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THE UPGRADING OF PETROLEUM RESIDUUM AND COAL IN CATALYTIC COPROCESSING

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Abstract—The combined catalytic reactions using different types of petroleum residuum and coal were performed at 425°C and 60 minutes in the presence of hydrogen to upgrade both materials to high quality synthetic fuels. In order to improve this coprocessing technology, the effect of the chemical and physical properties of both materials on the coprocessing product yields was investigated through a parametric study. In all reaction combinations, substantial increase in maltene production and high coal conversions of over 84% were observed regardless of petroleum residuum type and coal rank. The petroleum residuum properties of specific gravity and conradson carbon residue had effects on asphaltene production and coal conversion. The results of quantitative analysis for the amount of coal upgraded during coprocessing lead to conclude that a large amount of coal converted to maltene fraction due to high catalytic activity and reactive hydrogen donor richness of coprocessing system. However, most of the heavier fractions were formed primarily from coal regardless of the type of residuum used.

Key words: *Upgrading, Petroleum Residuum, Coal, Coprocessing, Maltene, Asphaltene, Coal Conversion, Catalytic Reaction, Coal Liquefaction*

INTRODUCTION

Rising consumption and diminishing crude-oil reserves have led to considerable activity in search for alternative hydrocarbon sources [Moschopedis et al., 1980; Probstein and Hicks, 1982]. As a possibility for the replacement of conventional crude, a hybrid of hydrocracking of heavy oil and coal liquefaction has been studied [Monnier, 1980; Yan and Espenscheid, 1983]. It is now known as "oil-coal coprocessing" or simply "coprocessing" [Audeh, 1983; Curtis et al., 1980]. In coprocessing, heavy oil such as atmospheric or vacuum petroleum residua is mixed with coal and hydrogenated under high temperature and pressure. Petroleum residuum used in this coprocessing is a hydrogen rich material which has a H/C ratio of approximately 1.5, while coal is a hydrogen poor material with an average H/C ratio of 0.8 [Moschopedis, 1980]. This fact leads to the conclusion that the amounts of hydrogen required in the combined processing of petroleum residuum and coal should be less than those required to obtain the same quality of products in coal liquefaction itself. Thus combined processing of petroleum residuum and coal has been considered as a feasible technology to upgrade both materials and to produce a possible synergy, yielding more and higher quality products at lower processing cost [Curtis et al., 1985; Moschopedis et al., 1982].

EXPERIMENTAL

1. Feedstocks

The petroleum residua used in this study were selected in the range from the more waxy and naphthenic to the more aromatic and asphaltic types. The properties and characteristics of the residua are given in Table 1. The coals ranked from the bituminous coal to the lignite were also used, and given in Table 2. The catalyst used in the reactions was an equilibrium catalyst obtained from a heavy oil hydrotreating unit and, consequently, contained substantial amounts of carbonaceous materials. The catalyst was prewashed with toluene and then with tetrahydrofuran in a sonicator bath for 3 days to remove any residual organic material which could be washed out from the catalyst pores, and then was dried at 95°C in a vacuum oven for 12 hours while blowing N_2 gas over the sample.

Table 1. Properties of petroleum residuum

Property	Resid 1	Resid 2	Resid 3
Specific gravity, g/cc	1.054	1.019	1.019
Conradson carbon resid, wt%	26.4	17.1	15.0
Maltene (HS), wt%	71.8	82.6	83.8
Asphaltene (HI), wt%	28.2	17.4	16.2
C, wt%	84.6	84.6	85.1
H, wt%	9.9	10.4	10.5
N, wt%	0.1	0.4	0.6
S, wt%	5.4	4.6	3.8
H/C	1.40	1.47	1.48
Ni, ppm	118	50	112
V, ppm	680	228	450

maltene (HS): hexane solubles
asphaltene (HI): hexane insolubles and toluene solubles

