COPROCESSING USING H_2S AS A PROMOTER

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INTRODUCTION

Coprocessing heavy oils, bitumens or petroleum residues with coal can be considered as a bridge between coal liquefaction and hydrocracking. The existing technologies of liquefaction and hydrocracking can be applied with modification to coprocessing. In terms of operation, coprocessing is less complicated than liquefaction because recylce solvent is eliminated. Since the coprocessing solvent is upgraded simultaneously with coal the reactor volume is utilized more effectively. If residuum conversion levels during coprocessing are as high as those in hydrocracking then coprocessing also offers a significant saving in feedstock costs by substituting a significant portion of the heavy oil with less expensive coal.

CANMET coprocessing involves the simultaneous upgrading of coal and heavy oil or bitumen in a once-through mode of operation using a disposable iron catalyst. The CANMET additive (pulverized coal impregnated with iron sulphate), hereinafter referred to as $FeSO_4$, has been identified as both an hydrogenation and coke-reducing catalyst. Process feasibility has been investigated using a variety of coals and heavy oils/bitumens(1). Also, it has been demonstrated that in terms of product yields for subbituminous coals, CANMET coprocessing is superior to liquefaction and is comparable to hydrocracking (2-3).

The effect of H_2S in hydrocracking of model compounds and in liquefaction is well documented (4-11). The ability of H_2S to reduce coke formation and increase liquid yield in coal liquefaction has been patented by Exxon Research and Engineering Company (12). It has also been shown that H_2S has benefical effects in non-catalytic crude oil hydrorefining processes (13).

In a previous batch autoclave study the use of H_2S in coprocessing subbituminous coal and bitumen resulted in high coal conversion and distillate yield (14). The increase in product yields in the presence of H_2S was attributed to its ability to donate its hydrogen to radicals derived from coal and bitumen (15).

The objective of the present study was to verify the positive effects of H_2S under coprocessing conditions using a continuous-flow bench scale pilot plant and to compare the activity of H_2S with $FeSO_4$ under similar operating conditions.

EXPERIMENTAL

Process Unit

Coprocessing experiments were carried out in a 1-L continuous-flow stirred tank reactor with a nominal capacity of 1 kg/h of slurry feed while product samples were collected over 1-h periods at steady state. For all the experimental runs reported in this paper, the material balances were within ±5 wt %. For comparison purposes, all the data were normalized to 100% material balance by proportioning the losses over each of the product fractions. Other details of the experimental unit are available elsewhere (2).

Feedstocks

The analysis of Forestburg subbituminous C coal and Cold Lake vacuum bottoms (CLVB) is shown in Table 1. Additives or promoters were $FeSO_4$ or H_2S or both. The H_2S was obtained from Matheson and used as received. In experiments where H_2S was used it was pumped as a liquid using a Waters LC pump model 6000A.

RESULTS AND DISCUSSION

Product Yields

Previous batch autoclave experiments indicated that H_2S is most effective at low to moderate severities in terms of improving product yields when compared to coprocessing without any additive. AT moderate-high severity, using the feedstocks reported in this paper,relatively high coke formation was observed even in the presence of H_2S. For this reason, the CSTR experiments which involved H_2S only were performed at low to moderate severities. For moderate-high severity experiments, iron sulphate was used to assure smooth process operation and to prevent coke formation. Attempts to perform coprocessing experiments in the CSTR unit using CLVB and Forestburg coal without any catalyst even at low severity resulted in coke formation and plant shutdown. Thus, it is not possible to compare the results of experimental runs using H_2S only with those using no additive or promoter as was done in the batch autoclave studies (15). The fact that coprocessing experiments could be performed in the CSTR with H_2S and no other catalyst at low and moderate severities is significant and verifies earlier batch results which indicated that H_2S prevents coke formation under the conditions employed (14-15).

