

MILD GASIFICATION OF COAL AND HEAVY OIL MIXTURES
TO ENHANCE LIQUID YIELD/QUALITY+

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INTRODUCTION AND BACKGROUND

Our previous studies demonstrated that relatively high quality (high H/C) liquid fuels from coal can be produced by low-temperature devolatilization (1). However, the liquids produced by low-temperature pyrolysis are typically of low yield. Therefore, there is an interest to identify ways to increase the yield of the liquids produced during pyrolysis.

Coprocessing of coal and heavy petroleum residue at relatively mild conditions may provide an avenue to enhance yield. Some important advantages of coprocessing can be the following: (a) upgrading of a petroleum residue in a reaction with coal; (b) conversion of coal to synthetic crudes which can be further upgraded into premium liquid fuels. In coprocessing, the petroleum residues may serve as the "liquefaction solvent" or hydrogen donor and the aromatics present in coal liquid may serve as hydrogen "shuttlers" by efficiently transferring hydrogen to moieties where it is most deficient. Coal also can enhance the conversion of petroleum residues to lighter liquid products through the catalytic effects of the mineral matters present in the coal. Liquefaction of coal and petroleum residues are typically performed at temperatures in the range of 400° to 500°C under pressurized hydrogen atmosphere. Catalysts are generally also added for the hydroconversion of coal and petroleum residues.

Coprocessing of the coal with petroleum, heavy crudes, and petroleum residues through catalytic hydrogenation (2-7) or solvent extraction (8-10) has been extensively studied. However, relatively little has been reported in the literature regarding the coprocessing of coal with petroleum residues by simple pyrolysis (i.e., without the complicating influences of pressurized hydrogen or hydrogenation catalysts).

+This work was performed at Morgantown Energy Technology Center

Sekrieru, et al. (11), investigated copyrolysis of brown coal and petroleum products. Vikhorev, et al. (12), also investigated copyrolysis of brown coal and coal tar or petroleum residue. Both of these studies apparently noted increases in liquid yield during copyrolysis. It was suggested that the additives (coal tar and petroleum residue) can swell or weaken the coal structure leading ultimately to a higher liquid yield. Huttinger and Sperling (13) studied flash hydrocopyrolysis of coals doped with aromatics, hydroaromatics (2 percent of loading) and observed that coprocessing of coal with additives resulted in an increase in the tar yield (by 5 to 10 percent) at the expense of char yield. In contrast, Malhotra, et al. (14), pyrolyzed coal with 10 percent of coal tar and prehydrogenated coal tar at various heating rates. Their limited results show that the addition of coal tar and prehydrogenated coal tar (containing 10 to 20 percent of hydroaromatics) to coal had no beneficial effect on pyrolysis yield. However, extensive characterization data on any of the studies were not reported.

Khan, et al. (16), studied the pyrolysis of raw coal, pyridine extract and extracted coal residue by a thermogravimetric analyzer (TGA) and found that the combined weight loss of extract and extracted coal residue at 600°C is considerably lower than the weight loss obtained for the raw coal alone. Therefore, it was suggested that the presence of hydrogen-rich portions of the coal (i.e., extract) in the coal structure increases the overall weight loss for coal during pyrolysis. The extractable portion of coal may serve as the source of internal hydrogen during pyrolysis by supplying hydrogen to hydrogen deficient moieties that would otherwise undergo coking reaction (forming solid residue) rather than desirable volatiles. In other words, the extractable portion of coal, being more hydroaromatic, can serve as hydrogen-donors in partially hydrogenating the insoluble portion of coal during pyrolysis, thereby increasing the yield of volatile matter from the residue.

It is generally believed in coal liquefaction, that hydrogen-donor solvent can donate hydrogen and "cap-off" the thermally generated free radicals to form stable volatiles. The rate of coal liquefaction process apparently depends on the rate at which hydrogen can be donated from the solvent. McMillen, et al. (17), suggested a mechanism for the formation of liquid products during pyrolysis in which strong linkages (such as diarylmethane, alkylaromatic, and dialylether) are cleaved at 400°C as a result of hydrogen transfer from solvent-derived cyclohexadienyl radicals in a direct bimolecular step. Existing literature data suggest that petroleum residue may serve as an external hydrogen source by enhancing the bond-scission reactions via formation of cyclohexadienyl radicals (18) during coprocessing. It is our hypothesis in this study that copyrolysis of coal with petroleum residue at a relatively low temperature (500°C) can increase the tar yield while improving the quality of the tar perhaps by hydrogen transfer and hydrogen-transfer-promoted, bond-scission reactions. To fully test our hypothesis and to extend the data available in the literature, a copyrolysis study was initiated. The copyrolysis products were extensively characterized. Relatively little has been reported in the literature regarding the characteristics of the liquids generated by copyrolysis of coal and heavy residue (in the absence of a catalyst or high-pressure hydrogen).

