

## COAL/OIL COPROCESSING USING SYNGAS

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### ABSTRACT

Coal and model compounds were hydrogenated and desulfurized in the presence of petroleum solvents and catalyst under coprocessing conditions by using syngas with steam in place of hydrogen. Nickel molybdate and cobalt molybdate catalysts impregnated with potassium carbonate exhibited good activities for hydrogenation and desulfurization of coal and model compounds (anthracene and benzothiophene) at 400-425°C with the use of syngas. Some water gas shift conversion also took place simultaneously. The extent of hydrogenation and desulfurization obtained are comparable to those obtained in coprocessing using pure hydrogen. Iron catalysts such as synthetic pyrite exhibited good activities for coal conversion in coprocessing using hydrogen, but only moderate activities in coprocessing using syngas. Results from coprocessing of model compounds indicate that these iron catalysts have relatively low activities in the desulfurization of benzothiophene.

### INTRODUCTION

In coprocessing of coal and petroleum residues to produce liquid fuels, the process economics could be improved significantly by using syngas ( $H_2+CO$ ) and steam instead of hydrogen as feed gas to the reactor. The use of syngas, even only at the first stage of the current two-stage process being developed, could substantially reduce the hydrogen consumption and improve the overall thermal efficiency. It has been demonstrated that lignite<sup>1</sup> and bituminous coal<sup>2</sup> are liquefied and coal liquid<sup>3</sup> is hydrogenated by the use of carbon monoxide or carbon monoxide-containing gas.

In this study, coal model compounds (anthracene and benzothiophene) are coprocessed with petroleum solvents in the presence of catalyst, and the results of hydrogenation and desulfurization during coprocessing using syngas and hydrogen were compared. The catalysts used include NiMo, CoMo, and disposable Fe and  $ZnCl_2$  catalysts. In general the catalyst activities are somewhat lower with the use of syngas than with hydrogen. It is shown, however, that NiMo and CoMo catalysts exhibit good activities with syngas and the performances are comparable to those obtained with hydrogen. Some coprocessing experiments using coal and petroleum solvents with syngas yielded moderately good coal conversions, but reaction conditions relating to  $H_2/CO$  ratio, steam/syngas ratio, solvent composition, catalyst, and process severity should be optimized to achieve better results.

### EXPERIMENTAL

The coprocessing reactions of model compounds were conducted in a shaking 20-ml microreactor with syngas ( $H_2:CO=1:1$ ) or  $H_2$  at initial pressures of 70 Kg/cm<sup>2</sup> and temperatures of 350-400°C for 45 minutes. Anthracene and benzothiophene were used as the model compounds, and mixtures of n-paraffin and cycloalkane and that added with tetralin were used as petroleum solvents. The ratio of solvent to coal model compounds was 5:1. With syngas, 10 weight % of  $H_2O$  based on the total amounts of the model compounds and solvent was added. The amount of ground catalyst powder added was also 10 weight %.

The conventional NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts and disposable synthetic pyrite (Mitsui Coal Liquefaction Co.) were used for coprocessing experiments using H<sub>2</sub>. For experiments using syngas, the NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts and synthetic pyrite were impregnated with aqueous potassium carbonate solution (10 wt%). Additional catalysts tested for comparison purpose included a solid superacid catalyst of sulfate-promoted iron oxide<sup>4,5</sup> and a zinc chloride catalyst<sup>6</sup> (30 wt%) supported on silica-alumina. The Fe<sub>2</sub>O<sub>3</sub>/SO<sub>4</sub><sup>2-</sup> (2 wt%) was prepared starting from iron(III) nitrate precipitated with an aqueous ammonia. The powdered precipitate was treated with ammonium sulfate, and then dried and calcined at 500°C.

Some coprocessing experiments using coal and petroleum solvents with syngas were also conducted. Illinois No. 6 bituminous coal (River King) with an ultimate analysis of C, 78.3; H, 5.4; N, 1.32; O, 11.12; S, 3.86; Ash, 10.9 (maf. basis) was used. The coal conversion was determined from tetrahydrofuran insolubles, and the solubles were analyzed by Yanaco G-6800 gas chromatograph using OV-1701 fused silica capillary column (60m x 0.25mm φ).

## RESULTS AND DISCUSSION

**Hydrogenation of Anthracene.** Anthracene was initially hydrogenated in the presence of petroleum solvents and synthetic pyrite using H<sub>2</sub> and syngas. The results in Table 1 show that the hydrogenation proceed well at 350°C with H<sub>2</sub> irrespective of the type of solvent used. Paraffins and cycloalkanes did not participate in the reaction and hydrogen transfer from tetralin was not an important factor. The reaction with syngas at the same temperature gave only 65.9% anthracene conversion. It is observed that the conversion increased as the temperature increased to 400°C, and that this was accompanied by the increase of CO shift conversion.

