominant and produced  $\text{H}_2$  while the hydrogenation reaction occurred to a lesser extent and consumed  $\text{H}_2$ . The net amount of hydrogen transferred was calculated by subtracting the  $\text{H}_2$  consumed by reaction 2 from that produced from reaction 1.

Table 1  
Upgrading of Residuum

| Product                                | Thermal<br>400°C |                   | NiMo/Al <sub>2</sub> O <sub>3</sub> |                   |             | Mo Naphthenate |             |                   |
|--|------------------|-------------------|-------------------------------------|-------------------|-------------|----------------|-------------|-------------------|
|  | Maya<br>TLR      | Maya<br>TLR + TET | Maya<br>TLR                         | Maya<br>TLR + TET | Maya<br>TLR | Maya<br>TLR    | Maya<br>TLR | Maya<br>TLR + TET |
| Gas                                    | 1.9              | 2.0               | 2.1                                 | 2.4               | 3.7         | 1.3            | 2.7         | 1.7               |
| PS                                     | 80.0             | 79.1              | 85.4                                | 88.1              | 86.0        | 80.5           | 86.7        | 85.2              |
| BS                                     | 17.1             | 17.4              | 7.7                                 | 5.3               | 4.5         | 15.9           | 9.9         | 11.0              |
| MCMS                                   | 0.4              | 0.3               | 0.7                                 | 1.2               | 0.4         | 0.6            | 0.2         | 0.9               |
| THFS                                   | 0.5              | 0.4               | 0.7                                 | 1.1               | 0.2         | 0.2            | 0.1         | 0.6               |
| IOM                                    | 0.1              | 0.8               | 3.4                                 | 1.9               | 5.2         | 1.5            | 0.4         | 0.6               |
| H <sub>2</sub> (g) Consumed,<br>mmoles | 19.5             | 14.2              | 31.3                                | 28.5              | 44.3        | 23.1           | 19.5        | 12.82             |
| H <sub>2</sub> Transferred,<br>mmoles  | NA*              | 2.6               | NA                                  | 0.5               | NA          | NA             | NA          | 0.62              |
| Total H <sub>2</sub> Used,<br>mmoles   | 19.5             | 16.8              | 31.3                                | 29.0              | 44.3        | 23.1           | 19.5        | 13.44             |
| Oil Production, %                      | 11.4             | 10.2              | 39.6                                | 53.5              | 44.1        | 16.0           | 43.6        | 39.5              |

NA: Not Applicable

In the thermal upgrading reaction with TET, 2.6 mmoles of  $\text{H}_2$  were transferred from TET to the residuum and an average of 14.2 mmoles of molecular hydrogen were consumed; therefore, the total hydrogen utilized by the residuum was 16.8 mmoles. Although the total amount of  $\text{H}_2$  transferred to and consumed by the residuum was greater in the reaction without TET, the increased hydrogen utilization by the residuum did not result in higher conversion of BS to PS; both reactions had nearly equivalent oil production.

**Catalytic Upgrading.** In the catalytic upgrading of Maya TLR with NiMo/Al<sub>2</sub>O<sub>3</sub>, two-thirds of the original BS were reacted, forming both lighter and heavier products (Table 1). A substantial amount of IOM, 3.4%, was produced compared to 0.1% in the thermal reaction. Catalytic hydrotreatment increased oil production to ~40% compared to 11.4% in the thermal reaction and hydrogen consumption was doubled. With NiMo/Al<sub>2</sub>O<sub>3</sub>, trace but measurable quantities of DEC, TET, and NAPH were observed in both the PS and BS product fractions. These results indicate that while substantial upgrading, i.e., high oil production and hydrogen consumption, occurred, coking also occurred, producing heavy products from the residuum.

In Table 2, the hydrogen contents of the PS and BS fractions from the upgrading reactions are given. Comparing the hydrogen content obtained from

catalytic to the thermal hydrogenation shows increases in the hydrogen content in both PS and BS fractions with NiMo/Al<sub>2</sub>O<sub>3</sub>. Thus, it appears that the increased hydrogen consumption resulted in a direct increase of the hydrogen content of the products. Comparison of the gas chromatograms obtained from both the PS and BS fractions prior to the reaction to that obtained after the thermal and catalytic reactions, however, did not show any visible changes in the product fingerprint. Changes in the compounds present or the addition of new compounds to these product fractions was not discernible in the chromatograms.