EXPERIMENTAL

Feedstocks Origin and Pyrolysis Procedure: The experimental procedures for the production of pyrolysis liquids from solid fuels including reactor system, experimental procedures, and reproducibility of results have been described by Khan (1a). A fixed-bed reactor known as slow heating rate organic devolatilization reactor (SHRODR) was used to generate the pyrolysis liquids at 500°C. In addition, a thermogravimetric analysis (TGA) reactor was used for our studies. The Pittsburgh No. 8 coal (high volatile bituminous) and the Wyodak subbituminous coals were used in this study. All sample preparation and handling procedures were performed in inert atmospheres. The Kern River heavy residue was provided by the Stanford Research Institute. Additional details on the origin of these samples can be found elsewhere (1b).

RESULTS AND DISCUSSION

The proximate and ultimate analyses of Pittsburgh No. 8 coal, Wyodak coal (PSOC 1520) and Kern River heavy residue are shown in Table 1. The pyrolysis weight loss in a TGA during heat-treatment to 500°C at 20°C/min (Table 2) for the Pittsburgh No. 8 coal was 25.7 weight percent (daf) and that for the heavy residue was 80.0 weight percent (daf). The weight loss of 50/50 mixture was 62.9 weight percent (daf), which is 9.0 weight percent higher than that for the projected value (53.9 weight percent) based on the yields of the individual components. These results suggest that the presence of heavy residue increases the overall weight loss during pyrolysis of Pittsburgh No. 8 coal. The heavy residue (hydrogen-rich) may serve as hydrogen-donor providing some of the labile hydrogen to the coal (hydrogen-poor) moieties and thereby suppressing the regressive reactions during pyrolysis. Figure 1 shows the pyrolysis (derivative thermogravimetric analysis) DTG curves of Pittsburgh No. 8 coal, heavy residue, and their 50/50 mixture. There is only one major peak shown in the DTG curve for coal. Two major peaks were shown in the DTG curves of heavy residue and 50/50 mixture. The first peak in the DTG curves of heavy residue and 50/50 mixture is related to the decomposition and devolatilization of light molecules (or components), and the second peak is presumably related to the decomposition and devolatilization of original and newly formed heavy molecules (or components). As shown in Figure 1, coprolysis of coal with heavy residue slightly shifts the first peak to a lower temperature while simultaneously lowering the second peak by 40°C as compared to the pyrolysis of heavy residue alone. These findings provide credence to the concept of synergistic effects during coprolysis of coal and heavy residue.

Figure 2 presents the yield of gas, tar, and char products from pyrolysis of Wyodak coal, heavy residue, and the 50/50 mixture at 500°C in the fixed-bed reactor. The tar yield from pyrolysis of 50/50 mixture is 52.2 weight percent (daf), which is 5.1 weight percent higher than the predicted value (47.1 weight percent [daf]). This observation is consistent with the TGA coprolysis data.

Table 3 shows the ultimate analyses and heating values of tars from pyrolysis of Wyodak coal (PSOC 1520), heavy residue, and their 50/50 mixture at 500°C in the fixed-bed reactor (SHRODR). It appears that the elemental composition of tar from 50/50 mixture is similar to that for the tar from heavy residue. The tar from 50/50 mixture has higher H/C ratio, lower O/C ratio, and higher

heating value than those for the tar from coal. This confirms that copyrolysis of coal with heavy residue produces a better quality tar as compared to the pyrolysis of coal alone. Table 4 shows the elemental analyses of chars from pyrolysis of Wyodak coal, heavy residue, and the mixture. It is expected that the elemental composition of char from the mixture is similar to that for the char from Wyodak coal. The char from pyrolysis of 50/50 mixture has slightly higher heating value than that for the char from pyrolysis of coal. These results indicate that copyrolysis of coal with heavy residue upgrades the tar quality without necessarily degrading the char quality.

