

COPROCESSING REACTIONS OF ILLINOIS #6 COAL WITH HONDO PETROLEUM RESID

Yanlong Shi, Thomas A. Cutler and Edward M. Eyring
Department of Chemistry, University of Utah, Salt Lake City, UT 84112

Anthony V. Cugini
Federal Energy Technology Center, Pittsburgh, PA 15236-0940

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INTRODUCTION

Petroleum crude is becoming heavier and the amount of vacuum tower resids produced in refining has been steadily increasing. Many have suggested that the combination of coal liquefaction and heavy resid upgrading has economic and processing advantages over the direct liquefaction of coal.¹⁻¹² Because petroleum resids are still hydrogen rich materials ($H/C \approx 1.5$) when compared to coal ($H/C \approx 0.8$), the amount of hydrogen required in a combined process should, in principle, be less than that required to produce the same quality products from a stand-alone coal liquefaction facility. It is generally believed that the petroleum resid in coprocessing serves as hydrogen transfer agents for coal conversion; in essence the resid replaces the donor solvent in direct coliquefaction. On the other hand, coprocessing can also improve the quality of the petroleum resid used by the removal of the vanadium and nickel complexes since the undissolved coal could act as a trap for the metal removed from the resid.¹³ Thus, coprocessing is beneficial in reducing the deposition of coke and trace metals on a hydroliquefaction catalyst.^{2,3,14-15} The liquids produced by combined processing may also be more amenable to downstream processing and further refining via existing technology and equipment, than liquids from a purely coal fed plant would be. It seemed appropriate to investigate the reaction pathways and explore the conditions for the maximum conversion of both coal and resid to a liquid fuel precursor.

Vanadium and nickel, the principal metals in petroleum resid, are present in structures such as porphyrins and the more condensed asphaltenes in concentrations ranging up to 1300 ppm by weight.¹⁶ During catalytic hydroprocessing for sulfur and nitrogen removal, these metal-bearing molecules undergo hydrodemetallation (HDM) reactions leading to metal deposition and catalyst poisoning. The removal of vanadium and nickel has been investigated widely for this purpose. However, most researchers only selected model compounds of vanadium and nickel porphyrins as subjects for study because of the complication of real petroleum resid systems.^{2-3, 16-21}

The objectives of the present study are: (1) to identify conditions for maximum removal of metals, mainly Ni and V, present in petroleum resid using coal with the resultant product becoming a feed to catalytic desulfurization and cracking that does not severely shorten catalyst life; (2) to optimize conditions for the conversion of both coal and resid to a liquid fuel precursor. The catalytic coprocessing of Illinois #6 coal with Hondo resid (850 °F or whole resid) was carried out using $(NH_4)_2MoS_4$ as catalyst at different temperatures and at 1000 psig of H_2 (cold). The influence of reaction time, and the ratio of resid to coal on the reactivity and product distribution from coprocessing were investigated. The effect on the coprocessing of hydrogenating Hondo resid in a pretreatment step was also studied. The effects of catalysts on coprocessing were studied using $(NH_4)_2MoS_4$, presulfidized $CoMo/Al_2O_3$, $Mo/Fe_2O_3/SO_4^{2-}$ and no catalyst. Ni and V removal was quantified by ICP measurements.

EXPERIMENTAL

The Hondo resid (whole resid: Anal. %C, 83.87; %H, 10.19; %N, 1.01; %S, 4.07; Ni, 78 ppm; V, 150 ppm and hexane insolubles, 25.6% or 850 °F resid: Anal. %C, 83.60; %H, 10.11; %N, 1.00; %S, 4.23; Ni, 150 ppm; V, 290 ppm and hexane insolubles, 29.5%) obtained from the Federal Energy Technology Center at Pittsburgh and was stored under ambient conditions. The resid is semisolid at room temperature so that it was necessary to heat it to about 100 °C to make it fluid enough to pour into the reactor. Illinois #6 coal was selected for the coprocessing because it has the best demetallation effect.¹³ Illinois #6 coal (-60 mesh) was obtained from the Pennsylvania State Coal Sample Bank. The hydrogenation catalyst $NiMo/Al_2O_3$ (Katalco, 6.7% NiO% and 27.0% MoO_3) was presulfidated at 350 °C for two hours. The hydrogenation experiments were completed using 27 cm³

