

CO-PROCESSING OF NEW MEXICO COAL WITH HONDO RESIDUUM

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INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has developed a process for co-processing coals with heavy petroleum crudes and residua. The process utilizes one or more ebullated bed reactors in series and brings together experience in resid processing (H-Oil process) and coal liquefaction (H-Coal and CTSL processes). Co-processing has been demonstrated with bench-scale and PDU-scale tests.

During last few years, HRI has assessed co-processing performance of several coal and petroleum feedstock combinations. Coals of varying rank including Texas lignite, Black Thunder (Wyoming), Forestburg (Alberta), New Mexico (McKinley mine), and Taiheiyo (Japan) subbituminous coals, Ohio 5/6, Lingan (Nova Scotia) and Westerholt (Germany) bituminous coals were tested. Petroleum residua tested include Maya (Mexico), Orinoco (Venezuela), Cold Lake (Canada), and Hondo (California).

This paper presents results obtained on co-processing of New Mexico coal with a vacuum residuum from Hondo heavy crude. This feedstock combination was found to be particularly reactive in co-processing. Some results on comparative reactivities of Hondo, Maya, and Cold Lake residua, using Texas lignite as a reference coal, are also presented.

EXPERIMENTAL

The bench tests were conducted in a 50 lb/day (nominal size) continuous unit equipped with two close-coupled ebullated bed reactors. Both reactors were charged with commercial NiMo hydroprocessing catalyst which was sulfided during start-up. Unlike commercial operation, each bench test was conducted with a fixed charge of catalyst with no intermediate catalyst additions and withdrawals.

Table 1 shows the analyses of New Mexico (McKinley mine) subbituminous coal and Texas lignite (cleaned, from Homer city). Analyses of Hondo, Cold Lake, and Maya vacuum resids are also shown in Table 1.

RESULTS AND DISCUSSION

New Mexico coal was co-processed with Hondo vacuum resid according to the run plan indicated in Table 2. Condition 1 was the baseline condition at the base space velocity, base reference (internal reactor) temperature of 810°F in both reactors, 33 W % coal concentration in feed, and once-through operation. Coal concentration, space velocity and reactor temperatures were varied over conditions 2 through 4. In condition 2, with coal concentration at 50 W % of fresh feed, atmospheric bottoms were used as recycle (to reduce the feed viscosity) at recycle-to- fresh-feed ratio of 0.5. Condition 5 was identical to condition 1 and was used to assess the extent of catalyst deactivation.

The process performance obtained in co-processing of New Mexico coal with Hondo vacuum resid is shown in Table 2 and in Figures 1 and 2. The product yields are based on ASTM distillations. Coal conversion was calculated based on solubility in quinoline. Residuum (975°F+) conversion was calculated from D-1160 distillation on product vacuum-still-bottoms. Hydrodesulfurization (HDS) and Hydrodenitrogenation (HDN) were calculated from heteroatom contents of the products and the total feed (including ash). Demetallization was based on the metals (Ni + V) content of the liquid product. Net C₄-975°F yield was calculated by subtracting the gas oil content of the feed from the C₄-975°F content of the product and expressing it as a percentage of the feed 975°F+ (MAF) content. Hydrogen efficiency is defined as the ratio of net distillate produced to hydrogen consumption.

Coal conversion for New Mexico coal ranged from 91.0 to 93.1 W % (MAF). There was virtually no effect of catalyst deactivation on coal conversion. Coal conversion dropped from 93.1 W % in condition 1 to 92.5 W % in condition 5. The lowest coal conversion (91.0 W %) was obtained in condition 3 (at high space velocity), however, the decrease was small. Residuum (975°F+) conversion ranged from 85.9 to 93.2 (MAF) W %. There was a small effect of catalyst deactivation, 975°F+ conversion dropped from

93.2 W % in condition 1 to 91.1 W % in condition 5. Again, the lowest conversion was obtained in condition 3. The effect of high space velocity was more pronounced on 975°F+ conversion than on coal conversion, with 975°F+ conversion dropping to 85.9 W % in condition 3.

Hydrodesulfurization (HDS) level was very high throughout the run, ranging from 96.7 W % to 97.7 W %. In conditions using oil-to-coal ratio of 2, more than 95% of the sulfur content of the feed was associated with Hondo. The extremely high level of HDS is an indication of the high reactivity of Hondo. Hydrodenitrogenation (HDN), unlike HDS, was very dependent upon catalyst age, decreasing from 87.4 W % in condition 1 to 67.3 W % in condition 5. High level of demetallization, over 96 W %, was obtained throughout the run.