Table 2 compares coprocessing results obtained in the presence of H_2S and iron sulphate at two levels of severities. At both levels replacement of $FeSO_4$ with H_2S resulted in higher distillate yield, pitch and coal conversions. The results of batch studies indicated

that product yields depend on H_2S concentration. At moderate temperature maximum coal conversion and distillate yield were obtained at about 3.5 wt % H_2S based on maf slurry feed (15). However, the results reported in this work are based on only one experimental run and are at approximately 8 wt % H_2S based on maf slurry feed. No optimization of H_2S concentration on product yields was carried out in this CSTR study.

The increase in conversions and distillate yield in the presence of H_2S can be rationalized by its hydrogen-donor ability. Hydrogen sulphide can donate its hydrogen directly to coal and bitumen-derived radicals or the available hydrogens in H_2S can be transferred to radicals via coal-derived liquids. The evidence for direct hydrogen donation by H_2S comes from batch autoclave hydrocracking studies using CLVB (14). At low severity, the presence of H_2S resulted in a substantial improvement and at moderate severity a slight increase in distillate yield. The considerable increase in distillate yield in the presence of H_2S suggests that at least in part, hydrogen from H_2S is transferred to bitumen-derived radicals. The previous study (14) also showed that while the conversion of Forestburg coal in anthracene oil increased with H_2S, distillate yield did not. However, in coprocessing (batch and CSTR) both coal conversion and distillate yield improved substantially when H_2S was used. These results may indicate that H_2S promotes upgrading of bitumen during coprocessing. An apparent synergism between coal and H_2S is also suggested by less coke formation during coprocessing in the presence of H_2S relative to the hydrocracking of bitumen only using H_2S as a promoter (15). Table 2 indicates that at least at low and moderate severities the performance of H_2S under coprocessing conditions in a CSTR is as good as or better than $FeSO_4$.

Table 3 compares the activities of iron sulphate with and without H_2S. At very low and low severities addition of H_2S to $FeSO_4$ resulted in an increase in coal conversions whereas distillate yields and pitch conversions did not change. However, at moderate severity, H_2S had a significant effect on distillate yield, coal and pitch conversions. The presence of H_2S at moderate-high severity had small effect on distillate yield and pitch conversion but no effect on coal conversion. It appears that at higher severities the positive effect of H_2S is masked by the presence of $FeSO_4$. A comparison of Tables 2 and 3 reveals that at low severity a higher distillate yield was obtained with the H_2S only run. However, at moderate severity, no improvement was observed using H_2S+$FeSO_4$ compared to H_2S only. Also, the comparison clearly shows that at moderate severity coal conversion in the presence of H_2S only (80.4 wt %) approaches that at moderate-high severity using $FeSO_4$ only (86.3 wt %).

Product Characteristics

a) Distillates

Table 4 shows the characteristics of distillate products at four different severities and compares product qualities obtained in the presence of H_2S with those obtained using $FeSO_4$ or H_2S + $FeSO_4$. At very low severity it appears that the distillate products obtained using H_2S + $FeSO_4$ are relatively heavier than those obtained in the presence of $FeSO_4$ only. The sulphur content of the distillate did not change when H_2S was added to $FeSO_4$, however, the aromaticity increased from 26 to 31. This increase parallels that of increased coal conversion upon H_2S addition (see Table 3) and may imply that some coal-derived liquid contributed to the distillate. Again at low severity, higher coal conversion in the presence of H_2S only compared to $FeSO_4$ or H_2S + $FeSO_4$ resulted in a relatively heavier distillate. The sulphur content of the distillate decreased slightly in the H_2S only run. At moderate severity, the use of H_2S alone resulted in a heavier liquid product, lower H/C ratio and higher molecular weight than the distillate obtained using either $FeSO_4$ or H_2S + $FeSO_4$.