tubing reactors at 1500 psig of H_2 (cold) for 1 h at 350 °C. Coprocessing experiments were carried out in the same tubing reactors as for the hydrogenation. Reactants were brought to the set-point temperature, usually within 10 min, by immersing the reactor in a preheated, fluidized sand bath. The reactor was shaken horizontally (3 times/s) to ensure adequate mixing. At the end of a 1 h reaction time, the reactor was removed from the sand bath and allowed to cool at room temperature for 5 mins, and was then quenched in cold water. Reaction products and solids were removed and extracted with THF, and then the solvent was removed with a rotary evaporator. The THF soluble portion was dried under vacuum for two hours and weighed. The THF insoluble residue remaining in the Soxhlet extractor thimble was also dried for two hours under vacuum. Next the dried THF solubles were extracted with cyclohexane. The cyclohexane was removed from the oil sample using a rotary evaporator. The cyclohexane insoluble residue is referred to as asphaltenes. The cyclohexane soluble portion is referred to as oil. $(NH_4)_2MoS_4$ (Aldrich) was used as received to impregnate the coal from aqueous solution by the incipient wetness technique. The coprocessing catalyst was added to the coal before coprocessing based on 300 ppm of Mo. The ICP analyses were completed by DataChem Laboratories and American West Analytical Laboratories, Salt Lake City, UT. Elemental analyses were completed by Atlantic Microlabs, Norcross, Georgia. Total conversion of coal, asphaltenes conversion and conversions to product fractions were defined on an ash-free basis as follows :

total coal conversion: $Y_T = 100(1-Y)$; $Y = (W_i - W_C - W_{sub})/W_{mf}$

asphaltenes conversion (from coal and resid): $Y_{AC} = 100[1 - (W_A + W_{sub})/(W_{mf} + W_{RA})]$

coal conversion to asphaltenes: $Y_{CCA} = 100[W_A - W_{RA}(1 - Y_{AC})]/W_{mf}$

coal conversion to oils and gases: $Y_{O+G} = 100(Y_T - Y_{CCA})$

where W_i , W_C , W_{sub} , W_A , W_{mf} and W_{RA} are masses of THF insoluble products, catalyst, ash, asphaltenes (cyclohexane insolubles), moisture- and ash-free coal and asphaltenes from resid respectively; Y_T , Y_{AC} , Y_{CCA} and Y_{O+G} denote the yields of total conversion, asphaltenes conversion (from coal and resid), coal conversion to asphaltenes and coal conversion to gas + oil, respectively.

RESULTS AND DISCUSSION

Effect of Hydrogenation of Petroleum Resid on the Coprocessing. Table 1 shows the effects of a hydrogenation pretreatment of the Hondo resid (whole or 850 °F) on the catalytic coprocessing of Hondo resid with Illinois #6 coal. After hydrogenation pretreatment of Hondo resid (whole or 850 °F) using presulfidized $NiMo/Al_2O_3$, the coal conversions from the coprocessing were increased from 84.3% and 82.9% to 96.6% and 91.4%, respectively for whole and 850 °F resids. These results clearly demonstrate that the hydrogenated Hondo resid (whole or 850 °F) is a better coprocessing solvent than unhydrogenated Hondo resid. The difference is probably attributable to the formation of dropolyaromatics in the hydrogenated Hondo resid. This trend has been observed by other investigators^{2,8} and our previous work on the coprocessing of coal and hydrogenated vacuum pyrolyzed tire oil.²² The difference of the coal conversion between the whole and 850 °F resid is very small because the 850 °F resid represents 91% of the whole resid. It seems that the asphaltenes conversion from both resid and coal to gas and oil is independent of the hydrogenation pretreatment.

The ICP analyses for Ni and V of the coprocessing products from Illinois #6 with Hondo resid and hydrogenated Hondo resid are summarized in Table 2. After coprocessing, the Ni and V in oil (cyclohexane solubles) were not detected above the limit of detection for the coprocessing of whole resid or hydrogenated whole resid with the coal. Most of the Ni and V was trapped in the ash/char. There was more Ni than V in asphaltenes even though the concentration of V was larger than Ni in the original resid samples.

