EFFECT OF PRETREATING OF HOST OIL ON COPROCESSING

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OBJECTIVES

The principal objective of this research was to determine if coprocessing performance (i.e., coal conversion and oil yield) could be significantly improved by pretreating the heavy resid prior to reacting it with coal. For this purpose, two petroleum vacuum resids (1000°F+), one from the Amoco Co. and another from the Citgo Co., were used as such and after they had been pretreated by catalytic hydrogenation and hydrocracking reactions. The pretreatments were aimed at improving the host oil by; (1) converting any aromatic structures in the petroleum to hydroaromatic compounds capable of donating hydrogen, (2) cracking the heavy oil to lower molecular weight material that might serve as a better solvent, (3) reducing the coking propensity of the heavy oil through the hydrogenation of polynuclear aromatic compounds, and (4) removing metals and heteroatoms that might poison a coprocessing catalyst. Highly dispersed catalysts, including fine particle Fe- and Mo-based, and dicobalt octacarbonyl, $Co_2(CO)_8$, were used in this study. The untreated and pretreated resids were extensively characterized in order to determine chemical changes brought about by the pretreatments. The modified heavy oils were then coprocessed with an Illinois No.6 coal as well as with a Wyodak coal, and compared to coprocessing with untreated resids under the same hydroliquefaction conditions. The amount of oil derived from coal was estimated by measuring the level of phenolic oxygen (derived mainly from coal) present in the oil products.

INTRODUCTION

The world's supply of petroleum crude is becoming heavier so that the amount of vacuum tower bottoms (resid) has been steadily increasing. Coprocessing of coal with petroleum resid (1000°F+) may be an attractive way of obtaining valuable distillates from these readily available and relatively inexpensive hydrocarbon sources.[1,2,3,4]

In general, petroleum is a poor coal liquefaction solvent and coal conversion in heavy oil in the absence of a liquefaction catalyst is usually less than that achieved in the coal-derived recycle solvent used in conventional liquefaction processes.[5,6] This is mainly because petroleum contains fewer aromatic and hydroaromatic compounds. Some hydroaromatic compounds are known to donate hydrogen and certain polynuclear aromatic compounds shuttle hydrogen atoms during coal liquefaction. Both of these steps are important for bringing about high levels of coal dissolution.

One approach for improving coprocessing coal conversion involves modifying the heavy oil prior to reacting it with coal. Takeshita and Mochida[7] obtained a coal conversion of 88% with a petroleum pitch that had first been hydrotreated at high pressure over a $Ni/Mo/Al_2O_3$ catalyst. A similar approach was taken by Sato and coworkers[8] who obtained high conversions and high distillable oil yields from a Japanese subbituminous Taiheiyo coal in a tar sand bitumen that was prehydrotreated with a Ni-Mo catalyst. Curtis and coworkers[9,10,11] showed that high levels of coal conversion can be obtained in a host that contained a mixture of both heavy oil and hydrogen donor compounds.

EXPERIMENTAL

Material

This project used two different petroleum vacuum tower resids (1000°F+); one from the Amoco Oil Company the other from the Citgo Oil Company. Properties of the resids are given in Table 1. Experiments were first conducted with the Amoco resid in order to explore reaction conditions required to hydrogenate and hydrocrack a resid, and to evaluate the sensitivity of reaction parameters such as time, temperature and pressure on product yields. The Citgo resid, however, was chosen as the primary heavy oil to test because it came from an identifiable crude oil source, Venezuela. The Amoco resid, on the other hand, was derived from a wide mixture of crude oils from around the world.

Two different coal samples were used; an Illinois No 6 bituminous coal and a Wyodak subbituminous coal. Most of the work was done with the Illinois No 6 coal. Both coals are Argonne premium samples that had been ground to -100 mesh and stored in sealed glass vials. Properties of the coals are listed in Table 2.

Several different finely dispersed catalyst systems were used; Fe_2O_3/SO_4, $Mo/Fe_2O_3/SO_4$, $Mo(CO)_6+Fe(CO)_5$ and Mo naphthenate. The sulfated iron oxides, synthesized in our laboratory, have been previously described and successfully tested in coal liquefaction and coprocessing reactions.[12,13,14] Iron and Mo carbonyls were obtained from Aldrich Chemical Co. and Mo naphthenate, which contained 6% Mo by weight, was obtained from ICN Biomedical Inc. It is known that the iron compounds used in this study are transformed to pyrrhotites ($Fe_{1-x}S$) at reaction conditions in the presence of sulfur, which was supplied in our experiments by adding either H_2S gas or elemental sulfur in excess to the reactants. It is generally accepted that pyrrhotites, along with H_2S gas, function as hydrogenation catalysts. Under similar conditions, the Mo compounds used in this study are transformed to MoS_2, which acts as a catalyst.

A homogeneous catalyst, dicobalt octacarbonyl, $Co_2(CO)_8$, and a 1:1 synthesis gas system was used based on findings that cobalt carbonyl, $Co_2(CO)_8$, can partially hydrogenate polynuclear aromatic compounds at relatively low temperatures, below 250 °C, in the presence of CO and H_2.[15,16]. Project SEACOKE[17], carried out by ARCO, also demonstrated the action of transition metal carbonyls using coal model compounds as well as coal derived liquids.