Table 2  
Elemental Composition of PS and BS Fractions from Upgrading Fractions

| Reactants | Temperature<br>°C | Catalyst                            | PS   |      | BS   |     |
|-----------|-------------------|-------------------------------------|------|------|------|-----|
|           |                   |                                     | % C  | % H  | % C  | % H |
| Maya TLR  | No Reaction       |                                     | 84.7 | 11.5 | NM*  | NM  |
|           |                   |                                     | 84.7 | 11.4 | NM   | NM  |
| Maya TLR  | 400               | None                                | 85.7 | 11.2 | 82.8 | 7.0 |
|           |                   |                                     | 85.6 | 11.4 | 83.1 | 7.0 |
| Maya TLR  | 400               | NiMo/Al <sub>2</sub> O <sub>3</sub> | 87.1 | 12.0 |      |     |
|           |                   |                                     | 86.8 | 11.8 | 83.9 | 8.5 |
| Maya TLR  | 400               | Mo Naphthenate                      | 84.9 | 11.3 | 82.7 | 6.5 |
|           |                   |                                     | 84.6 | 11.2 | 82.9 | 7.6 |
| Maya TLR  | 425               | Mo Naphthenate                      | 86.1 | 11.8 | 85.3 | 7.4 |
|           |                   |                                     | 88.0 | 12.1 | 85.3 | 7.3 |
| Maya TLR  | No Reaction       |                                     | 86.9 | 10.0 | NM   | NM  |
| + TET     |                   |                                     |      |      |      |     |
| Maya TLR  | 400               | None                                | 86.6 | 10.2 | 83.6 | 7.3 |
| + TET     |                   |                                     | 86.7 | 10.3 | 83.6 | 6.8 |
| Maya TLR  | 400               | NiMo/Al <sub>2</sub> O <sub>3</sub> | 87.9 | 10.9 | 79.3 | 8.7 |
| + TET     |                   |                                     | 87.6 | 10.8 | 78.2 | 8.4 |
| Maya TLR  | 425               | Mo Naphthenate                      | 86.8 | 10.3 | 84.9 | 7.3 |
| + TET     |                   |                                     | 87.0 | 10.3 | 84.3 | 7.4 |

\*NM: Not measured

When TET was added, a higher oil production (53.5%) and a decrease in BS were observed, although the total amount of heavy products (MCMS, THFS, and IOM) was similar to the reaction without TET. In these reactions, the catalyst and TET were both positive factors in producing PS materials. The molecular hydrogen consumed by the residuum was nearly equivalent to the reaction without TET. Only 0.39 mmoles of NAPH were produced which was approximately one-sixth that produced in the thermal reaction, indicating that hydrogenation of NAPH formed during the reaction to TET occurred in the presence of NiMo/Al<sub>2</sub>O<sub>3</sub>.

The catalytic upgrading reactions with Mo naphthenate were performed at 400 and 425°C. Compared to the thermal reaction, only a small change in product slate was observed with Mo naphthenate at 400 °C. At an increased reaction temperature of 425°C, the activity of the Mo naphthenate catalyst appeared to be enhanced since substantial increases in the upgrading of Maya TLR were observed; BS was converted to PS and only small amounts, <0.4%, of IOM were formed. An oil production of 43.6% was achieved yielding a substantial increase over that (16%) observed at 400°C. When TET was added, the product slate was very similar to that without TET although the total mmoles of H<sub>2</sub> utilized by the residuum was slightly less (Table 1). Only 0.44 mmoles of NAPH were produced, again indicating the rehydrogenation of NAPH to TET in the presence of Mo naphthenate.