From the results shown in Table 4 it appears that the effect of $FeSO_4$ as a hydrogenation catalyst is more pronounced at relatively higher severities. At moderate severity, although similar coal conversions and distillate yields were obtained with both H_2S and H_2S + $FeSO_4$, a better distillate quality was obtained with H_2S + $FeSO_4$. Again the higher molecular weight in the H_2S only run may suggest that more coal-derived liquid contributes to the distillate but the product is not upgraded to the same degree as when $FeSO_4$ is used. The oxygen content of the distillate decreased when H_2S was used instead of $FeSO_4$. Addition of H_2S to $FeSO_4$ further reduced the oxygen content which indicates that H_2S reacts with the oxygen functionalities in coal. However, sulphur content of the distillate increased slightly in the presence of H_2S only. At moderate-high severity, the product quality improved slightly in the presence of H_2S in terms of higher H/C ratio, lower oxygen content, aromaticity and molecular weight.

b) Residues

The compositions of residues obtained under different process severities are shown in Fig. 1. At very low severity, the addition of H_2S to $FeSO_4$ resulted in slightly higher yields of asphaltenes, preasphaltenes and lower THF insolubles. At low severity, the lowest yield of THF insolubles was obtained with H_2S which reflects a higher coal conversion than the $FeSO_4$ and H_2S+$FeSO_4$ runs. Under these conditions, the relative yields of oils, asphaltenes, and preasphaltenes remained unchanged. At moderate severity, the residue in the $FeSO_4$ run contained more residual oil than the H_2S run. However, as shown in Table 2 the total distillate yield as well as the pitch conversion in the H_2S run are higher. This suggests that the upgrading of heavy material in coprocessing is more efficient using H_2S than $FeSO_4$ at least at moderate severities. Little or no change

occurs in the yields of asphaltenes and preasphaltenes at moderate severity using the different additives. At moderate-high severity, adding H_2S to $FeSO_4$ resulted in slightly higher pitch conversion and consequently lower residue yield (Table 3). The drop in residue yield is reflected mainly in lower preasphaltenes and asphaltenes yields.

The toluene insolubles of some of the coprocessing residues were also examined using optical microscopy. This technique, supplemented by semi-quantitative elemental analysis by scanning electron microscopy has shown that it is possible to distinguish the originality of coal-derived and bitumen-derived solids in coprocessing residues (16). At moderate severity, the toluene insolubles of the coprocessing residue obtained using H_2S contains 22.5 vol % coal-derived solids (altered coal or unreacted coal) whereas the residue from the $FeSO_4$ run contains 52.1 vol % coal-derived materials. These results are consistent with the higher coal conversion in the H_2S run relative to the $FeSO_4$ run. Also a small amount, (0.9 vol %) of anisotropic solids in both the H_2S and $FeSO_4$ runs was detected whereas none was detected in the H_2S + $FeSO_4$ run.

CONCLUSIONS

Hydrogen sulphide has been shown to be an effective promoter in achieving high coal conversions and distillate yields when coprocessing subbituminous coal with bitumen vacuum bottoms in a continuous-flow bench scale operation. Results indicate that, at least, at low and moderate severities of operation H_2S performs as good as or better than $FeSO_4$ in terms of product yields as well as qualities. However, at higher severities, $FeSO_4$ is superior to H_2S.

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Table 1

Analysis of Feedstocks

Forestburg Coal

Proximate analysis (wt %, as received)	
Moisture	19.7
Volatile	37.2
Fixed carbon	36.1
Ash	7.0
Ultimate analysis (wt % DAF)	
C	74.34
H	4.81
N	1.78
O	18.58
S	0.49

Cold-Lake vacuum bottoms

Specific gravity, 15/15°C	1.038
Pentane insolubles, wt %	23.8
Pitch content, wt %	83.2
Conradson Carbon, wt %	17.1
Elemental composition, wt %	
C	83.34
H	9.69
N	0.45
S	5.84
O	0.68
Metals, ppm	
V	235
Ni	93
Fe	18

Table 2

Comparison of the Effects of H_2S with $FeSO_4$

Severity	Low		Moderate	
H_2S (1)	no	yes	no	yes
$FeSO_4$	yes	no	yes	no
Distillate yield (2)	22.9	27.3	36.3	43.2
Coal conversion (3)	53.7	67.9	70.4	80.4
Pitch conversion (4)	15.8	20.3	34.1	42.5