Petroleum Resid Pretreatment Reactions and Product Workup

The petroleum vacuum resids were pretreated in a well-stirred stainless-steel 300 ml autoclave batch reactor. At the end of the reaction, the reactor was cooled to room temperature and gases were vented and collected for analysis. The reactor was then opened and products were removed by washing with tetrahydrofuran (THF). The THF-washed material was sonicated for 30 minutes and separated into two fractions according to their solubility in THF. The THF-soluble liquid, which contained oil and asphaltenes, was used as the host oil in coprocessing runs. Asphaltenes are soluble in THF but insoluble in pentane, and oil is soluble in both THF and pentane.

The product workup procedure was later improved by adding an atmospheric distillation step to remove any light (bp<380°F) products directly from the reactor prior to washing with THF. The light oil fraction was recombined with the heaver fraction before being used as a coprocessing host oil.

Products containing $Co_2(CO)_8$ were refluxed for three hours to destroy the carbonyl. To further facilitate removal of cobalt, silica-alumina powder was added to the product mixture prior to filtering.

Coal- Heavy Oil Coprocessing Reaction and Product Workup

Coprocessing experiments were performed in a horizontal, stainless-steel microreactor. The microreactor system has been previously described[12]. At the end of the reaction, the reactor was removed from the sand bath and cooled to room temperature. Gases were vented and collected for analysis; gas production was determined by weight loss. Oil products were recovered by washing the reactor with pentane. Asphaltenes were recovered by washing with THF. The material that was insoluble in both pentane and THF consisted of coke and coal-derived mineral matter. Pentane was removed from the filtered oil by a rotovapor under atmospheric pressure instead of vacuum pressure. This was done to minimize losses of light compounds during this product recovery step. However, under the mild separation condition, a small amount of pentane remained dissolved in the oil. This amount was latter measured by simulated distillation.

Reactant and Product Characterization Techniques

Product gases were analyzed for composition (H_2, H_2S and C1-C5) using an HP 5880A GC. Light pentane-soluble oils (free of ash and asphaltenes) were analyzed for composition with an HP 5890 series II GC/HP 5970 mass selective detector. A boiling curve for pentane-soluble oil samples was estimated using simulated distillation techniques[18] with an HP 5890 series II GC. Product oil and asphaltene samples were analyzed for their hydrogen type and aromatic content by ^1H NMR using a Bruker 3000 MSL spectrometer; samples were prepared in deuterated chloroform with tetramethylsilane for internal reference. Catalytic dehydrogenation[19] was used to measure the "available" hydrogen of untreated resids and pretreated host oils. Available hydrogen was defined as the amount of hydrogen gas evolved when an oil sample was catalytically dehydrogenated at atmospheric pressure in boiling phenanthridine (bp=350°C) for 285 min over a reduced $Pd/CaCO_3$ catalyst. Metal contents (V and Ni) of selected samples were measured by The Pittsburgh Applied Research Corp. using the ICP technique. The elemental composition (C, H, S and N) of selected samples was measured by Galbraith Laboratories Inc. and CONSOL Inc. The phenolic oxygen concentration of pentane-soluble oil samples was measured by CONSOL Inc. using an FTIR method.[20]

RESULTS AND DISCUSSION

Resid Pretreatment Experiments

A critical property of a liquefaction solvent is its ability to supply hydrogen to coal during coprocessing. From pretreatments with the Amoco oil, we found that the available hydrogen content of the pretreated resids was sensitive to pretreatment temperature.

Pretreatment of the Amoco resid at a reaction temperature of 440°C, using Mo naphthenate resulted in a decrease in available hydrogen content. When the same resid was pretreated at a lower temperature of 400°C, using either Mo/Fe_2O_3/SO_4 or Mo naphthenate, the available hydrogen content of the starting resid almost doubled.

Four different pretreatments of the Citgo resid were performed around 400°C; one above it and three below it. Conditions for these runs are summarized in Table 3. The first pretreatment, referred to as A, involved cracking the resid at 440°C for two hr with the main objective of reducing molecular weight and removing sulfur and metals. The other three pretreatments, referred to as B through D, involved hydrogenating the resid at temperatures below 400°C where cracking is suppressed. The objective of these runs was to increase available hydrogen.

Properties of the untreated Citgo resid and the four pretreated Citgo host oils are listed in Table 4. The A host oil was lighter, based on wt% of distillate (bp<565°C), than the untreated Citgo resid as well as the other pretreated oils. This was expected due to the higher pretreatment temperature used. The atomic H/C ratio of this host oil was slightly higher than that of the untreated resid and its C/S ratio was higher, indicating that sulfur atoms had been removed. The atomic C/N ratio of A was slightly lower than that of the starting resid, suggesting that nitrogen atoms were not removed. The available hydrogen content of A was slightly higher than that of the untreated resid. The available hydrogen content of the host oils from the mild temperature pretreatments (B, C and D) was much higher than that of the untreated resid and A. The increase in available hydrogen content for the host oil from pretreatments B, C and D was slightly below the amount of hydrogen gas consumed during these runs, indicating significant hydrogen utilization. The atomic H/C, C/S and C/N ratios of the host oils exposed to mild temperature pretreatments were essentially unchanged.

Effect of Host Oil Type and Coal Feed Concentration on Coal Conversion

Coprocessing experiments were conducted in order to evaluate the four pretreated host oils (A, B, C, and D) under thermal (no added catalyst) as well as catalytic conditions. Results of these experiments were compared to base-line runs made with the untreated Amoco and Citgo resids. The bulk of the work was done with Illinois No. 6 coal at the following thermal coprocessing conditions; 425°C, 1000 psig (cold) H_2 and 30 min reaction time. In these runs, the coal-feed concentration was varied from 10 to 50 wt%.