Figure 3 compares the composition of evolved gases from pyrolysis of Wyodak coal, heavy residue, and the mixture. It is obvious that pyrolysis of Wyodak coal resulted in a relatively high yield of CO and CO₂, which is due to the decomposition of oxygenated functional groups in Wyodak coal. Pyrolysis of heavy residue produced a relatively high yield of CH₄ and C₂H₄. This is probably due to the higher concentration of long-chain aliphatic components present in the heavy residue. Heavy residue has lower content of sulfur as compared to Wyodak coal. However, pyrolysis of heavy residue alone produces a higher yield of H₂S. This implies that the sulfur-containing compounds in heavy residue (e.g., thiol and disulfide) is more volatile than those present (e.g., thiophene, thiopyrone) in the Wyodak coal. Pyrolysis of 50/50 mixture produced lower yield of H₂S (18 percent lower) than that for the projected value. Therefore, the carbonate minerals in the Wyodak coal may also act as scavengers of hydrogen sulfide during copyrolysis of coal with heavy residue. In general, the yield of various gases for pyrolysis of the mixture ranked in the region between pyrolysis of Wyodak coal and heavy residue.

The tars from pyrolysis of coals (Wyodak coal and Pittsburgh No. 8 coal), heavy residue, and the mixture were separated by sequential elution solvent chromatography (data not shown). In general, the tars from pyrolysis of the mixture contain higher content of alkane/alkene neutral aromatics, lower content of monophenols, polyphenols, and other oxygen-containing compounds as compared to the tars from pyrolysis of coal alone. This implies that copyrolysis of coal and heavy residue upgrades the quality of coal tars.

The average structure parameters of tars from pyrolysis of Wyodak coal, heavy residue, and the mixture have been characterized by using proton NMR analysis (data not shown). The carbon aromaticity of tar from the mixture is similar to that for the tar from pyrolysis of heavy residue and much lower than that for the tar from pyrolysis of coal. The tar from the mixture contains lower content of mono-aromatics and higher content of di- and tri-aromatics than that for the tar from coal. It is interesting to note that the tar from the mixture contains higher content of naphthenic carbon and naphthenic rings/molecule than those for the tar from coal. This finding suggests that the tar from the mixture can be much easily upgraded to match the specifications of high-density jet fuel.

SUMMARY AND CONCLUSIONS

Our previous results demonstrated that relatively high-quality liquid fuel can be produced from coal by low-temperature devolatilization. Ongoing studies are aimed at producing a high-quality liquid while achieving a high yield of liquids. To better understand whether copyrolysis is a viable option to enhanced liquid yield, a coal and a heavy residue sample were copyrolyzed in a

fixed-bed reactor at a relatively low temperature and the products were characterized. Results demonstrated that there is a synergism during copyrolysis of coal and heavy residue. This synergism enhances both the yield and quality of the liquid products during copyrolysis.

In general, the tars from pyrolysis of the mixture contain higher content of alkane/alkene neutral aromatics, lower content of monophenols, polyphenols, and other oxygen-containing compounds as compared to the tars from pyrolysis of coal alone. The tars from the mixture also contain lower content of mono-aromatics and higher content of di- and tri-aromatics than that for the tar from coal. Therefore, they can be much easily upgraded to match the specifications of high-density jet fuel.

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REFERENCES

- 1a. Khan, M. R., Fuel Science and Technology International, 1987, 5(2), 185.
- 1b. Khan, M. R., Seshadri, K. and Kowalski, T. accepted for publication in Energy and Fuels, 1989.
2. Lenz, U, and J. Wavyzinek; Am. Chem. Soc. Div. Fuel Chem. Prepr., 1988, 33(1), 27.
- 3a. Curtis, C. W., J. A. Guin, M. C. Pass, and K. J. Tsai; Fuel Science and Technology International, 1987, 5(3), 245.
- 3b. Curtis, C. W., K. J. Tsai, and J. A. Guin; Ind. Eng. Chem. Process Des. Dev., 1985, 24, 1259.
4. Aulich, T. R., P. L. Holm, C. L. Knudson, and J. R. Ridut; Am. Chem. Soc. Div. Fuel Chem. Prepr., 1988, 33(1), 103.
5. Schwartz, M. M., and A. L. Hensley; Am. Chem. Soc. Div. Fuel Chem. Prepr., 1988, 33(1), 163.
6. Fouda, S. A., J. F. Kelly, and P. M. Rahimi; Am. Chem. Soc. Div. Fuel Chem. Prepr., 1988, 33(1), 179.
7. Oelert, H. H., R. Bloss, and P. F. Zhang; Am. Chem. Soc. Div. Fuel Chem. Prepr., 1988, 33(1), 185.
8. Mochida, I., Y. Moriguchi, Y. Korai, H. Fujitsu, and K. Takeshita; Fuel, 1981, 60, 746.
9. Moschopedis, S. E., R. W. Hawkins, J. F. Fryer, and J. G. Speight; Fuel, 1980, 59, 647.
10. Yan, T. Y., and W. F. Espenscheid; Fuel Processing Technology; 1983, 7, 121.
11. Sekriera, V. I., Z. S. Smutkina, and T. A. Titova; Solid Fuel Chemistry, 1978, 12(5), 45.
12. Vikhoven, A. A., A. M. Syroezhko, V. A. Proskuryakov, and N. A. Akhmedov; Solid Fuel Chemistry, 1987, 21(2), 78.
13. Huttlinger, K. J., and R. E. Sperling in proceedings of the 1987 International Conference on Coal Science, J. A. Moulijn, K. A. Nator, and H. A. G. Chermin, Editors; Elsevier Science Publishers B. V., Amsterdam, 1987, p. 699.

