PREMIUM DISTILLATE PRODUCTS FROM DIRECT LIQUEFACTION OF COAL

P.-Z. Zhou, Burns and Roe Services Corp. (BRSC), Pittsburgh, PA 15236;
R. A. Winschel, CONSOL Inc., Library, PA 15129;
and E. B. Klunder, Pittsburgh Energy Technology Center (PETC)/
U. S. Dept. of Energy (USDOE), Pittsburgh, PA 15236

Key words: Coal, Liquefaction, Product Quality, Refining

INTRODUCTION

It has long been the prevalent impression that coal-derived liquids are heavy, viscous, aromatic, hetero-compound-rich, and very difficult and expensive to refine into transportation fuels. An extensive research and development program over the past two decades, sponsored by the U. S. DOE/PETC, has resulted in dramatic improvements in coal liquefaction product quality. High-quality coal-derived distillates are now obtainable from modern catalytic two-stage liquefaction (TSL) processes. Recently, the net products of four liquefaction runs that represent variations of state-of-the-art technology were characterized in detail. The four samples were generated at the Wilsonville 6 ton/day pilot plant (Runs 259G and 260D) and the Hydrocarbon Research Inc. (HRI) 2 lb/hr bench unit (Runs CC-15 and CMSL-2), as described in Table 1. Complete background and characterization data of the samples appear in the original reports of this work.[1-5]

DISCUSSION

The distillation curves (Figure 1) of the four coal liquids have similar slopes over most of the boiling range, reflecting the similar fractional composition of the four liquids, despite the different feed coals and process conditions. All four liquids are resid-free and have end points (ca. 370-420 °C) much lower than those of early generation coal liquids. The HRI products are somewhat lower boiling than the Wilsonville products, partly as a result of different distillation operations. The specific gravities of these liquids range from 0.85 to 0.91, and the differences are primarily related to boiling range differences. These coal distillates possess excellent low-temperature characteristics: low viscosities (1.5-3.1 cSt @ 38 °C) and very low pour points (usually below -50 °C).

The four products are relatively high in hydrogen contents (11.2-12.7 wt %), and their H/C atomic ratios (1.54-1.74) are comparable to that of petroleum, resulting in fairly high characterization factors (10.9-11.1). The coal liquids have low N (0.03-0.3 wt %) and S (0.02-0.05 wt %) contents and contain negligible amounts of metals. The mid-percent curves of elements and hydrocarbon types in these coal liquids are plotted in Figures 2-8. For all four, the H content decreases gradually and the N content generally increases with increasing boiling point. The oxygen distribution shows a maximum in the 177-204 °C fraction, in which the single-ring phenols are concentrated. Sulfur content is very low throughout most of the boiling range. The N contents of the subbituminous coal liquids (W260D and CC-15) are higher than those of the bituminous coal liquids; this may reflect the use of only a single supported catalyst reaction stage in the subbituminous coal runs.

The aromatics content increases rapidly with increasing boiling point, yet these modern coal liquids are much less aromatic than early-generation liquefaction products. Figure 6 shows that it is feasible to produce from the coal liquids 30-40 LV% straight-run gasoline containing less than 22 LV% of aromatics, the projected specification for the turn of the century. These coal liquids contain approximately 60 LV% saturated hydrocarbons and the <177 °C naphthas contain as much as 91 LV% saturates. The paraffins level decreases substantially while naphthenes content decreases slightly with increasing boiling point. These liquids contain only about 3-5 LV% of olefins. Generally, the HRI liquids contain more H and less N, O, S, and aromatics over their boiling range.