Table 5 lists reaction conditions and results (coal conversion and product yields) for coprocessing experiments made with the Illinois No.6 coal. The data are grouped by host oil type. At baseline reaction conditions (30 min reaction time, 425°C, 1000 psig H_2, host oil:coal feed ratio of 2:1), the Illinois No.6 coal reacted with the untreated Citgo resid, resulting in 74 wt% (maf) of coal converted to THF-soluble products and gases. When the Illinois coal was coprocessed with untreated Amoco resid under the same reaction conditions, 56 wt% of coal (maf) was converted. The fraction of coal converted to gases and soluble products was not measured directly, but was determined by the amount of unconverted THF-insolubles. The following equation was used to calculate coal conversion.

$$Y_T = 100 * [1.0 - \frac{W_i - W_{ash} - W_{cat} - W_{pc}}{W_{maf}}]$$

where,

Y_T = coal conversion, %

W_{ash}, W_{cat}, W_i, W_{maf}, W_{pc} = mass of ash, catalyst, THF insolubles, maf coal, and petroleum coke, g

The low coal conversions obtained with the two untreated petroleum resids illustrate that petroleum is a poor liquefaction solvent, due mainly to its low supply of donatable hydrogen. Increasing the supply of active hydrogen by addition of 2000 ppm of Mo to the Citgo resid, with other reaction parameters held constant, resulted in an increase in Illinois coal conversion, from 74 wt% to 88 wt%. However, the aim of this study was to increase coal conversion by improving the properties of the host-solvent through pretreatment.

Figure 1 shows that the conversions of Illinois No. 6 coal in the host oils that were pretreated at mild reaction temperatures (B, C and D) were higher than levels achieved with the untreated Citgo resid or the host oil from the high temperature pretreatment, A. Coal conversions in the Citgo resid and in A decreased as the concentration of coal in the feed was increased. This trend demonstrates the limited ability of these host oils to bring about coal conversion. On the other hand, coal conversions in B, C and D remained high at all coal loadings tested. Coal conversions in B, C and D were slightly higher than conversions obtained when the coal was catalytically coprocessed in the Citgo resid using either Mo naphthenate (2000 ppm Mo) or $Mo/Fe_2O_3/SO_4$ (2 wt%).

These results demonstrate that the pretreated oils B, C and D are superior to untreated Citgo resid or A to obtain high levels of coal conversion. These results can be rationalized in terms of available hydrogen. The available hydrogen content of B, C and D was higher than that of A or the untreated Citgo resid (Table 4).

Effect of Host Oil Type and Coal Feed Concentration on Product Yield and Quality

Products from coal-heavy oil coprocessing include gases, pentane-soluble oil, asphaltenes, and THF-insoluble coke (excludes coal-derived minerals and, when used, catalyst). Asphaltene yields were determined by difference. Pentane-soluble oil yields were corrected to exclude dissolved pentane, by simulated distillation. We found that product yield was affected by the concentration of coal in the feed. This can be seen in Figure 2, which shows that, for coprocessing runs with host C, oil yield reached a maximum at a coal-feed concentration between 10 % and 33 wt%. With every host oil, asphaltene yields were highest at coal loading of 50 wt%, the highest coal-feed concentration studied. In general, asphaltene yields were lowest at coal-feed concentration where the oil yields were highest; both gas and coke yield remained at a low level and did not change much with coal-feed concentration. These results suggest that high level of oil production is brought about by conversion of asphaltenes (petroleum- or coal-derived) to oils. Furthermore, oil yields appear to be enhanced by the presence of small amounts, less than 33 wt%, of coal. In coprocessing runs made with A, the oil yield decreased as coal was added to the feed, while asphaltene and coke yield increased.

Distribution of products from coprocessing Illinois coal with untreated Citgo resid and the various pretreated host oils is shown in Figure 3. Based on oil yield, the host oils are ranked in the following order; D > C > untreated Citgo resid > B > A. The differences between the oil yield for D, C and untreated Citgo resid are small; little improvement in oil yield was realized as a result of our pretreatments of the Citgo resid.

Properties of the oil and asphaltene from the various coprocessing runs are listed in Table 6. In general, the product oils had atomic H/C ratios above 1.6, had a low concentration of nitrogen (about 0.3%) and contained a significant amount of oxygen (higher than 1.4%) and sulfur (above 1.5%). Essentially all the oxygen is presumably from the coal. The oil from the coprocessing run with A was the lightest oil produced; over 55 wt% of this oil had a simulated distillation boiling range below 650°F. Oil A was lighter than the other host oils. Product oils from the other coprocessing runs contained over 25 wt% of resid material; over 65 wt% of the oil boiled above 650°F, indicating that only a small fraction of the starting host oil and coal was converted to light distillate products. Further, the fraction of light distillate products that boiled in the gasoline and diesel range remained small at all coal loadings studied.

The asphaltenes had about the same concentration of S and O as the corresponding oils, but were richer in N and contained metals. The asphaltenes had a high aromatic carbon content (over 60 %) and had an average atomic H/C ratio of less than one.