**Coprocessing of Model Compounds.** Anthracene and benzothiophene were coprocessed with petroleum solvents to study the hydrogenation and desulfurization during coprocessing. It is seen in Table 2 that anthracene was hydrogenated easily with H<sub>2</sub> in the presence of synthetic pyrite, but desulfurization of benzothiophene did not take place easily. In the presence of NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>, both hydrogenation and desulfurization progressed markedly. In the run using an n-dodecane/decalin mixture as the solvent, 23.8% of decalin was dehydrogenated (17.7% to tetralin and 6.1% to naphthalene). It is of interest to note that trans/cis ratio of the remaining decalin has increased to 4.6 from the original trans/cis ratio of 1.6 after the coprocessing reaction. Similar increase of trans/cis ratio was also observed in the run using an n-dodecane/decalin/tetralin solvent mixture. The occurrence of isomerization to trans decalin during extraction of coal was also observed by Clarke et al<sup>7</sup>.

For comparison purpose, a sulfate-treated iron oxide catalyst and a ZnCl<sub>2</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst were prepared and tested. Both catalysts showed moderately good activities for hydrogenation and desulfurization in coprocessing using H<sub>2</sub>.

In coprocessing using a paraffin/ethylcyclohexane/tetralin solvent with syngas, NiMo and CoMo catalysts impregnated with K<sub>2</sub>CO<sub>3</sub> exhibited good activities for both hydrogenation and desulfurization, as shown in Table 3. When a paraffin/decalin/tetralin solvent was used, the extent of hydrogenation and desulfurization decreased. It was noticed that no net conversion or dehydrogenation of decalin took place in this case. The trans/cis ratios of the remaining decalin were much lower than those observed for coprocessing using H<sub>2</sub>, indicating limited occurrence of isomerization during coprocessing with syngas. As was suggested by Clarke et al<sup>7</sup>, decalin could participate in hydrogen donation reactions in the presence of polyaromatic compounds, and this was more pronounced in the reaction with H<sub>2</sub> than with syngas. It is speculated that hydrogen donation reactions of decalin somehow relate to the occurrence of isomerization. With syngas,

synthetic pyrite, sulfate-treated iron oxide, and  $ZnCl_2/SiO_2-Al_2O_3$  exhibited moderate activities for hydrogenation, but poor activities for desulfurization. Presence of significant concentrations of hydrogen donating tetralin alone was not sufficient to give high conversion in coprocessing using syngas. It is also observed, in general, that hydrogenation and desulfurization progress with the progress of CO shift conversion.

**Coprocessing of Coal with Petroleum Solvents.** Table 4 shows the test results of coprocessing bituminous coal with paraffin/decalin/tetralin solvents. Fairly high coal conversions were obtained with  $NiMo/Al_2O_3$ ,  $CoMo/Al_2O_3$ , and synthetic pyrite using  $H_2$ . The coal conversions obtained with syngas were only moderate, but it should be emphasized that the reaction conditions have not been optimized in these runs. Improved conversions should be obtainable if variables including steam/syngas ratio,  $H_2/CO$  ratio, solvent composition, catalyst, and process severity are properly chosen.

In the run using an n-dodecane/decalin/1-methylnaphthalene mixture as the solvent, high coal conversion was obtained even without the use of tetralin. Product analysis indicates that significant amounts of 1-methylnaphthalene may have participated in hydrogen exchanges with decalin and coal. In the similar run with syngas, the active participation of 1-methylnaphthalene was not evident, and the decalin conversion decreased. For syngas runs, again the trans/cis ratio of the remaining decalin was lower, probably suggesting that only limited participation of decalin in hydrogen donation reactions has taken place.

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Table 1 Hydrogenation of Anthracene Using H<sub>2</sub> and Syngas  
(Initial Pressure: 70Kg/cm<sup>2</sup>, Time: 45min)

Gas	H <sub>2</sub>					Syngas (H <sub>2</sub> :CO=1:1)	
	FeS <sub>x</sub> <sup>a</sup>					FeS <sub>x</sub> <sup>b</sup>	
Catalyst							
Solvent <sup>c</sup>	T	D/E	D/E/DL	D/E/T	D/E/T	D/E/T	D/E/T
Temperature, °C	350	350	350	350	400	350	400
Anthracene conversion, %	92.8	92.2	90.0	92.4	82.8	65.9	81.0
DIA formed, %	68.8	74.3	74.3	66.8	47.2	65.9	67.6
Conversion of tetralin, %	3.8	-	1.8 <sup>d</sup>	6.7	20.2	1.5	8.3
CO conversion, %	-	-	-	-	-	2.0	8.3

<sup>a</sup> Synthetic pyrite <sup>b</sup> Impregnated with K<sub>2</sub>CO<sub>3</sub> solution