Effect of the Coprocessing Reaction Time. Table 3 shows the results of the coprocessing of Hondo resid (850 °F) with Illinois #6 coal at different reaction times. The asphaltenes conversion from both resid and coal to gas and oil was increased from 46.1% at 10 min to 71.7% at 80 min. Parallel with the asphaltenes conversion, the asphaltenes for maf coal was decreased from 29.0% at 10 min to 8.75% at 8.7 min, and the gas and oil increased from 49.7% at 10 min to 77.0% at 80 min. In contrast, the total coal conversion did not change much with increasing reaction time. The ICP analyses of Ni and V shown in Table 5 indicate that for most cases the Ni and V in oil were below the detection limits and most of the Ni and V were trapped in the ash/char. It seems that Ni in asphaltenes and in ash/char is independent of reaction time; however, V in asphaltenes decreases with increasing reaction time and V in ash/char increases with increasing reaction time. Hung and Wei observed the same phenomenon when they investigated the hydrometallation kinetics of vanadyl

etioporphyrin (VO-Etio) and Nickel etioporphyrin (Ni-Etio).¹⁷

Dependence on Resid/Coal. The results of changing the resid/coal ratio on the coprocessing of Hondo resid (850 °F) and Illinois #6 coal are given in Table 4. When the amount of coal was fixed at 1 g, the asphaltenes conversion from both resid and coal to gas and oil was decreased from 64.9% at 1 g of resid to 55.4% at 3 g of resid. Correspondingly, the total coal conversion was decreased from 93.0% to 70.5%, asphaltenes from maf coal increased from 4.9% to 25.2%, and the gas and oil decreased from 88.1% to 45.3%. These trends are related to the limited hydrogen gas available since we used the same amount of hydrogen gas at 1000 psig (cold). When the resid was raised to 5 g, the total coal conversion dropped to only 6%, the asphaltenes conversion came mainly from the resid and was increased to 71.7%. When coal/resid was 0.2 g/1.8 g, no coal conversion was observed and a 60.4% asphaltenes conversion was totally dominated by the resid. When the ratio of coal to resid was adjusted to 1.6 g/0.4 g and 1.8 g/0.2 g, the total coal conversions were 23.1% and 20.1%, respectively. Table 5 shows that higher coal/resid ratios favor the V and Ni removal from resid.

CONCLUSIONS

Hydrogenated Hondo resid (whole or 850 °F) prepared using a presulfidized NiMo/Al₂O₃ is a better coal liquefaction solvent than unhydrogenated Hondo resid. However, the asphaltenes conversion from both resid and coal to gas and oil is independent of the hydrogenation pretreatment. vanadium removal by Illinois #6 coal is dependent on the reaction time, but nickel removal is independent of the reaction time. Higher coal/resid ratios favor the V and Ni removal from resid.

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Table 1. Coal and Asphaltenes Conversions of the Coprocessing of Illinois #6 Coal with Hondo Resid and Hydrogenated Hondo Resid (Reaction Conditions: (Resid/Coal) = 2g/1g, 430 °C, 1000 psig of H₂ (cold), 1 h and 300 ppm Mo loaded to coal using (NH₄)₂MoS₄)

Hondo Resid	Asphaltenes Conv.	Total coal conv.	Asphaltenes.	Gas + Oil
	% from resid and coal	% for maf coal	% for maf coal	% for maf coal
whole	72.5	84.3	8.3	76.0
850 °F ^a	59.6	82.9	6.4	76.5
whole (Hydro.) ^a	71.8	96.6	11.2	85.4
850 °F ^a (Hydro.) ^b	65.5	91.4	15.2	76.2

a: The hydrogenation conditions: presulfidized NiMo/Al₂O₃, 350 °C, 1 h, 1500 psig of H₂ (cold), and resid: catalyst = 5.5g:1g (the presulfidation was carried out at 350 °C for 2 hrs);

b: The same hydrogenation conditions as in a;