The Amount of Coal Liquids in the Oil Products

The various products from coprocessing of coal and heavy oil are a mixture of coal-derived and petroleum-derived material that cannot easily be separated. To estimate the fraction of coal liquids and petroleum in the pentane-soluble oil products, the phenolic oxygen concentration of oil samples was measured and correlated to the fraction of coal liquid in the products. Since the Illinois coal contains much more oxygen than that of the Citgo resid (Tables 1 and 2) and a significant portion (about half) of oxygen in coal is associated with phenols, it was expected that the phenolic oxygen in the oil was essentially from the coal. The concentration of oxygen as phenolic OH for oils produced by coprocessing Illinois coal with the five Citgo host oils is shown in Figure 4. The data point at zero coal-feed concentration was measured on oil obtained by processing the untreated Citgo resid without coal; all other conditions were the same as those used in the coprocessing runs. From this measurement, we assigned the petroleum-derived oil component an average phenolic oxygen concentration of 0.26 wt%. The two data points at 100 % coal-feed concentration were the phenolic oxygen of the pentane-soluble products from processing Illinois coal in the non-hydrogen donor solvent, diphenylmethane (DPM); all other conditions were the same as those used in the coprocessing runs. The values, which average 1.78 wt%, have been corrected to account for the presence of DPM, and they reflect the estimated phenolic oxygen concentration of the coal-derived oil. As shown in Figure 4, the phenolic oxygen concentration of the oil products fell between the two end points and increased as the concentration of coal in the feed was increased; and the amount of coal liquid in the oils increased as the concentration of coal in the feed was increased.

An estimate of the fraction of coal liquid present in the oils allowed study of the effect of host oil type and coal-feed concentration on the yield of coal-derived and petroleum-derived oils. Using phenolic oxygen concentration, the weight fraction of coal liquid in the oil products was calculated by the following equation.

$$x=\left[\frac{C_t-C_p}{C_c-C_p}\right]$$

where,
x = fraction of coal-derived liquid in oil product
C_c, C_p, C_t = concentration of phenolic-oxygen in coal-derived oil, petroleum-derived oil and oil product, wt%

The equation assumes that the phenolic-oxygen concentration of the coal and petroleum components did not change as a result of interactions between coal and heavy oil during coprocessing. Three oil yield curves for coprocessing runs made with C are shown in Figure 5. The top curve represents the overall oil yield. The yield of coal-derived oil, as measured by phenolic oxygen content, is represented by the lower curve. It starts at zero and ends at 28 wt%. This last point was obtained by processing the Illinois coal in DPM. The yield of petroleum-derived oil is represented by the middle curve. The starting point for this curve was determined by processing the host oil without coal, with all other reaction conditions the same as those used in coprocessing runs. The straight dashed lines drawn between the end points represent the oil yields assuming no interaction between coal and pretreated resid. These lines are simply the linear extrapolation of produced oil yields obtained when the coal and host oil were processed separately. Any deviation of the experimental data points above or below the dashed lines would imply an interaction between coal and host oil which either resulted in an enhancement or reduction in the oil yield.

In coprocessing runs with host C and D (not shown) the presence of small amounts of coal (less that 33 wt%) seemed to enhance the yield of petroleum-derived oil; the data points were above the line. This behavior was also seen in coprocessing runs with the untreated resid. Conversely, the presence of coal with B caused a slight reduction in the yield of petroleum-derived oil, and the yield of oils from A were adversely affected by the presence of coal.

The untreated Citgo resid and oil A had no enhancing effect on the production of coal-derived oil; the data points fell on the dashed line. On the other hand, the resids that were pretreated at mild temperatures (B, C and D) brought about a higher yield of coal-derived oil than were obtained in DPM.

CONCLUSIONS

Certain pretreatments caused the available hydrogen content of the resids to increase, and these pretreated oils became better liquefaction solvents; higher coal conversions were obtained in these oils as compared to untreated resid. However, only a small fraction of the host oil and coal were converted to light distillate products during coprocessing. The yield of product oil with pretreated hosts was about the same as that obtained with untreated resid. Oil and asphaltene yields were strongly affected by the concentration of coal in the feed.

The fraction of coal liquid in the oil products, determined by phenolic oxygen concentration, increased as the amount of coal in the feed was increased. The presence of small amounts, less than 33 wt%, of coal enhanced the yield of oil from the untreated Citgo resid as well as from oils that were pretreated it mild temperatures. The oil yield from the host that was pretreated at 440°C was adversely affected by the presence of coal.

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BIBLIOGRAPHY

1. Shinn, J.H., Dahlberg, A.J., Keuhler, C.W., and Rosenthal, J.W., "The Chevron Co-Refining Process", presented at the Ninth Annual EPRI Contractors Conference on Coal Liquefaction, Palo Alto, CA, May 1984.

2. Greene, M., Gupta, A., and Moon, W., "LCI's Two-Stage Co-Processing Route: Continuous Bench-Scale Operations", presented at the DOE Direct Liquefaction Contractors' Review Meeting, Pittsburgh, PA, October, 1986.

3. Duddy, J., Panvelker, S., and Popper, G., "HRI's Co-Processing Program", presented at the Fifteenth Annual EPRI Conference on Fuel Science, Pal Alto, CA, August, 1991.

4. Kelly, J.F., Fouda, S.A., Rahimi, P.M., and Ikura, M., 'CANMET Co-Processing: A Status Report", presented at the CANMET Coal Conversion Contractors' Review Meeting, Calgary, Alberta, November, 1984.

5. Cugini, A.V., Lett, R.G., and Wender, I., "Coal/oil Coprocessing Mechanism Studies", Energy and Fuels, Vol. 3, 120-126 (1989).

6. Miller, T.J., Panvelker, S.V., Wender, I., and Tierney, J.W., " Thermal Non-Catalytic Coprocessing of Illinois No. 6 Coal with Maya Resid and Boscan crude", Fuel Processing Technology, Vol.23, 23-38 (1989).

7. Takeshita, K. and Mochida, I., Jap. Pat. 80-45703 (1980)

8. Sato, Y., Yamamoto, Y., Kamo, T., Inaba, A., Miki, K., and Saito, I., "Effect of Hydrotreatment of Various Heavy Oils as Solvent for Coal Liquefaction", Energy & Fuels, Vol 5, 90-102 (1991).