2. Experimental Equipment and Procedures

The coprocessing reactions were performed in a 50 cm^3, one

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Table 2. Properties of coal

Property	Coal 1	Coal 2	Coal 3
Rank	Bituminous	Subbituminous	Lignite
Moisture, wt%	6.3	27.8	28.3
Ash, wt%	9.8	7.3	11.4
C, wt%	81.9	73.9	72.2
H, wt%	5.4	5.2	5.4
N, wt%	1.9	0.7	1.2
S, wt%	1.1	0.5	1.4
O, wt%	9.7	19.7	19.8
H/C	0.79	0.84	0.89

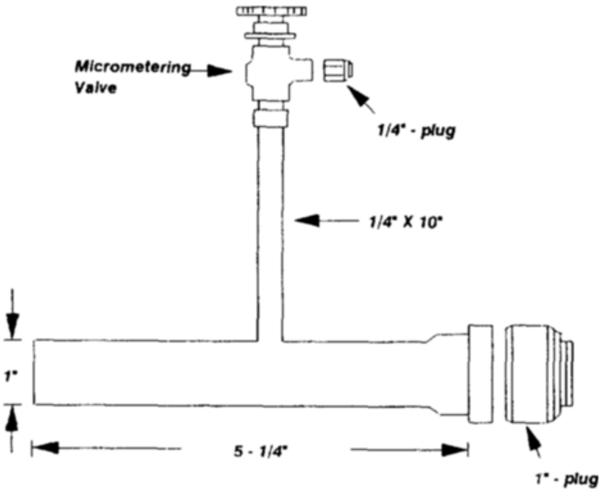

Fig. 1. Diagram of 316 stainless steel tubing bomb microreactor.

Table 3. Coprocessing reactions with different conditions

Reaction conditions	Maltene production (%)		Asphaltene production (%)		Coal conversion (%)	
	(A)	(B)	(A)	(B)	(A)	(B)
Thermal						
400°C /30 min	12	3	−15	13	35	34
425°C /30 min	25	3	−19	7	46	47
Catalytic						
400°C /30 min	22	21	4	14	62	59
400°C /60 min	37	28	−17	15	77	74
425°C /30 min	45	39	−20	10	83	83
425°C /60 min	57	52	−36	5	84	90

(A): Combination of Resid 1 and Coal 1
(B): Combination of Resid 2 and Coal 1

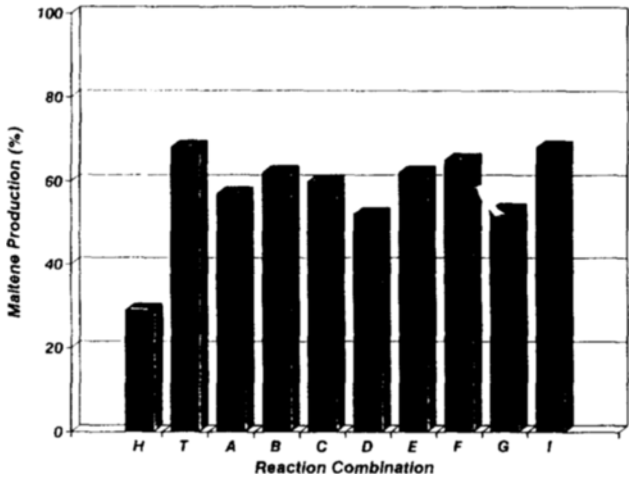

Fig. 2. Comparison of reactions with different combinations in terms of maltene production.

inch O.D. with 0.065 inch wall thickness, 316 stainless steel tubing bomb microreactor as shown in Fig. 1. The reactor was agitated at 800 rpm, and reaction temperature was maintained by immersing the reactor in a fluidized heated sandbath controlled within ±2°C with a Tecam TC4D temperature controller. The reactor was charged with 12 grams of petroleum residuum, coal and catalyst in a gram ratio of 6 : 3 : 3. Hydrogen was introduced into the reactor at the level of 1250 psig at ambient conditions. The gases evolved during the reaction and the hydrogen consumption by the reaction products was determined by gas chromatography. The liquid products were evaluated by fractionating the coprocessed products into maltene (hexane solubles); asphaltene (hexane insolubles and toluene solubles); preasphaltene (toluene insolubles and tetrahydrofuran solubles) and IOM (Insoluble Organic Matter, tetrahydrofuran insolubles) on a moisture, ash and catalyst free basis.