(1) 8 wt %, based on maf slurry feed (2) wt %, based on maf slurry feed
(3) wt %, based on maf coal, defined as THF solubility (4) $\frac{\text{maf (+525 °C) in - maf (+525°C) out}}{\text{maf (+525°C) in}}$

Table 3

Comparison of The Effects of $FeSO_4$ and H_2S + $FeSO_4$

Severity	Very low		Low		Moderate		Moderate-high	
H_2S (1)	no	yes	no	yes	no	yes	no	yes
$FeSO_4$	yes	yes	yes	yes	yes	yes	yes	yes
Distillate yield (2)	15.8	16.5	22.9	22.9	36.3	42.1	60.9	63.1
Coal conversion (3)	27.4	41.1	53.7	61.3	70.4	83.7	86.3	85.9
Pitch conversion (4)	8.1	7.5	15.8	18.6	34.1	42.4	64.8	69.7

(1) 8 wt %, based on maf slurry feed (2) wt %, based on maf slurry feed
(3) wt %, based on maf coal, defined as THF solubility (4) $\frac{\text{maf (+525°C) in - maf (+525°C) out}}{\text{maf (+525°C) in}}$

Table 4

Distillate Characteristics

Severity	Very low		Low			Moderate			Moderate-high	
H_2S	no	yes	no	yes	yes	no	yes	yes	no	yes
$FeSO_4$	yes	yes	yes	no	yes	yes	no	yes	yes	yes
API°	15.2	13.3	17.0	15.9	15.8	22.4	19.8	22.9	25.4	25.9
H/C	1.59	1.53	1.56	1.57	1.54	1.62	1.58	1.63	1.58	1.62
N,wt %	0.26	0.37	0.39	0.41	0.41	0.44	0.47	0.43	0.50	0.50
S,wt %	3.15	3.11	2.98	2.83	2.98	2.30	2.44	2.27	1.64	1.69
O,wt %	0.89	1.30	1.28	1.23	1.31	1.40	1.28	1.02	1.46	0.85
fa	26	31	29	28	30	25	29	24	30	·25
$\overline{M}n$,g/mole	-	-	307	320	322	272	305	279	293	278
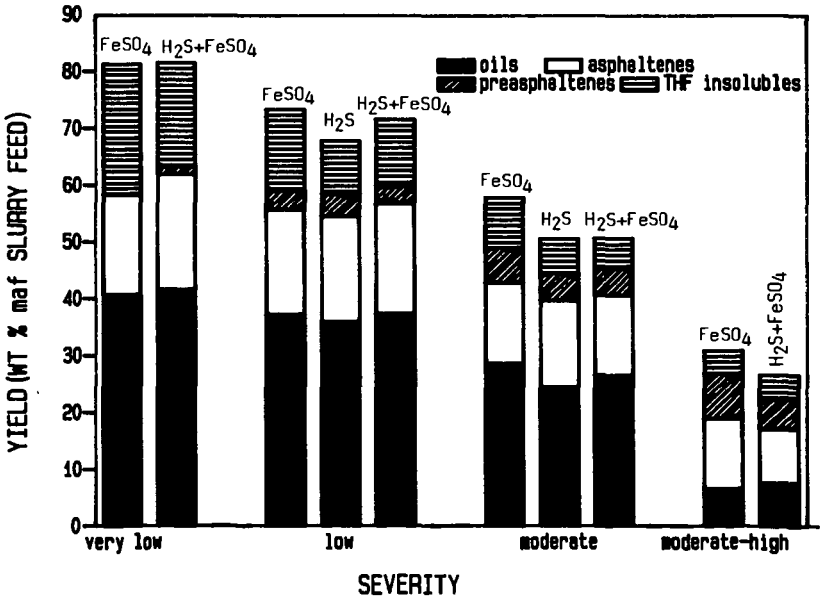
FIGURE 1 RESIDUE COMPOSITION