9. Curtis, C.W., Tsai, K.-J. and Guin, J.A., "Effect of Solvent Composition on Coprocessing Coal with Petroleum Residua", Fuel Processing Technology, Vol 16, -17 87 (1987).

10. Bedell, M.W., Curtis, C.W. and Hool, J.L., "Reactivity of Argonne coals in the presence of cyclic olefins and other donors", Fuel Processing Technology, Vol 37, 1-18 (1994).

11. Owens, R.M. and Curtis, C.W., " An Investigation of Hydrogen Transfer from Naphthenes during Coprocessing", Energy & Fuels, Vol 8, 823-829 (1994)

12. Pradhan, V.R., Hu, J., Tierney, J.W., and Wender, I., "Activity and Characterization of Anion-Modified Iron(III) Oxides as Catalysts for Direct Liquefaction of Low Pyrite Coals", Energy & Fuels, Vol 7, 446-454 (1993).

13. Pradhan, V.R., Herrick, D.E., Tierney, J.W., and Wender, I., "Finely Dispersed Iron, Iron-Molybdenum, and Sulfated Iron Oxides as Catalyst for Coprocessing Reactions", Energy & Fuels, Vol 5, 712-720, (1991).

14. Pradhan, V.R., Holder, G.D., Wender, I., and Tierney, J.W., "Kinetic Modeling of Direct Liquefaction of Wyodak Coal Catalyzed by Sulfated Iron Oxides", I&EC Res. Vol. 31 (1992) 2051-2056

15. Friedman, S., Metlin, S., Svedi, A., and Wender, I., "Selective Hydrogenation of Polynuclear Aromatic Hydrocarbons", J. Org. Chem, Vol 24, 1287, (1959).

16. Wender, I., Levine, R., and Orchin, M., J. Am. Chem. Soc., Vol.72 (1950) 4375

17. ARCO Chemical Company, "Catalytic Hydrogenation of Coal-Derived Liquids", Project SEACOKE, Phase II, Final Rep., Contract No. 14-01-0001-472, Off. Coal Res., U.S. Dept. of Interior, Washington, DC (1966)

18. ASTM Designation: D 2887-89, Annual Book of ASTM Standards

19. Whitcomb, J.H., M.S. Thesis, University of Pittsburgh, 1993.

20. Robbins, G.A., Winschel, R.A., and Burke, F.P., "Phenolic -OH as a Process-Performance Indicator in Two-Stage Liquefaction", Am. Chem. Soc. Div. Fuel Chem. Prepr., 155-163, (1986).

Table 1 Properties of Two Petroleum Resids (1000 °F+)

	Citgo Resid	Amoco Resid
S.G. @ 60°F		1.03
C, wt%	85.4	84.3
H, wt%	10.1	10.2
S, wt%	3.4	4.6
N, wt%	0.8	0.5
O, wt%	0.3	0.4
Atomic H/C	1.42	1.45
V, ppm	555	251
Ni, ppm	110	57
Fe, ppm	12	13
Pentane insolubles, wt%	29	20
Available H/100 C atoms	9.8	
f_a, fraction of total C	0.33	0.32

Table 2 Properties of Argonne Coal Samples

	Illinois No.6	Wyodak
Moisture, wt%	8.0	28.1
Ash, wt%	14.3	6.3
Volatile matter, wt%	35.8	32.2
Rank	hvB	Subbituminous
C, wt% (maf)	77.7	75.0
H, wt% (maf)	5.0	5.3
N, wt% (maf)	1.4	1.1
S, wt% (maf)	2.4	0.5
Cl, wt% (maf)	0.06	0.03
O, wt% (maf)	13.5	18.0
Atomic H/C	0.77	0.85
f_a	0.71	0.62

f_a = Fraction of aromatic carbon, determined by ^{1}H NMR using the Brown and Ladner method (1960).

Table 3 Reaction Conditions and Product Yields for Pretreatments of Citgo Resid

Conditions	Oil-A	Oil-B	Oil-C	Oil-D
Catalyst, concentration	MN, 1000 ppm	MN, 1000 ppm	$Mo/Fe_2O_3/$ SO_4, 200 ppm Mo 13000 ppm Fe	$Co_2(CO)_8$ 6.2 wt%
Gas used	H_2	H_2	H_2	CO/H_2 (1:1)
Temperature, °C	440	375	375	135
Pressure (cold), psig	1,000	1,000	1,000	2,000
Time, hrs	2	5	5	2
Gas yield, wt%	25	1	3	0
Liquid yield, wt%	72	97	95	100
Coke yield, wt%	3	2	2	0

MN=Mo naphthenate (6 wt% Mo)

Note: elemental sulfur was added in pretreatments A, B and C in excess of amount needed to sulfide the catalyst.

Table 4 Properties of Citgo Pretreated Host Oils

	Citgo Resid	Oil-A	Oil-B	Oil-C	Oil-D
b.p.<565°C[a], wt%		62.6	29.7	33.3	17.9
b.p.>565°C, wt%		37.4	70.3	66.7	82.1
C, wt%	85.4	85.1	85.9	85.6	84.8
H, wt%	10.1	10.6	10.4	10.8	10.0
S, wt%	3.4	2.2	2.7	2.9	2.9
N, wt%	0.8	0.9	0.9	0.8	0.8
O, wt%	0.3	1.2	0.1	0.0	1.5
Atomic H/C	1.42	1.49	1.45	1.51	1.42
Atomic C/S	67	103	85	79	78
Atomic C/N	124	110	111	125	124
V, ppm	555	393		472	
Ni, ppm	110	67		95	
Available[b] Hydrogen per 100 C atoms	9.9	12.4	16.8	14.0	17.5
wt% H_2 added		1.4	0.5	0.5	0.5

a: b.p.<565°C consists of pentane-soluble oil having a simulated distillation b.p.<565°C (1050°F). b.p.>565°C consists of pentane-insoluble asphaltenes and pentane-soluble oil having simulated distillation b.p.>565°C.

b: Value based on catalytic dehydrogenation.