The potential product yield structures of the four coal liquids are shown in Table 2. Clearly, only atmospheric distillation is required. The <177 °C naphtha yield is 24-28 LV%, with one exceptionally high case (CC-15) of 40 LV%. The yield of 204-288 °C light distillate, normally a diesel fuel fraction, is 34-36 LV%, except for W260D due to its high end point. The 177-204 °C swing cut (3.3-7.4 LV%) is also suitable for the recovery of single-ring phenolics. The yield of 288-343 °C heavy distillate, which can be refined into heavy diesel fuels/fuel oils or catalytically cracked/hydrocracked for gasoline and light diesel fuels, ranges from 18 to 26 LV%. The >343 °C atmospheric resid, which is equivalent to light vacuum gas oil and can be a part of the cracking feedstock, is less than 10 LV%, except for the high end-point W260D. These projections require verification by further refining studies of the coal liquids.

Major properties of the naphtha, light, and heavy distillates from these coal liquids are summarized in Tables 3-5 and compared with current ASTM and Federal

Phase I specifications and projected data for the year 2000. The aromatics and benzene contents of the naphthas are well below projected future specifications. This is a direct contradiction of the belief, no longer correct, that coal naphtha is highly aromatic. The olefins content (3-5 LV%) of the coal-derived naphthas is also very low compared with that of the current gasoline pool (about 10 LV%), and could readily meet projected future requirements. The octane numbers of the coal naphthas are within the range of straight-run naphthas from petroleum. The heteroatoms contents of the coal naphthas are low. They easily meet the current S specification and the HRI naphthas even meet the 1995 S requirement. The nitrogen levels are also low, particularly that of the CMSL-2 naphtha (0.01 wt %). Thus, the coal naphthas, after hydrofinishing, could be an excellent gasoline blending stock. Hydrotreating will simultaneously resolve the copper corrosion, oxidation stability, and existent gum deficiencies. The high-naphthene coal naphthas can also be good reformer feedstocks, if so required. In general, the coal naphthas exceed the 10% and 50% distillation-point maxima; however, this can always be adjusted through normal refinery blending operations.

The light distillates have excellent low-temperature properties (fr. pt. generally <-50 °C) and very low S contents, two advantages for jet fuel production. The major deficiency is high aromaticity, which must be reduced by high-severity hydrotreatment. Compared to jet fuels, diesel fuel oils have much less stringent specifications and are thus easier to produce from coal distillates. In spite of the low cetane index, the very low S level makes the light distillates an attractive blending stock for the diesel pool. A moderate hydrotreatment may be needed to improve their stability and to benefit the cetane index. The heavy distillates qualify as a No. 4 diesel/fuel oil, meeting the low S requirement. They may also be considered as a feedstock for catalytic cracking or hydrocracking, and the >343 °C fraction can be included for this purpose. However, hydrotreating may be necessary to boost the H content for improved cracking behavior.

CONCLUSIONS

The net liquid products from modern coal liquefaction processes are lower boiling and have much lower end points (mostly under 400 °C) than crude petroleum. Coal liquids have very low concentrations of heteroatoms, particularly S, and metals, and are free of resids and asphaltenes. High yields of low-S (0.01-0.03 wt %) naphtha, kerosene, and diesel fuel fractions can be obtained simply by atmospheric distillation, with a total yield of light fuel fractions ranging from 68 to 82 LV% (W260D exclusive). The coal naphtha has a low aromatics content (5-13 LV%), readily meeting projected year-2000 requirements. Its low Reid vapor pressure allows light components from other sources to be blended. The coal light distillate of an appropriate boiling range will be a good low-S blending stock for the light diesel fuel pool. The heavy distillate can be refined into a low-S No. 4 diesel fuel/fuel oil. This fraction, along with the >343 °C atmospheric bottoms, can be catalytically cracked or hydrocracked to make light liquid fuels. Thus, modern coal liquids should no longer be envisioned as thick liquids (or even solids) with high concentrations of aromatics and asphaltenes. Products obtained from advanced coal liquefaction technologies are more like light naphthene-base petroleum, but with lower heteroatoms and metals contents, and they are free of resids. Coal liquids are likely to be co-refined in existing petroleum refineries; and hydroprocessing of various severities would be needed for different fractions to produce quality blending stocks for refinery fuel pools.