Catalytic coprocessing reaction conditions of 425°C and 60 minutes were selected on the basis of the largest differences observed in the products achieved with two quite different combinations of (A) and (B) during a parametric study. The primary factors used in making the choice of the temperature and time of the coprocessing reactions were the amount of maltene and asphaltene contents achieved and the amount of coal conversion achieved. Two different petroleum residua of the asphaltene-rich Resid 1 and the maltene-rich Resid 3 were used for this parametric study because of large differences in their maltene and asphaltene contents, and the results are presented in Table 3. Thermal reactions were also conducted to establish a base line for thermal reactivity of the coal and petroleum residuum coprocessing system.

The products from the catalytic reactions showed substantial changes (25-35%) in coal conversion at each temperature compared to the thermal reactions for both combinations of (A) and (B). The catalytic reactions at 425°C showed increased maltene productions by 18 to 24 wt% and increased coal conversion of 10 to 20 wt% compared to reactions at the same time at 400°C for each combination. Also, the longer reaction time of 60 minutes increased maltene production by 7 to 20 wt% and coal conversion by 1 to 15 wt% compared to the same conditions at 30 minutes. More importantly, the largest differences in terms of asphaltene production between two combinations were observed at 425°C and 60 minutes. Thus, these results led to conclude that the catalytic reaction conditions of 425°C and 60 minutes are the most feasible conditions to ascertain the compatibility of different petroleum residuum and coal combinations discussed later in this paper.

RESULTS AND DISCUSSION

1. Coprocessing Reactions

The catalytic reactions of Coal 1 with hexadecane were preliminarily conducted to ascertain the dependence of hydrogen donor reactivity of petroleum residuum feedstock on coprocessing pro-

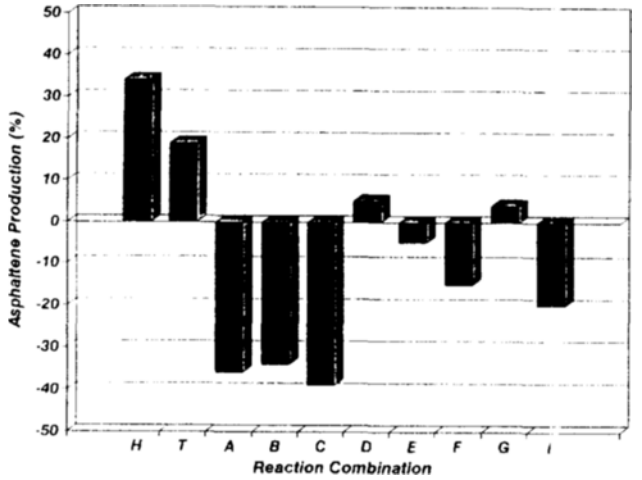

Fig. 3. Comparison of reactions with different combinations in terms of asphaltene production.

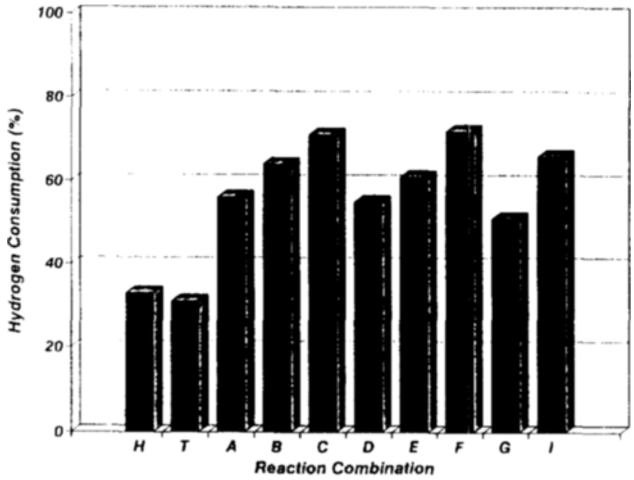

Fig. 5. Comparison of reactions with different combinations in terms of hydrogen consumption.