The net yield of C₄-975°F product was high and ranged from 72.6 W % to 77.9 W % (expressed as percentage of 975°F+ MAF content of feed). The lowest yield was obtained in low-severity (high space velocity) condition. Excluding this condition, the yield range was quite small with very low effect of catalyst deactivation.

The effect of coal concentration on process performance can be assessed by interpolating the performance at condition 1 and condition 5 to condition 2 and comparing it with that observed in condition 2. It is, however, difficult to use this method to assess the effect on HDN due to high, non-linear deactivation effect on HDN performance. The effect of coal concentration on coal and 975°F+ conversions was slightly negative, with that on 975°F+ conversion a little more pronounced. Higher coal concentration also gave a lower net yield of C₄-975°F distillate and showed lower hydrogen efficiency. The latter was caused due to lower hydrogen content of the feed and higher gas (C₁-C₃) and water yields obtained using higher coal concentration. As shown in Table 2, the yield of vacuum gas oil (VGO) (650-975°F) fraction in the product slate was lower in condition 2. However, when yields are calculated on a net basis (by subtracting VGO portion of the feed), the distillate selectivity for condition 2 is not much different from that in condition 1. In both cases, the net yield of VGO was quite small indicating the reactive nature of New Mexico coal and Hondo vacuum resid.

In condition 3, low severity was employed by increasing the space velocity from the base value by 60%. Consequently, lower process performance was obtained. As mentioned earlier, coal conversion decreased by a small amount and the 975°F+ conversion and net C₄-975°F yield decreased by a greater amount. The hydrogen consumption fell considerably.

The reference reactor temperature was increased by 15°F in condition 4 maintaining the high space velocity. The increased severity increased process performance to the high levels obtained in the baseline condition. Hydrogen efficiency in condition 4, although lower than that in condition 3 due to higher gas yield, was still quite high. The effect of temperature and space velocity on net distillate selectivity is shown in Figure 3. In condition 3 (base temperature, high space velocity), the net selectivity of VGO was quite high - 14.5 W % (of C₄-975°F product) versus less than 2 W % in condition 5 (base temperature, base space velocity). When the temperature was increased in condition 4 by 15 F, the net selectivity of VGO dropped to 3.1 W % giving a very light product slate. The selectivity in condition 4 was very similar to that in condition 5. The results indicate that the operating variables used in condition 4 would produce a more economical product as compared to the baseline conditions (1/5) due to lower capital cost arising from higher space velocity. Higher temperature operation usually results in higher gas make-up and higher catalyst deactivation. However, the above results suggest that these factors are of small consequence for New Mexico/Hondo feedstock combination.

A noteworthy feature of this test was the effect of catalyst deactivation on performance. The effect of deactivation on coal conversion and HDS was negligibly small. It affected 975°F+ residuum conversion, however, the magnitude was quite small. HDN and hydrogen consumption, especially the former, were markedly affected by catalyst deactivation. Table 3 shows the analyses of the product TBP cuts. All distillate products had very low sulfur contents. There is a significant effect of deactivation on the product quality of heavier cuts. For instance, the 975°F+ liquid portion obtained on day 21 had very low hydrogen content and higher sulfur, nitrogen, and metals contents as compared to that obtained on day 5. It is very interesting to note that there is a large effect on the sulfur content (0.07 W % on day 5 versus 0.48 W % on day 21) although the effect on HDS level is very small (97.7 W % on day 1 versus 96.7 W % on day 21). This is due to very low yields of 975°F+ liquid product.

The small effect on catalyst deactivation on coal and residuum conversions and HDS might be hypothesized as due to predominantly thermal character of these reactions. This is quite true for coal conversion and partly true for residuum conversion. It is quite unlikely that the desulfurization of the thiophenic components typically found in heavy oils would occur by a thermal path. A possible explanation of the behavior observed here might be the non-uniform deactivation of catalyst sites. It is known that hydrotreating catalysts such as the one used here have distinct hydrogenation and hydrogenolysis sites. The former type of sites might have deactivated while the latter type relatively unaffected. HDS rate is dependent upon hydrogenolysis and does not require hydrogenation. HDN reactions require hydrogenation prior to hydrogenolysis and could get affected by deactivation of hydrogenation sites depending upon the limiting step in the reaction network.