CURRENT DEVELOPMENTS

DOE continues to support work on improving and evaluating product quality. Additional detailed product inspections are planned. A newly initiated program will include actual refining and testing of the refined products. A recent development in coal liquefaction technology is to include in-line fixed-bed hydrotreating of the products. The resultant liquid products are expected to be of even higher quality for conversion into transportation fuels.

ACKNOWLEDGEMENT

This work was supported by the U.S. Dept. of Energy under contracts DE-AC22-89PC89883 and DE-AC22-89PC88400. Valuable suggestions from Drs. R. G. Lett, M. A. Nowak (DOE/PETC), and R. D. Srivastava (BRSC) are appreciated.

REFERENCES

1. Kramer, R. L. in Report DOE/PC89883-24, June 1991.
2. Kramer, R. L. in Report DOE/PC89883-34, Nov. 1991.
3. Sturm, Jr., G. P.; Kim, J.; and Shay, J. in Report DOE/PC89883-92, January 1994.
4. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; and Burke, F. P. Reports DOE/89PC89883-27, September 1991, -43, March 1992, and -86, March 1994.
5. Zhou, P.-Z. "Assessment of Coal Liquids as Refinery Feedstocks," 1992, and "Characterization of Direct Liquefaction Distillate Products," 1994, BRSC Reports, DOE Contract No. DE-AC22-89PC88400.

Table 1. Sources of Coal Liquid Samples

Plant/Run	Feed Coal	Process Description
Wilsonville 259G	Pittsburgh Seam	Catalytic/Catalytic Shell 324 441/421 °C
Wilsonville 260D	Wyodak and Anderson	Catalytic/Thermal Shell 324 421/412 °C
HRI CC-15	Wyodak and Anderson	Thermal/Catalytic Shell 317 427/413 °C
HRI CMSL-2	Illinois No. 6	Catalytic/Catalytic Shell 317 400-414/424-433 °C

Table 2. Potential Product Yield Structures

	Coal Liquids Yield, LV %			
Boiling Range, °C	W259G	W260D	CC-15	CMSL-2
IBP-177	26.7	24.4	40.2	27.9
177-204	6.4	3.3	7.4	5.7
204-288	35.5	22.6	34.9	34.4
288-343	21.7	17.9	17.5	25.6
>343	9.7	31.8	--	6.3

Table 3. Characteristics of Coal-Derived Naphtha Fractions

Properties	W259G IBP-193°C	W260D IBP-193°C	CC-15 IBP-193°C	CMSL-2 IBP-177°C	Current[1] Gasoline Specifications	Federal Phase I (1995)	Projected (2000)
Specific Gravity @ 15.6°C	0.7844	0.7758	0.7798	0.7771			
Elemental Analysis, wt%							
H	13.3	13.6	14.0	14.2			
S	0.05	0.08	0.03	0.01	0.1 max	0.03 max	0.003 max
N	<0.1	0.1	0.09	0.01			
Basic N	0.028	0.046	0.082	0.006			
Hydrocarbon Group, LV%							
Paraffins	19.3	}88.0	38.0	36.9			
Naphthenes	67.5		45.7	53.9			
Aromatics	13.2	7.0	8.7	5.3		25 max	22 max
Olefins	--	5.0	4.6	3.2			4.0 max
Benzene	--	--	0.089	0.20		1 max	0.80 max
Octane, Research	--	--	61.6	60.1			
Octane, Motor	--	--	60.7	58.7			
Octane, by GC	86.5	87.1	74.8	75.2			
Reid Vapor Pressure, psi	2.8	3.1	2.54	2.74	9.0 max	9 max[2]	
Copper Corrosion	1a	1a	3b	3b	1 max		
Existent Gum (Washed), mg/100 mL	7.6	40.2	11.2	1.0	5 max		
Oxidation Stability (D525), minutes	pass	fail	105	1440	240 min		
086 Distillation, °C							
10%	91	80	88	96	70 max		
50%	126	115	123	127	77-121		
90%	172	171	169	166	190 max		149 max