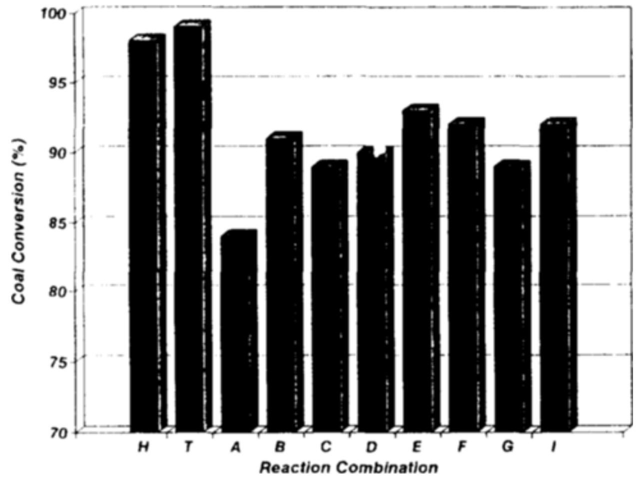

Fig. 4. Comparison of reactions with different combinations in terms of coal conversion.

Table 4. Description of tick levels used in Figs. 2 to 4

Tick level	Description
H	reaction combination of Hexadecane with Coal 1
T	reaction combination of Tetralin with Coal 1
A	reaction combination of Resid 1 with Coal 1
B	reaction combination of Resid 1 with Coal 2
C	reaction combination of Resid 1 with Coal 3
D	reaction combination of Resid 2 with Coal 1
E	reaction combination of Resid 2 with Coal 2
F	reaction combination of Resid 2 with Coal 3
G	reaction combination of Resid 3 with Coal 1
I	reaction combination of Resid 3 with Coal 3

duction yields. Hexadecane was chosen as a relatively non-reactive hydrogen donor solvent, on the contrary, tetralin was chosen as a reactive one. Large differences as shown in Figs. 2 and 3, 40% for maltene production and 15% for asphaltene production, were observed between the coprocessed products using tetralin (designated as "T" in Figs.) and hexadecane (designated as "H" in Figs.). As shown in maltene production of 68%, significant upgrading to maltene occurred with tetralin showing the greater benefit to the coprocessing system compared to that of 29% with hexadecane.

Catalytic reactions using eight different coal and petroleum residuum combinations were performed at 425°C and 60 minutes and the results are presented in Figs. 2 to 5. The description of tick levels used in these Figs. is given in Table 4. For all combinations, the coprocessing products showed substantially large increases in the maltene content resulting from maltene production of over 52%. For all combinations using Coal 2 ranked as subbituminous coal and Coal 3 ranked as lignite, the asphaltene productions were negative. This fact leads to suggest that a portion of asphaltene of the original feedstock was upgraded to lighter fraction during a reaction. This negative value of asphaltene production was also observed in all combinations of Resid 1 regardless of type of coal used. Most combinations showed high coal conversion of over 84% resulting from the less amount of an insoluble organic matter (IOM) produced either from petroleum residuum or from coal. The hydrogen consumption during the coprocessing reactions with Coal 2 and Coal 3 was higher than with Coal 1 containing lower amount of hydrogen as shown in Table 2. In order to determine how the original feed materials were converted during the coprocessing, additional comparison of product distributions for catalytic reaction with those for original feed materials of Resid 1 and Coal 1 is also represented diagrammtically in Figs. 6 and 7.