Table 5 Reaction Conditions and Results of Illinois No.6 Coprocessing Runs (Conditions: 1000 psig (cold) H_2, 30 min reaction time, other conditions shown in table)

Host Oil	Run No.	Cat.	Oil: Coal	Tavg, °C	Pavg, psig	Coal Conv, wt%	Gas yield, wt%	Oil yield, wt%	Asph. yield, wt%	Coke yield wt%
Amoco Resid	69	none	2:1	427	2104	56	10.1	73.1	in oil	16.8
Citgo Resid	85	none	2:1	415	2046	74	3.3	69.4	13.9	8.7
Citgo Resid	87	none	1:1	427	2227	58	6.0	40.4	28.7	17.8
Citgo Resid	119	Fe	2:1	423	1889	81	6.7	70.2	12.3	6.1
Citgo Resid	136	MN	2:1	425		88	5.0	70.0	16.0	4.2
Oil-A	115	none	2:1	425	2097	74	4.7	48.4	34.5	7.6
Oil-A	114	none	1:1	425	2257	71	3.9	40.0	37.3	11.7
Oil-B	96	none	9:1	426	1756	85	4.9	95.1	-4.2	2.8
Oil-B	142	none	4:1	424	1805	85	7.1	78.0	8.3	3.7
Oil-B	91	none	2:1	427	1766	92	6.5	65.0	20.5	3.3
Oil-B	95	none	2:1	428	1790	93	5.1	67.3	19.8	3.0
Oil-B	141	none	1.5:1	424	1844	90	5.8	64.6	19.7	4.2
Oil-B	93	none	1:1	425	1849	89	6.0	46.8	34.8	5.2
Oil-C	100	none	9:1	425	1803	72	10.1	99.0	-16.2	5.6
Oil-C	143	none	9:1	423	1796	89	4.1	68.4	23.4	2.7
Oil-C	144	none	4:1	425	1813	94	3.3	61.3	29.9	2.6
Oil-C	117	none	2:1	425	1915	94	6.7	74.6	9.9	4.1
Oil-C	97	none	2:1	426	1874	93	4.1	46.9	39.9	4.4
Oil-C	145	none	1.5:1	425	1844	89	5.7	43.4	39.4	5.7
Oil-C	98	none	1:1	425	2311	56	6.0	31.0	36.7	19.1
Oil-C	107	none	1:1	425	1890	90	6.5	53.3	27.4	5.6
Oil-D	106	none	9:1	424	1697	86	3.3	71.3	20.7	3.3
Oil-D	118	none	9:1	424	1710	43	6.5	85.0	0.3	6.8
Oil-D	147	none	4:1	424	1777	85	11.3	63.7	17.7	4.5
Oil-D	102	none	2:1	425	1032	88	4.2	78.5	7.7	4.8
Oil-D	137	none	2:1	426	2071	44	13.6	42.4	23.4	16.1
Oil-D	146	none	1.5:1	425	1781	90	5.2	47.5	37.2	4.4
Oil-D	103	none	1:1	426	1764	91	4.3	56.7	27.2	4.7

Fe = Mo/Fe_2O_3/SO_4 (1 wt% Mo)
MN = Mo Naphthenate (6 wt% Mo)
Oil-A= Citgo resid hydrotreated with 1000 ppm Mo naphthenate at 440°C for 2 hrs.
Oil-B= Citgo resid hydrotreated with 1000 ppm Mo naphthenate at 375°C for 5 hrs.
Oil-C = Citgo resid hydrotreated with 2 wt% Mo/Fe_2O_3/SO_4 (1% Mo) at 375°C for 5 hrs.
Oil-D = Citgo resid hydrotreated with 6.2 wt% $Co_2(CO)_8$ and 1:1 H_2:CO at 135°C for 2 hrs.
Asph. = Asphaltenes (determined by difference)

Table 6 Properties of Coprocessing Oil and Asphaltenes (conditions: 425°C, 1000 psig (cold) H_2 , host oil:coal = 2:1, 30 min reaction time)

Properties	Citgo resid + Illinois No.6		Oil-A + Illinois No.6		Oil-B + Illinois No.6		Oil-C + Illinois No.6		Oil-D + Illinois No.6	
	Oil	Asph	Oil	Asph	Oil	Asph	Oil	Asph	Oil	Asph
< 421°F, wt%	13.4		19.5		12.6		9.5		14.2	
421-650°F, wt%	21.0		36.4		16.4		15.5		12.1	
650-1050°F, wt%	38.6		36.9		43.7		39.4		42.4	
1050°F +, wt%	27.0		7.2		27.3		35.6		31.3	
Atomic H/C	1.62	0.35	1.67	0.86	1.66	0.96	1.69	0.86	1.64	0.90
S, wt%	2.3		1.6		1.8	1.8	2.0		2.2	2.2
N, wt%	0.3	2.5	0.2	1.8	0.3	1.8	0.3	1.9	0.3	1.8
O, wt%	1.4		2.7		4.0	3.5	3.0		3.3	2.9
f_a	0.29		0.25	0.74	0.25	0.62	0.22	0.75	0.27	0.66
V, ppm		1015		206				750		
Ni, ppm		204		43				205		