[1]Class A
[2]Northeastern States

Table 4. Characteristics of Coal-Derived Light Distillates

Properties	W259G 193-266°C	W260D 193-266°C	CC-15 193-266°C	CMSL-2 177-204°C	CMSL-2 204-288°C	Jet A Specs	No. 2 Diesel Fuel Specs
Specific Gravity @ 15.6°C	0.8990	0.9260	0.8899	0.8492	0.8890	0.775-0.840	
Elemental Analysis, wt%							
H	11.5	10.6	11.77	12.72	12.27		
S	0.04	0.04	0.03	0.01	0.01	0.3 max[1]	0.50 max[3]
N	<0.1	0.3	0.33	0.03	0.03		
Basic N	0.093	0.22	0.27	0.023	0.029		
Mercaptan S	0.003	0.009	0.0045	0.0019		0.003 max	
Hydrocarbon Group, LV%							
Paraffins	--	}47.0	9.6	7.5	7.5		
Naphthenes	--		43.1	61.3	53.0		
Aromatics	44.0	50.0	41.4	28.4	37.5	25 max	
Olefins	3.0	3.0	5.8	2.8	2.0		
Naphthalene	--	4.94	4.23	0.48	--	3 max[2]	
Viscosity, cSt, @							
38°C	--	--	--	--	2.50		1.9-4.1
-20°C	1.75	18.94	10.80	4.68	--	8.0 max	
Freezing Pt., °C	-53.5	too dark	-24.4	-72.8	--	-40 max	
Smoke Pt., mm	10.8	9.8	10.9	15.6	--	25 min[2]	
Reid Vapor Pressure, psi	0.2	0.0	<0.01	0.02	--		
Thermal Stability (JFTOT)	Fail	--	Fail	--	--		
Copper Corrosion	1a	1a	1a	1a	1a	1 max	3 max
Net Heat of Combustion, MJ/Kg	42.1	42.0	41.7	42.8	--	42.8 min	
Cetane Index	22.9	21.8	26.4	20.8	32.7		40

[1]Reduced to 0.1 wt% in Federal Phase I.
[2]or smoke point 20 mm (min) and naphthalene 3 LV% (max).
[3]Reduced to 0.05 wt% in Federal Phase I.

Table 5. Characteristics of Coal-Derived Heavy Distillates

Properties	W259G 266°C+	W260D 266-343°C	CC-15 266-337°C	CMSL-2 288°C+	No. 4-D Diesel Fuel Specs	No. 4 Fuel Oil Specs
Specific Gravity @ 15.6°C	0.9574	0.9484	0.9223	0.9262	0.8762 min	
Elemental Analysis, wt%						
H	10.5	10.7	11.4	11.8		
S	0.04	0.03	0.01	0.01	2.00[1]	
N	0.1	0.3	0.22	0.06		
Basic N	0.093	0.22	0.19	0.03		
Hydrocarbon Group, LV%						
Paraffins			10.1			
Naphthenes			34.5			
Aromatics			52.1			
Olefins			3.3			
Viscosity, cSt @ 38°C	8.97	6.2	5.34	8.77	5.5-24.0[2]	5.5-24.0[2]
Pour Pt., °C			1.7	-12		-6 max
Copper Corrosion	1a	1a	1a	1a		
Flash Pt., °C		124	136		55 min	55 min
Cetane Index	26.5	27.7	34.2	35.2	30	