14. Malhotra, R., G. St. John, D. S. Tse, and D. F. McMillen; Am. Chem. Soc. Div. Fuel Chem. Prepr., 1988, 30(2), 257.
15. Brown, H. R., and P. L. Waters; Fuel, 1966, 45, 17.
16. Khan, M. R., R. Usmen, E. Newton, S. Beer, and W. Chisholm; Fuel, 1988, 67, 1668.
17. McMillen, D. F., R. Malhotra, G. P. Hum, and S.-J. Chang; Energy and Fuel, 1987, 1, 193.
18. McMillen, D. F., R. Malhotra, D. S. Tse, and S. E. Nigenda; Am. Chem. Soc. Div. Fuel Chem. Prepr., 1988, 33(1), 58.
19. Seshadri, K. S., and D. C. Cronauer; Fuel, 1983, 62, 1436.

TABLE 1

PROXIMATE AND ULTIMATE ANALYSES OF PITTSBURGH NO. 8 COAL, WYODAK COAL (PSOC 1520), AND KERN RIVER HEAVY RESIDUE

	Pittsburgh No. 8 Coal	Wyodak Coal	Kern River Heavy Residue
% C, daf	83.74	73.78	85.43
% H, daf	5.46	4.62	11.15
% N, daf	1.56	1.11	0.86
% S, daf	2.15	1.38	0.97
% O, daf (by difference)	7.09	19.11	1.59
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% Ash (as-received basis)	7.27	9.08	< 0.01
% Moisture	0.57	26.69	0
H/C Atomic (daf)	0.78	0.75	1.57
O/C Atomic (daf)	0.064	0.19	0.014

TABLE 2

TGA PYROLYSIS OF PITTSBURGH NO. 8 COAL, KERN RIVER HEAVY RESIDUE, AND 50/50 PITTSBURGH NO. 8 COAL/KERN RIVER HEAVY RESIDUE MIXTURE

Samples	Weight Loss (daf) at 500°C
Pittsburgh No. 8 Coal	25.7
Kern River Heavy Residue	80.0
50/50 Coal/Heavy Residue Mixture	62.9
Projected Weight-Loss for Mixture	53.9 ^a

^a Predicted weight loss (daf) of 50/50 mixture, assuming no synergism.

TABLE 3

ULTIMATE ANALYSES AND HEATING VALUES OF TARS FROM PYROLYSIS OF WYODAK COAL (PSOC 1520), KERN RIVER HEAVY RESIDUE AND 50/50 WYODAK COAL/KERN RIVER HEAVY RESIDUE MIXTURE AT 500°C

	Tar from Coal	Tar from Heavy Residue	Tar from 50/50 Mixture	Projected*
% C, daf	78.44	86.17	84.30	85.05
% H, daf	10.59	12.28	11.96	12.03
% N, daf	0.52	0.69	0.70	0.67
% S, daf	0.55	0.17	1.14	0.22
% O, daf	9.9	0.69	1.90	2.03
(by difference)				
H/C Atomic (daf)	1.62	1.71	1.70	1.70
O/C Atomic (daf)	0.09	0.006	0.017	0.018
Heating Value, Btu/lb	15,615	18,662	18,470	

* Projected values are calculated based on (a) the composition of individual components, and (b) their respective yield during pyrolysis. Assumes no synergism.