<sup>c</sup> Equal wt% of each component <sup>d</sup> Conversion of decalin

D:n-Decane, E:Ethylcyclohexane, T:Tetralin, DL:Decalin, DIA:9,10-Dihydroanthracene

Table 2 Coprocessing of Model Compounds Using H<sub>2</sub>  
(Coal Model: Anthracene/Benzothiophene, Initial Pressure: 70Kg/cm<sup>2</sup>, Time: 45min)

Catalyst	FeS <sub>x</sub>	FeS <sub>x</sub>	Fe <sub>2</sub> O <sub>3</sub>	ZnCl <sub>2</sub>	NiMo	CoMo	NiMo	NiMo
			/SO <sub>4</sub> <sup>2-</sup>	/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>				
Solvent <sup>a</sup>	D/E/T	D/E/T	D/E/T	DO/E/T	D/E/T	D/E/T	DO/DL/T	DO/DL
Temperature, °C	350	400	400	400	400	400	400	400
Anthracene conversion, %	90.8	81.7	68.4	87.1	97.0	96.8	97.2	89.4
Benzothiophene conversion, %	10.2	26.0	80.8	50.2	96.2	100	100	100
Conversion of tetralin, %	11.5	13.8	13.5	33.2	38.5	33.0	16.7	-
Decalin remained, %							86.4	76.2
cis							15.0	13.7
trans							71.4	62.5
trans/cis ratio							4.8	4.6

<sup>a</sup> Equal wt% of each component

T:Tetralin, D:n-Decane, E:Ethylcyclohexane, DO:n-Dodecane, DL:Decalin

Table 3 Coprocessing of Model Compounds Using Syngas (H<sub>2</sub>:CO=1:1)

(Coal Model:Anthracene/Benzothiophene.

Initial Pressure:70Kg/cm<sup>2</sup>, H<sub>2</sub>O:10wt% of Reactants, Time:45min)

	FeS <sub>x</sub> <sup>a</sup>	FeS <sub>x</sub> <sup>a</sup>	NiMo <sup>a</sup>	NiMo <sup>a</sup>	NiMo <sup>a</sup>	CoMo <sup>a</sup>	Fe <sub>2</sub> O <sub>3</sub> /SO <sub>4</sub> <sup>2-</sup>	ZnCl <sub>2</sub> /SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
Solvent <sup>b</sup>	D/E/T	D/E/T	D/E/T	DO/DL/T	TD/DL/T	D/E/T	DO/E/T	DO/E/T
Temperature, °C	350	400	400	400	400	400	400	400
Anthracene conv., %	80.1	70.9	90.1	78.9	77.8	88.3	50.2	65.6
Benzothiophene conv., %	4.1	11.7	90.4	67.6	66.6	100	28.3	22.6
Conversion of tetralin, %	15.4	4.0	11.3	6.6	11.4	22.1	2.6	23.2
CO conversion, %	2.0	7.7	15.3	10.4	15.9	18.3	16.4	2.8
Decalin remained				102.4	102.4			
cis				33.4	30.8			
trans				69.0	71.6			
trans/cis ratio				2.1	2.32			

<sup>a</sup> Catalyst impregnated with K<sub>2</sub>CO<sub>3</sub> solution <sup>b</sup> Equal wt% of each component

D:n-Decane, E:Ethylcyclohexane, T:Tetralin, DO:n-Dodecane, DL:Decalin, TD:n-Tridecane

Table 4 Coprocessing of Bituminous Coal with Petroleum Solvents(425°C, 45min)

(Solvent:n-Dodecane/Decalin/Tetralin, Solvent:Coal=4:1)

Catalyst	H <sub>2</sub>				Syngas (H <sub>2</sub> :CO=1:1)		
	FeS <sub>x</sub>	NiMo	NiMo <sup>a</sup>	CoMo	FeS <sub>x</sub> <sup>b</sup>	NiMo <sup>b</sup>	NiMo <sup>a,b</sup>
Coal conversion, %	89.3	87.6	84.9	83.7	63.7	79.8	62.6
H <sub>2</sub> consumption, wt% of maf coal	3.1	3.1	3.9	5.3	0.8	-0.3	-0.2
CO conversion, %	-	-	-	-	6.2	22.1	19.3
Conversion of tetralin, %	17.3	10.1	-	12.9	14.1	8.2	-
Conversion of 1-methylnaphthalene, %	-	-	17.4	-	-	-	1.2
Decalin remained, %	98.6	90.7	88.6	95.8	95.7	87.2	94.5
cis	16.8	27.4	25.3	27.3	22.2	30.3	32.4
trans	81.8	63.3	63.3	68.5	73.5	56.9	62.1
trans/cis ratio	4.9	2.3	2.5	2.5	3.3	1.9	1.9

<sup>a</sup> Solvent:n-Dodecane/Decalin/1-Methylnaphthalene <sup>b</sup> Impregnated with 10%K<sub>2</sub>CO<sub>3</sub>