Coprocessing of Coal with Residuum. In thermal coprocessing, Maya TLR and Western Kentucky 9/14 coal were reacted in the presence and absence of TET at a one percent donable hydrogen level (Table 3). The reaction without TET achieved 47.9% coal conversion which was corrected to account for the IOM produced from the reaction using Maya TLR alone. The thermal coprocessing reactions utilized 12.3 mmoles of H<sub>2</sub> and achieved an oil production of 12.6%. When TET was added, coal conversion increased to 69.7%; however, oil production was lowered to 4.1%. Although the consumption of molecular hydrogen in the reaction with TET was ~2 mmoles less than in the reaction without TET, an additional 6.5 mmoles of H<sub>2</sub> was transferred from TET to the coal/petroleum system, yielding the total of 16.6 mmoles of H<sub>2</sub> utilized by the coal/residuum system. The increased H<sub>2</sub> utilization by the coal/residuum/TET system resulted in increased coal conversion and in the production of the heavier product fractions but not in increased oil production.

Table 3  
Coprocessing of Coal with Residuum at 400°C

| Product Distribution, %             | Thermal         |                     | NiMo/Al <sub>2</sub> O <sub>3</sub> |                       | Mo Naphthenate  |
|-------------------------------------|-----------------|---------------------|-------------------------------------|-----------------------|-----------------|
|                                     | Maya TLR + Coal | Maya TLR Coal + TET | Maya TLR + Coal                     | Maya TLR + Coal + TET | Maya TLR + Coal |
| Gas                                 | 1.7             | 1.9                 | 1.8                                 | 1.7                   | 1.9             |
| PS                                  | 53.2            | 48.3                | 63.6                                | 60.1                  | 54.7            |
| BS                                  | 17.3            | 18.6                | 17.9                                | 22.3                  | 18.4            |
| MCMS                                | 5.8             | 9.9                 | 3.1                                 | 5.5                   | 8.6             |
| THFS                                | 5.9             | 9.0                 | 1.6                                 | 1.9                   | 8.6             |
| IOM                                 | 16.1            | 12.3                | 12.0                                | 8.5                   | 7.8             |
| H <sub>2</sub> (g) Consumed, mmoles | 12.3            | 10.1                | 30.2                                | 45.7                  | 26.7            |
| H <sub>2</sub> Transferred, mmoles  | NA*             | 6.5                 | NA*                                 | 0.6                   | NA*             |
| Total H <sub>2</sub> Used, mmoles   | 12.3            | 16.6                | 30.2                                | 46.3                  | 26.7            |
| Corrected Coal Conversion, %        | 47.9            | 69.7                | 68.9                                | 81.8                  | 78.5            |
| Oil Production, %                   | 12.6            | 4.1                 | 23.3                                | 29.2                  | 3.8             |
| BS Production, %                    | 5.6             | 12.9                | 7.7                                 | 22.1                  | 9.7             |

NA: Not Applicable

Catalytic Coprocessing. Catalytic coprocessing of Western Kentucky coal with Maya TLR was performed in the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo naphthenate catalysts and also with and without TET. Analysis of the products achieved from these reactions are given in Tables 3 and 4. Catalytic treatment with NiMo/Al<sub>2</sub>O<sub>3</sub> achieved 68.9% coal conversion which was greater than thermal coprocessing (47.9%) and nearly equivalent to thermal coprocessing with TET (69.7%). The oil production from catalytic coprocessing was more than double that of the thermal reactions with and without TET. In addition, higher hydrogen consumption and lower yields of the MCMS and THFS fractions were obtained, indicating a more highly upgraded product. The combined effect of hydrogen donation from TET and hydrotreatment from NiMo/Al<sub>2</sub>O<sub>3</sub> synergetically promoted coal conversion since the addition of TET produced a higher coal conversion (81.8%) than did the catalyst alone (68.9%) or the thermal reaction with TET (69.7%). High quality products were produced during

the reaction with oil production reaching nearly 30%, higher BS and lower levels of MCMS and THFS fractions were also observed. A higher consumption of molecular hydrogen occurred with TET addition than without. During the reaction, three times more NAPH was produced than DEC; however, the NAPH production of 0.53 mmoles in the catalytic reaction was low compared to 3.4 mmoles produced in the thermal reaction. As in the upgrading reactions, the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> caused NAPH to be rehydrogenated to TET and a consumer of H<sub>2</sub>. The total amount of H<sub>2</sub> utilized by the coal/resid/TET system was 46.3 mmoles which was higher than the thermal reaction or the NiMo/Al<sub>2</sub>O<sub>3</sub> reaction without TET. A small increase in the hydrogen content of the PS was observed compared to the thermal reaction as shown in Table 5.