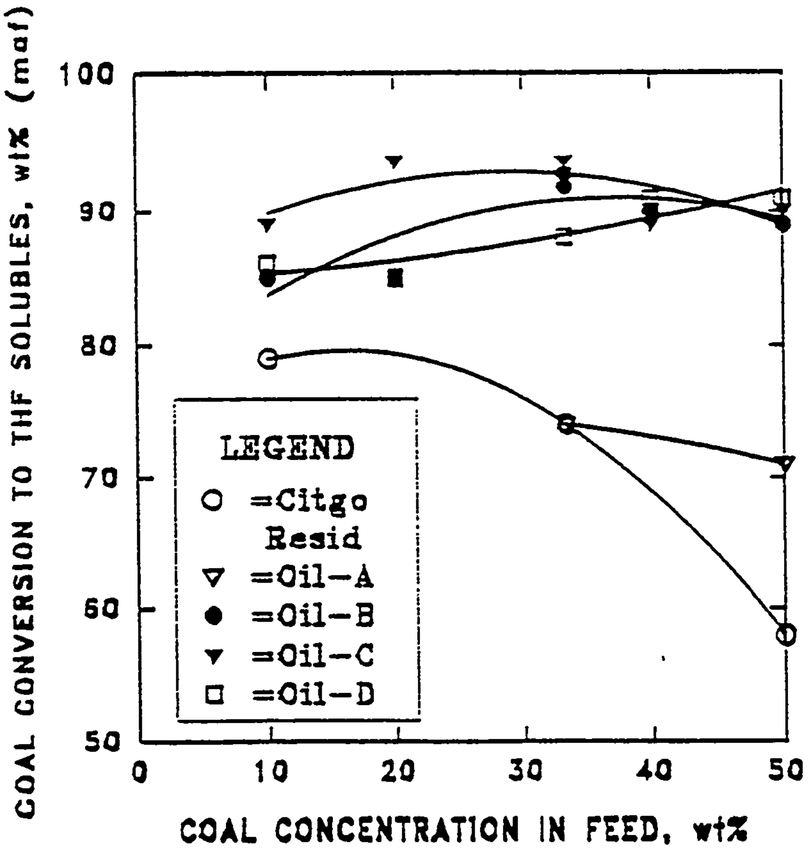

Figure 1 Illinois No.6 Coal Conversions When Coprocessed With Citgo Resid and Pretreated Host Oils (conditions: 425°C, 1000 psig (cold) H_2, 30 min)

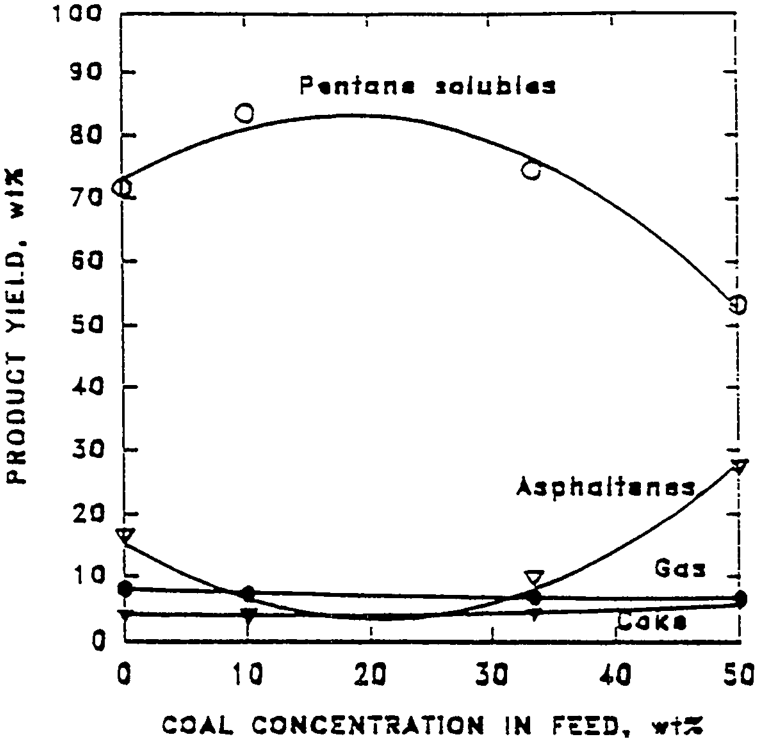

Figure 2 Product Yields from Coprocessing Illinois No.6 Coal and Host Oil-C (conditions : 425°C, 1000 psig (cold) H_2, 30 min)