Co-processing of New Mexico coal with Hondo vacuum resid gave very high level of demetallization (based on metals (Ni + V) content of the liquid product). Figure 4 shows the mode of demetallization. In all conditions, the total demetallization was in high 90's (W %). In condition 1, catalytic demetallization accounted for more than 80%. The balance was achieved through deposition on coal solids. During the course of the run, as the catalyst deactivated, the relative amount of catalytic demetallization dropped. In condition 5, it accounted for just over 55 W %, the balance was achieved by coal solids. Although this decline in catalytic activity towards demetallization is significant, it is our experience that the above retained activity is higher than that typically observed for a similarly aged catalyst.

The recovered first-stage catalyst had lower carbon content and higher contaminant metals than the second-stage catalyst. This is the usual behavior, however, the first-stage carbon content was lower than that usually found. This perhaps is the cause for higher retained activity towards 975°F+ conversion, HDS and demetallization.

The extremely high HDS level indicated that Hondo vacuum resid was very reactive. In order to compare its reactivity with other residua tested in this program, Texas lignite was co-processed with Maya, Hondo, and Cold Lake. Texas lignite was the reference coal for the program. The run plan and the results are shown Table 4 and in Figure 5. The residuum conversion with Hondo was 92.7 W % versus 90.3 W % with Maya and 88.1 W % with Cold Lake. Similarly, HDS level was higher with Hondo. The product distribution as reported in Table 4 did not show much variation, however, considering Hondo contained substantial amount of VGO, the net distillate product slate with Texas lignite - Hondo combination was more selective towards lighter products.

The reactivity of various coal/residuum combinations towards 975°F+ residuum conversion were modelled by the equation:

$$k = k_0 \cdot \exp(-E/RT) \cdot (1+C)^a \cdot \exp(-d \cdot A)$$

where,

- k = first-order rate constant calculated assuming two CSTRs in series,
- k₀ = constant representing initial reactivity at 0 W % coal
- E = activation energy
- R = gas constant
- T = temperature
- C = fractional coal concentration
- a = exponent indicating effect of coal concentration
- d = deactivation parameter
- A = catalyst age

This model fits the experimental data obtained under the entire program very well. Table 5 shows a comparison of the model parameters obtained for various feedstock combinations. New Mexico - Hondo combination was the most reactive feedstock and had very low deactivation rate.

CONCLUSION

New Mexico subbituminous coal was co-processed with Hondo vacuum resid in a continuous bench unit employing HRI's Coal/Oil Co-processing Technology. This feedstock was very reactive and gave high yield of distillate product. The hydrodesulfurization was extremely high. The effect of catalyst deactivation on residuum conversion, HDS, and net distillate yield was quite small, however, the effect on HDN was more pronounced. A separate test done on co-processing of Texas lignite with Maya, Hondo, and Cold Lake VSB showed that Hondo was the most reactive residuum.

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TABLE I
ANALYSES OF FEEDSTOCKS

COALS	New Mexico		Texas Lignite		
Moisture, W %	7.6		9.4		
Ultimate Analysis, W % (Dry)					
Carbon	69.3		64.7		
Hydrogen	5.2		4.4		
Nitrogen	1.3		1.3		
Sulfur	0.5		1.3		
Ash	9.8		12.6		
Oxygen (Difference)	13.9		15.7		
PETROLEUM VACUUM RESIDUA	Hondo		Cold Lake		Maya
API Gravity	7.8		2.6		3.1
Elemental Analysis, W %					
Carbon	82.8		83.5		83.4
Hydrogen	10.6		9.9		9.9
Nitrogen	0.8		0.7		0.7
Sulfur	5.4		5.7		5.1
Metals, WPPM					
Nickel	108		137		105
Vanadium	277		348		562
IBP, °F	750		882		835
IBP-975°F, W %	31.9		9.1		9.6
975°F+, W %	68.1		90.9		90.4