The relationship between the properties of petroleum residuum and the upgrading yields of petroleum residuum were evaluated in terms of maltene and asphaltene productions and coal conversion with the following properties of petroleum residuum; specific gravity, conradson carbon number and metal content. In examining the reactivity of these properties on the results of the different coprocessing reactions as represented in Tables 1, 2 and 4, the properties of specific gravity and conradson carbon number showed effects on the amount of asphaltene production and coal conversion. The amount of asphaltene production was inversely proportional to these properties of petroleum residuum, while the amount of coal conversion was directly proportional to these properties regardless of type of coal. However, the amount of

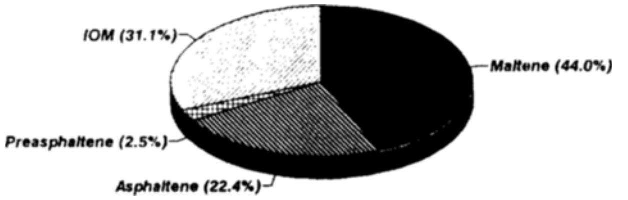

Fig. 6. Fractionization of original feed materials used in Resid 1 and Coal 1 coprocessing combination.

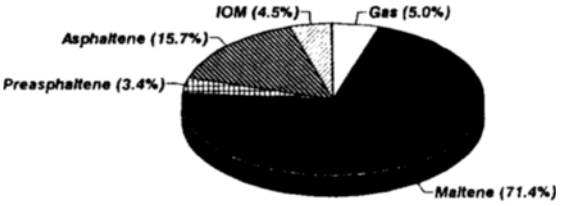

Fig. 7. Product distributions for catalytic coprocessing reaction of Resid 1 and Coal 1 combination.

Table 5. Contribution of coal in coprocessing product fractions

Reaction combination	% of product fraction derived from coal Gas	MAL	ASP	PRE	IOM
Hexadecane/Coal	100	9	100	100	100
Tetralin/Coal	100	20	100	100	100
Resid 1/Coal 1	32	20	58	61	84
Resid 1/Coal 2	44	28	44	38	74
Resid 1/Coal 3	52	23	42	69	78
Resid 2/Coal 1	40	20	75	65	91
Resid 2/Coal 2	48	26	64	46	86
Resid 2/Coal 3	53	25	53	59	89
Resid 3/Coal 1	45	17	82	57	84
Resid 3/Coal 3	52	23	62	60	91

MAL: maltene fraction
ASP: asphaltene fraction
PRE: preasphaltene fraction
IOM: insoluble organic matter which is ash free, tetrahydrofuran insolubles

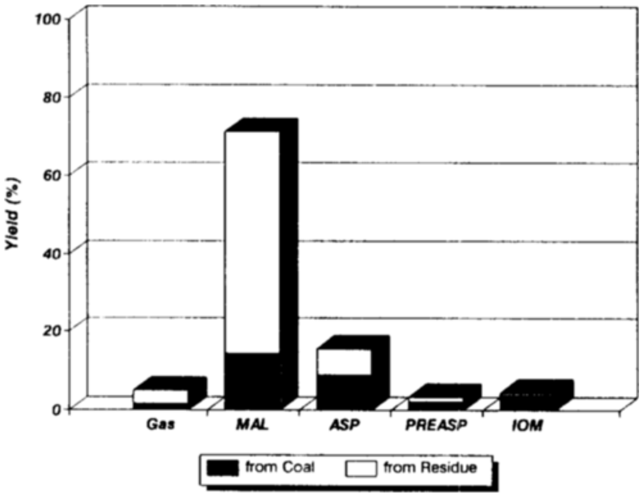

Fig. 8. Coprocessed product fractions from Coal 1 in catalytic reaction with Resid 1.