[1]Low sulfur specifiation 0.05 wt%
[2]at 40°C

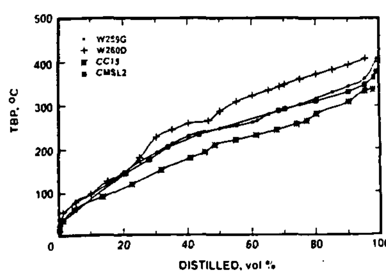

Figure 1. True-Boiling-Point Curves of Two-Stage Coal Liquids

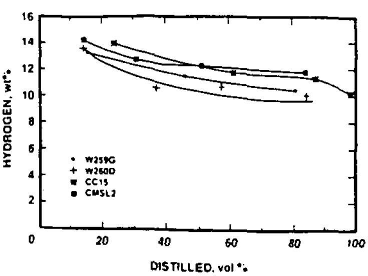

Figure 2. Hydrogen Mid-Percent Curves of Coal Liquids

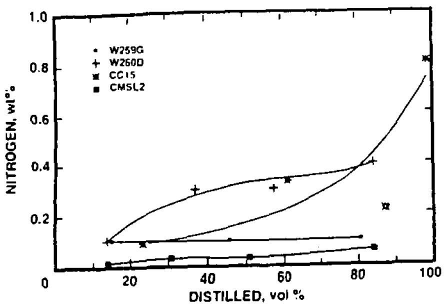

Figure 3. Nitrogen Mid-Percent Curves of Coal Liquids

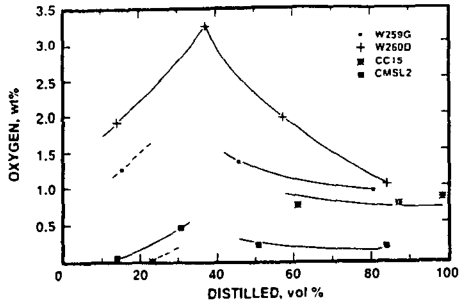

Figure 4. Oxygen Mid-Percent Curves of Coal Liquids

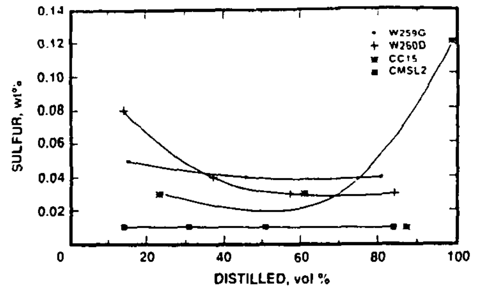

Figure 5. Sulfur Mid-Percent Curves of Coal Liquids

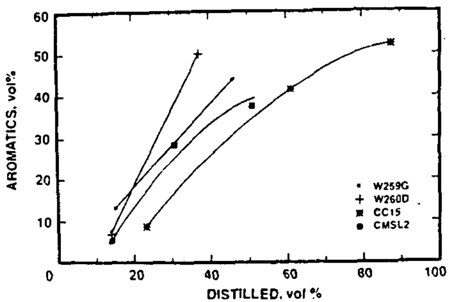

Figure 6. Aromatics Mid-Percent Curves of Coal Liquids

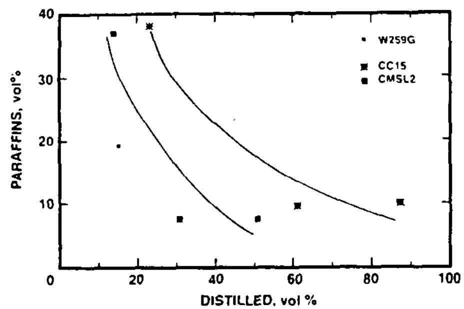

Figure 7. Paraffins Mid-Percent Curves of Coal Liquids

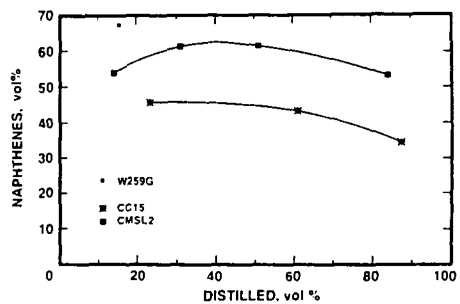

Figure 8. Naphthenes Mid-Percent Curves of Coal Liquids