TABLE 2
CO-PROCESSING OF NEW MEXICO COAL
WITH HONDO VACUUM RESIDUUM

Condition No.	1	2	3	4	5
Days	1-5	6-9	10-13	14-17	18-21
Relative Space Velocity	1.0	1.0	1.6	1.6	1.0
Reactor Temperature, °F	810	810	810	825	810
Coal Concentration in Fresh Feed, W %	33	50*	33	33	33
Yields (W % Fresh Feed)					
C ₁ -C ₂	6.1	6.3	4.6	6.3	6.4
C ₄ -350°F	16.0	17.2	13.7	18.4	18.0
350-650°F	40.9	38.2	33.0	38.2	38.5
650-975°F	23.2	19.7	29.2	23.1	22.2
975°F+ Liquid	3.0	4.1	7.9	3.5	4.4
Coal (IOM) + Ash	5.3	8.7	6.3	5.7	5.8
CO + CO ₂	0.3	0.4	0.5	0.6	0.2
NH ₃ + H ₂ S + H ₂ O	9.7	10.3	8.4	8.4	8.7
Total (100 + H ₂ Consumption)	104.5	104.9	103.5	104.1	104.0
Coal Conversion (W % MAF)	93.1	92.3	91.0	92.9	92.5
975°F+ Conversion (W % MAF)	93.2	90.3	85.9	92.5	91.1
HDS, W %	97.7	97.1	97.1	97.1	96.7
HDN, W %	87.4	77.4	66.5	67.6	67.3
DEMET, W %	99.1	98.4	99.9	97.6	96.6
C ₄ -975°F Yield (W % Dry Fresh Feed)	80.2	75.1	75.9	79.7	78.7
Net C ₄ -975°F Yield (W % 975°F+ MAF)	77.9	74.9	72.6	77.6	76.2
Hydrogen Efficiency (Net C ₄ -975/H ₂ Consumed)	13.0	12.2	15.4	14.3	14.3

* Atmospheric Bottoms were used as recycle (50 W % Fresh Feed) to facilitate pumping

TABLE 3
PRODUCT PROPERTIES
CO-PROCESSING OF NEW MEXICO COAL WITH HONDO VACUUM RESIDUUM

Condition No.	1	2	3	4	5
Day	5	9	13	17	21
IBP-350°F					
API Gravity	51.4	54.8	54.8	54.3	54.8
Carbon, W %	86.5	85.5	86.1	85.5	85.1
Hydrogen, W %	13.9	14.7	14.6	14.5	14.5
Sulfur, W %	0.01	0.01	0.01	0.01	0.01
Nitrogen, W %	0.02	0.11	0.12	0.12	0.11
350-650°F					
API Gravity	32.3	31.0	31.8	31.0	31.8
Carbon, W %	87.6	87.1	87.0	87.5	87.6
Hydrogen, W %	12.8	12.9	12.9	12.6	12.4
Sulfur, W %	0.01	0.01	0.01	0.03	0.02
Nitrogen, W %	0.14	0.22	0.31	0.35	0.24
650-975°F					
API Gravity	22.8	20.1	19.3	20.2	20.3
Carbon, W %	87.4	87.9	87.6	88.0	88.1
Hydrogen, W %	12.0	11.7	12.2	11.8	11.8
Sulfur, W %	0.03	0.02	0.10	0.08	0.11
Nitrogen, W %		0.55	0.45	0.50	0.49
975°F+ Liquid					
API Gravity	4.0	-1.3	-2.2	-8.2	-6.8
Carbon, W %	88.0	89.3	88.7	90.4	89.8
Hydrogen, W %	11.1	9.1	9.0	7.8	7.9
Sulfur, W %	0.07	0.17	0.42	0.30	0.48
Nitrogen, W %	0.51	0.91	1.05	1.27	1.31
Ni, WPPM	0.2	9	25	30	32
V, WPPM	2	5	4	12	4

TABLE 4
CO-PROCESSING OF TEXAS LIGNITE WITH
MAYA, HONDO, AND COLD LAKE VACUUM RESIDUUM

Condition No.	1	2	3
Days	1-5	6-8	9-11
Oil	Maya	Hondo	Cold Lake
Relative Space Velocity	1.0		
Reactor Temperature, °F	810		
Coal Concentration in Fresh Feed, W %	33		
Yields (W % Fresh Feed)			
C ₁ -C ₃	6.4	5.9	6.3
C ₄ -350°F	15.8	16.5	16.4
350-650°F	35.8	38.6	32.1
650-975°F	23.8	23.7	25.0
975°F+ Liquid	6.5	2.6	8.1
Coal (IOM) + Ash	5.8	6.5	6.1
CO + CO ₂	0.1	0.1	0.1
NH ₃ + H ₂ S + H ₂ O	10.6	10.8	10.5
Total (100 + H ₂ Consumption)	104.8	104.6	104.6
Coal Conversion (W % MAF)	92.5	90.6	91.4
975°F+ Conversion (W % MAF)	90.3	92.7	88.1
HDS, W %	95.2	96.7	95.0
HDN, W %	77.9	76.2	67.7
Net C ₄ -975°F Yield (W % 975°F+ MAF)	76.6	76.5	73.4