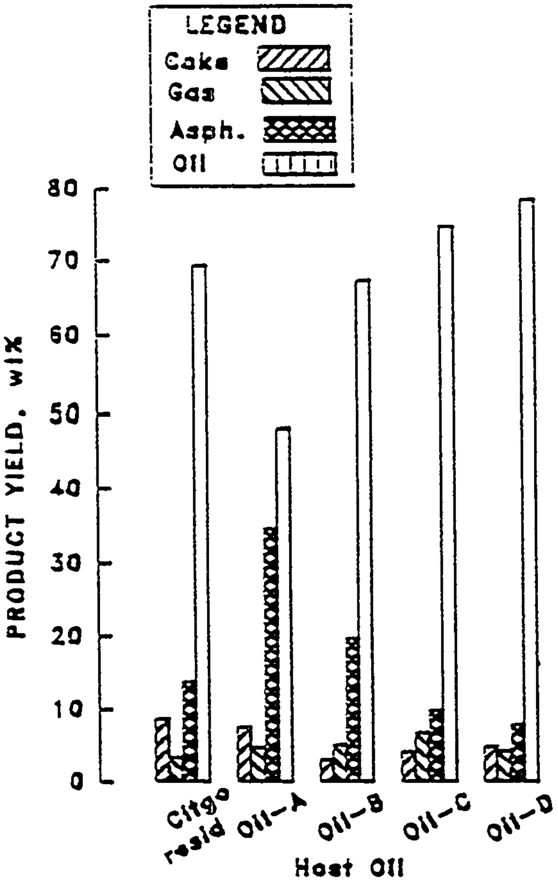

Figure 3 Product Yields from Coprocessing Illinois No.6 Coal and Citgo Host Oils (conditions : 425°C, 1000 psig (cold) H_2, 30 min, host oil:coal=2:1)

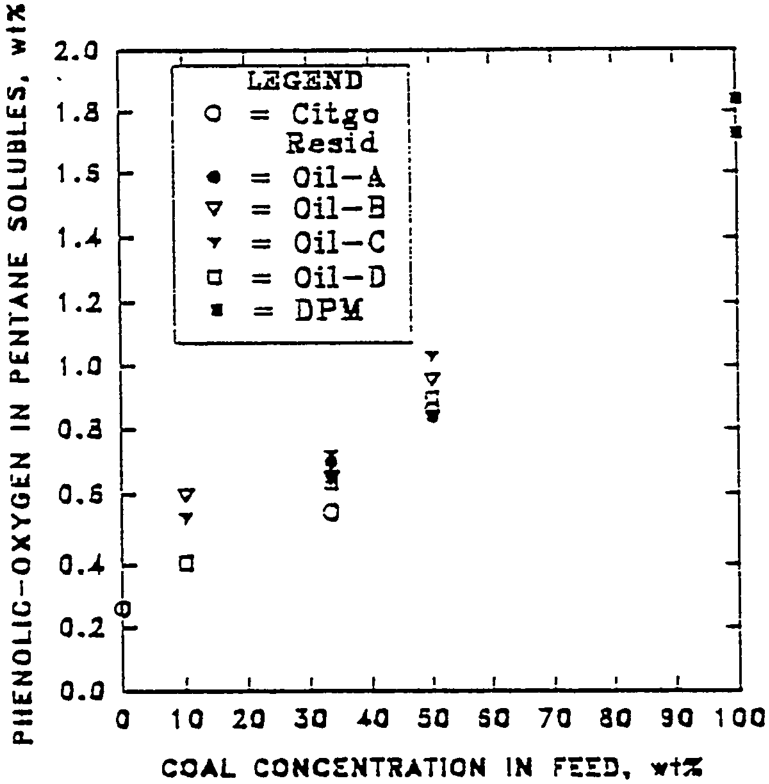

Figure 4 Concentration of Oxygen as Phenolic-OH in Pentane-Soluble Products from Coprocessing Illinois No.6 Coal with the Various Citgo Host Oils

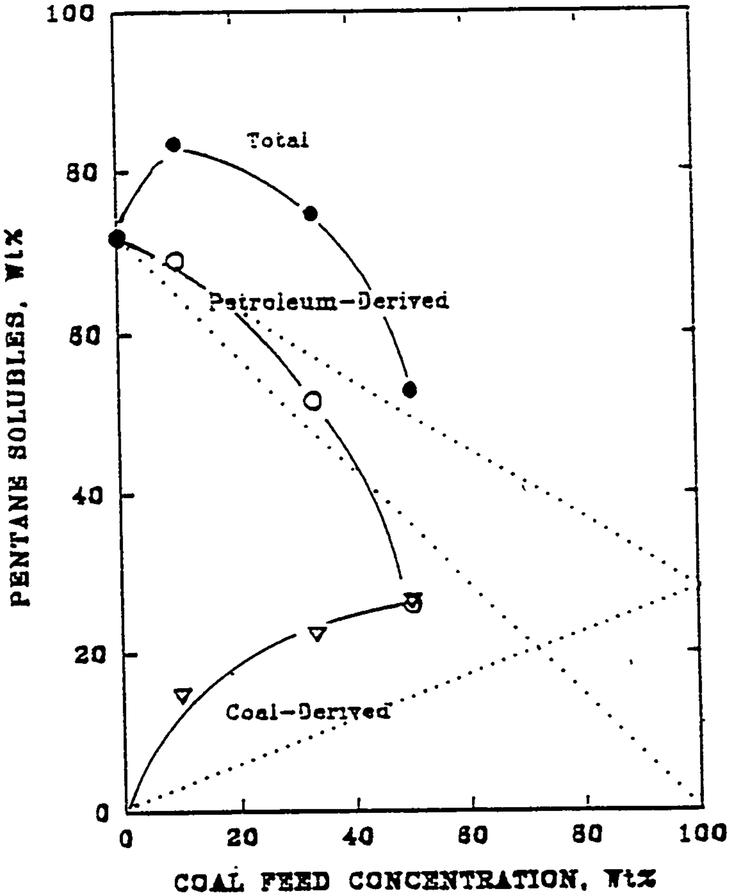

Figure 5 Petroleum-Derived and Coal-Derived Oil Yields from Coprocessing Illinois No.6 Coal with Host Oil-C (conditions: 425°C, 1000 psig (cold) H_2, 30 min)