Table 4  
Coproducting of Coal with Residuum at 425°C

| Product Distribution, %                | Thermal            | NiMo/Al <sub>2</sub> O <sub>3</sub> | Mo Naphthenate     |                          |
|--|--------------------|-------------------------------------|--------------------|--------------------------|
|  | Maya TLR<br>+ Coal | Maya TLR<br>+ Coal                  | Maya TLR<br>+ Coal | Maya TLR +<br>Coal + TET |
| Gas                                    | 4.1                | 3.5                                 | 4.0                | 3.6                      |
| PS                                     | 55.1               | 61.8                                | 66.8               | 61.9                     |
| BS                                     | 15.0               | 19.8                                | 19.3               | 21.8                     |
| MCMS                                   | 3.4                | 2.8                                 | 4.8                | 6.0                      |
| THFS                                   | 3.1                | 2.0                                 | 1.6                | 2.1                      |
| IOM                                    | 19.4               | 9.6                                 | 3.5                | 4.6                      |
| H <sub>2</sub> (g) Consumed,<br>mmoles | 29.8               | 41.6                                | 57.5               | 49.9                     |
| H <sub>2</sub> Transferred,<br>mmoles  | NA*                | NA                                  | NA                 | 2.6                      |
| Total H <sub>2</sub> Used,<br>mmoles   | 29.8               | 41.6                                | 57.5               | 52.5                     |
| Corrected Coal<br>Conversion, %        | 52.4               | 80.6                                | 89.5               | 89.3                     |
| Oil Production, %                      | 6.6                | 22.8                                | 31.4               | 32.0                     |
| BS Production, %                       | -1.8               | 11.3                                | 12.6               | 19.5                     |

\*NA: Not applicable

When Mo naphthenate was used in coprocessing at 400°C, coal conversion increased compared to the thermal reaction but little other effect was observed (Table 3). When the temperature was increased to 425°C (Table 4), substantial increases in coal conversion, hydrogen consumption, and oil production were observed in the reactions using Mo naphthenate. Since in these reactions both a catalyst was added and the temperature was increased, the effect of the temperature increase on the reaction must be ascertained. This effect can be evaluated from the data given in Table 4, by comparing the products produced during the thermal reaction at 425°C to those produced with Mo naphthenate. Since both coal conversion and oil production were low in the thermal reaction at 425°C, the high levels of coal conversion and oil production can then be attributed to the catalytic activity of Mo naphthenate not the temperature increase. Comparing Mo naphthenate to NiMo/Al<sub>2</sub>O<sub>3</sub> at 425°C, shows that Mo naphthenate is more active in terms of oil production and coal conversion even though the concentration level of Mo in the NiMo/Al<sub>2</sub>O<sub>3</sub> reaction was 22 times that in Mo naphthenate reaction.

Table 5  
Elemental Composition of PS and BS Fractions from Coprocessing

| Reactants    | Temperature<br>°C | Catalyst                            | PS   |      | BS   |     |
|--------------|-------------------|-------------------------------------|------|------|------|-----|
|              |                   |                                     | % C  | % H  | % C  | % H |
| Maya TLR     | 400               | None                                | 84.5 | 11.4 |      |     |
| + Coal       |                   |                                     | 84.0 | 11.3 | 82.8 | 7.1 |
| Maya TLR     | 400               | NiMo/Al <sub>2</sub> O <sub>3</sub> | 84.8 | 10.9 | 84.6 | 7.4 |
| + Coal       |                   |                                     | 84.8 | 10.9 | 86.8 | 7.3 |
| Maya TLR     | 400               | Mo Naphthenate                      | 84.3 | 10.8 | 83.6 | 7.2 |
| + Coal       |                   |                                     | 84.3 | 10.8 | 84.1 | 7.2 |
| Maya TLR     | 425               | Mo Naphthenate                      | 85.7 | 11.0 |      |     |
| + Coal       |                   |                                     | 84.6 | 10.6 | 86.3 | 6.4 |
|              |                   |                                     | 84.9 | 10.7 | 85.1 | 6.8 |
|              |                   |                                     | 85.1 | 10.6 |      |     |
| Maya TLR     | 400               | None                                | 86.3 | 10.1 | 83.8 | 6.9 |
| + Coal + TET |                   |                                     | 86.4 | 10.1 | 83.5 | 7.0 |
| Maya TLR     | 400               | NiMo/Al <sub>2</sub> O <sub>3</sub> | 87.8 | 10.5 |      |     |
| + Coal + TET |                   |                                     | 87.1 | 10.5 | 86.0 | 7.0 |
|              |                   |                                     | 85.7 | 10.3 | 84.7 | 7.1 |
|              |                   |                                     | 87.4 | 10.5 |      |     |
| Maya TLR     | 425               | Mo Naphthenate                      | 86.9 | 10.5 | 85.6 | 6.6 |
| + Coal + TET |                   |                                     | 86.5 | 10.3 | 85.7 | 6.6 |