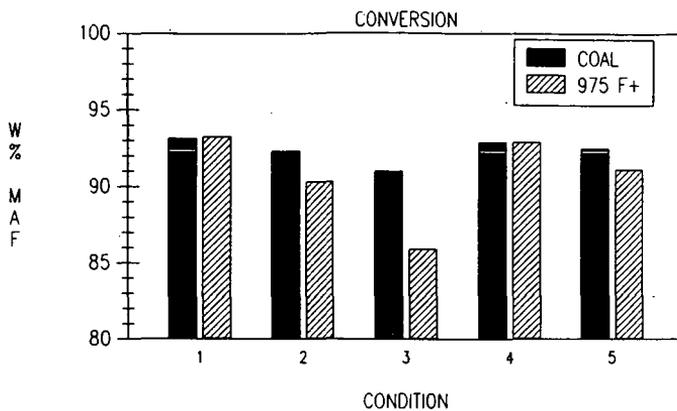
TABLE 5
COMPARISON OF FEEDSTOCK REACTIVITY

Feedstock Combination	Initial Reactivity* at 33 W % Coal	Deactivation* Parameter
Texas Lignite + Maya	1.00	1.00
Texas Lignite + Cold Lake	1.00	-
Texas Lignite + Hondo	1.33	-
Taiheiyo + Maya	0.78	0.42
Westerholt + Cold Lake	0.59	0.75
Forestburg + Cold Lake	0.78	0.71
New Mexico + Hondo	1.29	0.51

* Relative to Texas lignite + Maya combination

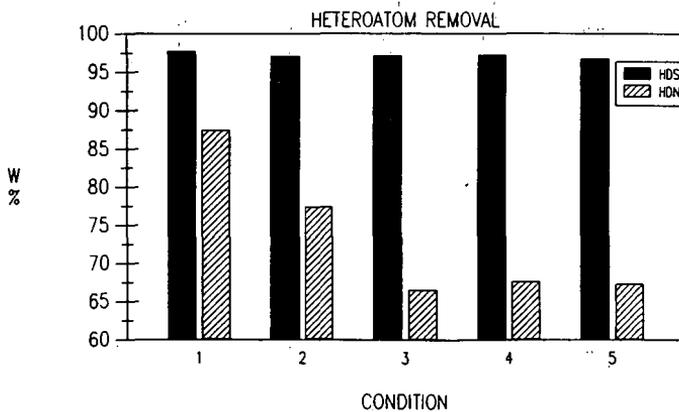
NEW MEXICO COAL PLUS HONDO

FIGURE 1



NEW MEXICO COAL PLUS HONDO

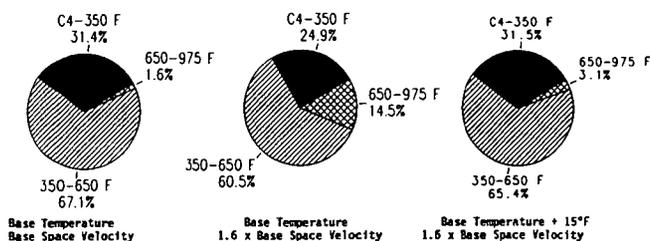
FIGURE 2



NET C4-975 F DISTILLATE PRODUCT

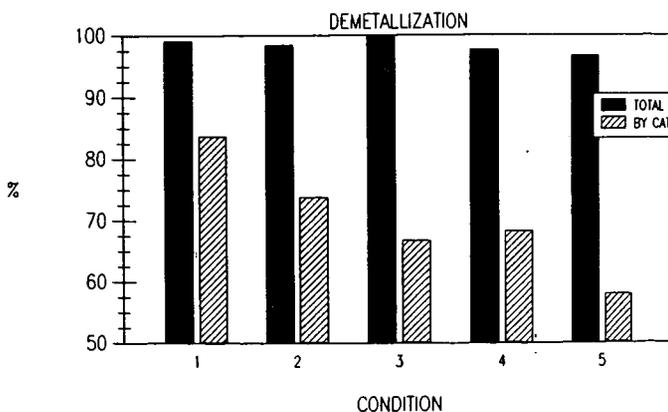
FIGURE 3

EFFECT OF TEMP / SPACE VELOCITY



NEW MEXICO COAL PLUS HONDO

FIGURE 4



TX LIGNITE + MAYA / HONDO / COLD LAKE ^{FIGURE 5}