Table 2. ICP Analyses of Ni and V from the Coprocessing of Illinois #6 Coal with Hondo Resid and Hydrogenated Hondo Resid (Coprocessing Conditions: Resid/Coal = 2g/1g, 430 °C, 1000 psig of H₂ (cold) and 1h)

Reaction System	Oil		Asphaltenes		Ash/Char	
	Ni	V	Ni	V	Ni	V
	ppm	ppm	ppm	ppm	ppm	ppm
Whole resid	78	150	---	---	---	---
Hondo resid (850 °F ^a)	150	290	---	---	---	---
Whole resid + Coal	*	*	150	36	1700	1200
850 °F ^a resid + Coal	*	0.62	320	150	2500	980
Hydrogenated whole resid ^a + Coal	*	*	84	19	4100	440
Hydrogenated 850 °F ^a resid ^a + Coal	*	0.45	150	53	2,100	250

a: The hydrogenation conditions: see Table 1;

*: Parameter not detected above limit of detection (Limits of detection: Ni: 2.3 ppm; V: 0.40ppm)

Table 3. Results from Catalytic Coprocessing of Illinois #6 Coal with Hondo resid (850 °F^a) at Different Reaction Time (Reaction Conditions: Coal/Resid = 1g/2g, 430 °C, 1000 psig of H₂ (cold) and 300 ppm Mo Loaded to Coal Using (NH₄)₂MoS₄)

Reaction Time min	Asphaltenes conv., % (from resid and coal)	Total conv., % (for maf coal)	Asphaltenes, % (for maf coal)	Gas + Oil, % for maf coal
10	46.1	78.7	29.0	49.7
20	49.2	82.3	31.6	50.7
40	59.8	88.3	20.9	67.4
60	59.6	82.9	6.4	76.5
80	71.7	85.7	8.7	77.0
120	61.3	84.7	19.4	65.3

Table 4. Results from Catalytic Coprocessing of Illinois #6 Coal with Hondo Resid (850 °F*) at Different Ratios of Coal/Resid (Reaction Conditions: 1 h, 430 °C, 1000 psig of H₂ (cold) and 300 ppm Mo Loaded to Coal Using (NH₄)₂MoS₄)

Coal/Resid	Asphaltenes conv., % (from resid and coal)	Total conv., % (for maf coal)	Asphaltenes, % (for maf coal)	Gas + Oil, % (for maf coal)
1g/1g	64.9	93.0	4.9	88.1
1g/2g	59.6	82.9	6.4	76.5
1g/3g	55.4	70.5	25.2	45.3
1g/5g	71.6	6.0	8.4	-2.4
0.2g/1.8g	60.4	0.0	0.0	0.0
0.4g/1.6g	55.5	50.7	25.5	25.2
1.6g/0.4g	65.3	23.1	1.7	21.4
1.8g/0.2g	56.6	24.1	-3.6	20.5

Table 5. ICP Analyses of Ni and V from the Coprocessing of Illinois #6 Coal with Hondo Resid (850 °F*) Under Different Conditions at 430 °C, 1000 psig of H₂ (cold) and 300 ppm Mo loaded to coal using (NH₄)₂MoS₄

Coal/ Resid g/g	Time min.	Oil		Asphaltenes		Ash/Char	
		Ni ppm	V ppm	Ni ppm	V ppm	Ni ppm	V ppm
1.0/2.0	10	*	*	370	520	310	510
1.0/2.0	20	*	65	240	450	2000	190
1.0/2.0	40	24	23	240	320	2100	610
1.0/2.0	60	*	0.6	320	150	2500	980
1.0/2.0	80	*	*	310	99	1400	1400
1.0/2.0	120	*	*	49	27	1700	1400
1.0/1.0	60	*	*	180	51	1400	820
1.0/3.0	60	*	*	310	350	710	970
1.0/5.0	60	*	*	130	120	800	980
0.2/1.8	60	*	*	240	100	8500	1500
0.4/1.6	60	*	*	130	*	1700	1500
1.6/0.4	60	*	*	*	*	420	200
1.8/0.2	60	*	*	*	*	630	120

*: Parameter not detected above limit of detection (Limits of detection: Ni: 5 ppm; V: 0.5 ppm)