The presence of TET in the coal/resid/Mo naphthenate system did not substantially change the product slate. Coal conversion, hydrogen consumption and oil production were the same as the reaction without TET. The total amount of NAPH formed during the reaction was 1.5 mmoles which fell between that for the thermal and NiMo/Al<sub>2</sub>O<sub>3</sub> reactions. Ten times as much NAPH was formed as DEC. The H<sub>2</sub> utilized by the Mo naphthenate systems, 57.5 mmoles without TET and 52.5 mmoles with TET, was high compared to the other reactions performed. The product slates from these Mo naphthenate reactions show the effective utilization of H<sub>2</sub> in terms of coal conversion and oil production.

Effect of the Catalyst Compared to Tetralin on the Product Slate. The addition of catalyst in the residuum upgrading reactions increased the amount of oil production achieved and, in the case of NiMo/Al<sub>2</sub>O<sub>3</sub>, substantially increased the IOM formed. The presence of TET had varying effect; but only in the reaction with NiMo/Al<sub>2</sub>O<sub>3</sub> did TET improve the oil production. In all upgrading reactions, the BS fraction was reduced during the reaction forming both lighter and heavier products. The catalytic reactions with NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo naphthenate at 425°C reduced the BS fraction the most. The combination of TET plus NiMo/Al<sub>2</sub>O<sub>3</sub> resulted in the greatest reduction of the BS fraction and subsequent increase in the PS fraction.

In the coprocessing experiments, both the addition of catalyst and the addition of tetralin promoted coal conversion. For the NiMo/Al<sub>2</sub>O<sub>3</sub> reactions, the combination of catalyst and tetralin synergetically promoted coal conversion. With Mo naphthenate, coal conversion was high (89.5%) without TET addition and no change was observed with the addition of TET. Thus, with a highly accessible and active catalyst, additional hydrogen donation from the solvent had little influence on coal conversion. Therefore, coal conversion in coprocessing appears to be dependent upon both catalyst and hydrogen donation except in the case of a highly active catalyst where catalytic activity predominates.

TET did not promote the production of PS materials in either the thermal or catalytic reactions. In fact, in the thermal reactions the presence of TET was detrimental to oil production.

The effect of TET and catalytic treatment on BS production is also instructive in examining the roles and relative importance of these two factors in coprocessing. BS production is defined as the difference between the final BS and the initial BS divided by the upgradeable material which is maf coal. Compared to the thermal reaction at 400°C, the addition of TET increased the amount of BS production (Table 3). Catalytic treatment at 400°C did not increase the BS production; however, the addition of TET to reaction system with NiMo/Al<sub>2</sub>O<sub>3</sub> at 400°C did enhance BS production. At 425°C, the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> and Mo naphthenate increased the BS production as shown in Table 4. The addition of TET to the Mo naphthenate reaction again increased the BS production. Since all of these reactions showed positive oil production, the increases observed in the BS production were directly related to the upgrading of liquefied coal to BS products. Thus, the presence of TET assisted in the production of BS but not in the production of PS. The presence of a hydrotreating catalyst was required for oil production in the coprocessing reactions.

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