Table 6. Coal conversion to coprocessing product fractionstions

Reaction combination	% of coal converted to Gas	MAL	ASP	PRE	IOM
Hexadecane/Coal	4	29	34	31	2
Tetralin/Coal	5	67	19	8	1
Resid 1/Coal 1	5	50	30	8	7
Resid 1/Coal 2	8	70	16	3	3
Resid 1/Coal 3	12	59	16	10	3
Resid 2/Coal 1	6	52	29	9	4
Resid 2/Coal 2	8	71	16	4	1
Resid 2/Coal 3	11	72	11	6	0
Resid 3/Coal 1	7	43	34	7	9
Resid 3/Coal 3	10	64	12	7	7

MAL: maltene fraction
ASP: asphaltene fraction
PRE: preasphaltene fraction
IOM: insoluble organic matter which is ash free, tetrahydrofuran insolubles

maltene production produced from the coprocessing reaction was insensitivity to any kind of petroleum residuum.

2. Quantitative Analysis of Upgraded Product Fractions

The amount of coal upgraded during coprocessing was quantitatively analyzed based on the following approaches: (1) what quantity of the different product fractions was formed from coal in the presence of petroleum residuum and catalyst; and (2) what quantity of maf coal was converted to each soluble fraction during the coprocessing. In the initial analysis, it was assumed that the upgrading performance of coal and petroleum residuum were independent and that the petroleum residuum would react in the same manner in the presence of coal as it did alone. Using this assumption, the percentage of each coprocessing product fractions produced from coal was calculated. The percentages given in Table 5 were calculated by substracting the product fractions upgraded from petroleum residuum itself from those obtained from coprocessing, and then dividing by the total product fractions. The coprocessed product fractions from Coal 1 in catalytic reaction with Resid 1 are diagrammatically represented in Fig. 8 indicating what quantity of the different product fractions was formed from coal on the basis of yield in coprocessing. In the second analysis, it was assumed that no degraded fractions such as IOM, preasphaltenes, and asphaltenes and gas were produced by the original maltene content of petroleum residuum during residuum upgrading. The original maltene content of petroleum residuum was maintained as an maltene fraction; only the asphaltene fraction reacted. On the basis of this assumption, the percentage of maf coal converted to each soluble fraction was also determined and given in Table 6.

It was observed that the portion of each product fraction formed coal and the portion of coal converted to each product fraction during the coprocessing were dependent on the type of coal used and not on petroleum residuum. The results from the initial analysis as shown in Table 5 indicated that the most of the heavier fractions of the products such as IOM, preasphaltene and asphaltene were formed primarily from coal for all combinations. In addition, the results from the second analysis as shown in Table 6 revealed that a large amount of maf coal converted to maltene fraction during the coprocessing, while a smaller amount was converted to asphaltene fraction.

CONCLUSIONS

The coprocessing of petroleum residuum and coal offered the potential for improving the efficiencies of coal liquefaction as well as upgrading both materials into high quality products. The following conclusions are obtained.

1. The coprocessing reaction system performed in this study showed a high catalytic activity and was somewhat dependent on the types of petroleum residuum. All coprocessing combinations showed high coal conversion of over 84%. This high coal conversion may also be due to both the high catalytic activity of coprocessing system and the reactive hydrogen donor richness of petroleum residuum feedstocks as observed in comparison of coprocessing reactions with hexadecane and tetralin.

2. The asphaltene production on the coprocessing system was inversely proportional to the petroleum residuum properties, specific gravity, conradson carbon number and metal content, while coal conversion was proportional to these properties regardless of type of coal used. However, the amount of maltene production was insensitivity to any kind of petroleum residuum properties, which was only dependent on the type of coal used.

3. The results of quantitative analysis for the amount of coal upgraded during coprocessing showed that a large amount of coal converted to maltene fraction even though the most heavier fractions of the coprocessed products came from primarily from coal.

NOMENCLATURE

Abbreviations

H/C : ratio of hydrogen to carbon
maltene (HS) : hexane solubles
MAL : maltene fraction
asphaltene (HI) : hexane insolubles and toluene solubles
ASP : asphaltene fraction
preasphaltene : toluene insolubles and tetrahydrofuran solubles
PREAS : preasphaltene fraction
IOM : insoluble organic matter which is ash free, tetrahydrofuran insolubles
maf : moisture ash free

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