TABLE 4

ULTIMATE ANALYSIS AND HEATING VALUES OF CHARS FROM PYROLYSIS OF WYODAK COAL (PSOC 1520), KERN RIVER HEAVY RESIDUE, AND 50/50 WYODAK COAL/KERN RIVER HEAVY RESIDUE MIXTURE AT 500°C

	Char from Coal	Char from Heavy Residue	Char from 50/50 Mixture	Projected*
% C, daf	85.92	89.69	85.76	86.32
% H, daf	3.26	3.26	3.43	3.26
% N, daf	1.49	3.04	1.17	1.65
% S, daf	1.30	0.95	1.59	1.27
% O, daf	8.03	3.06	8.05	7.50
(by difference)				
H/C Atomic (daf)	0.46	0.44	0.48	0.45
O/C Atomic (daf)	0.07	0.026	0.07	0.065
Heating Value, Btu/lb	11,806	14,755	12,104	

* See definition of projected values on Table 3.

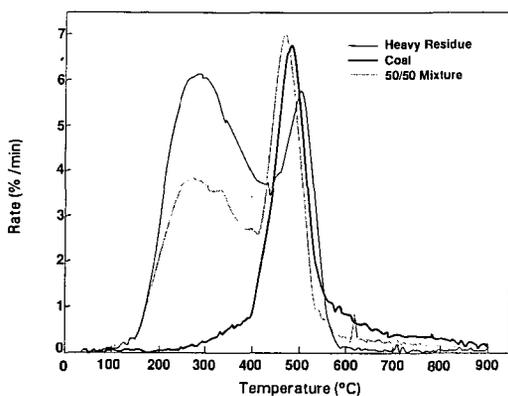


FIGURE 1 EFFECT OF CO-PROCESSING ON PYROLYSIS RATE PROFILES

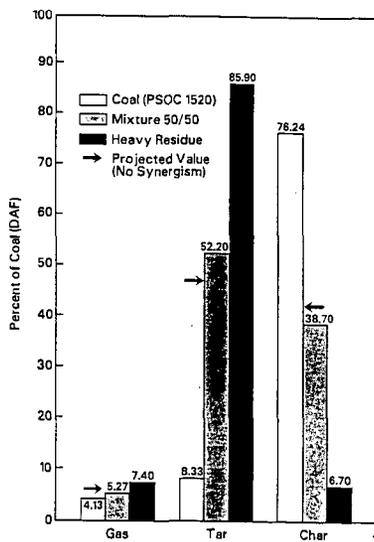


FIGURE 2 CO-PROCESSING OF COAL AND HEAVY RESIDUE

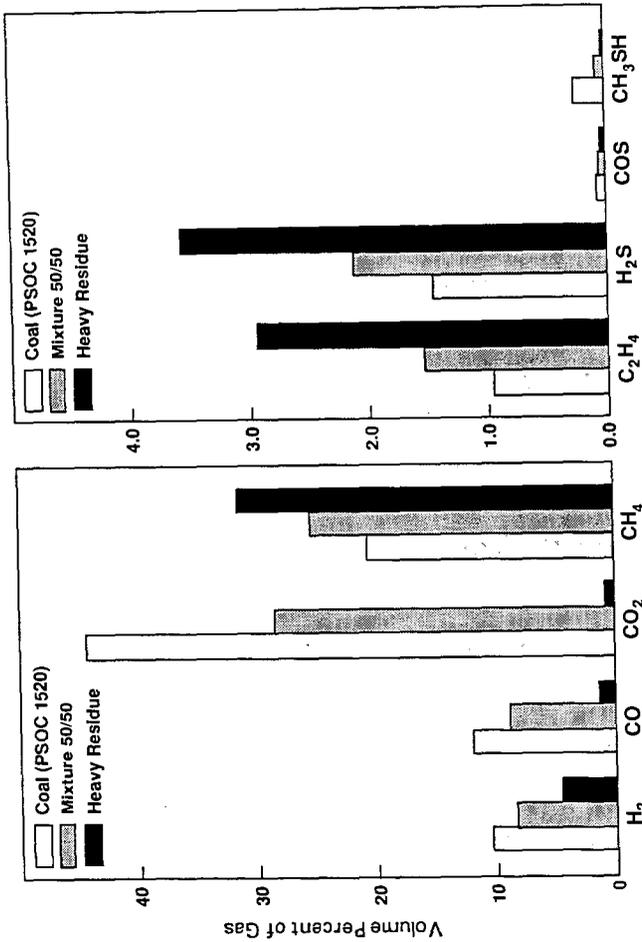


FIGURE 3 INFLUENCE OF CO-PROCESSING ON PRODUCT YIELD/COMPOSITION