

STRATEGIC CONSIDERATIONS OF COAL LIQUID REFINING

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The development of the two-stage coal liquefaction process over the past decade has resulted in remarkable improvements in process efficiency, including increased liquid yield, better product quality, improved hydrogen efficiency, and dramatic reduction in production costs. At this stage in liquefaction development, serious consideration should be given to the refining of coal liquids into marketable transportation fuels.

PROPERTIES OF COAL-DERIVED LIQUIDS

Properties of coal liquids representative of various single-stage and two-stage liquefaction (TSL) processes were compiled in a comprehensive review [Zhou and Rao, 1992]. The major differences between current two-stage liquefaction coal liquids and those from earlier processes are the higher hydrogen and lower heteroatom contents of the former. TSL liquids are usually richer in middle distillates than are single-stage liquids, probably due to the lower hydrogenation severity of the two-stage processes which leads to the lower hydrogen consumption and higher liquid yields.

Coal liquids produced from coals of the same rank under similar conditions are quite similar in properties. For coal liquids obtained from bituminous coals, the hydrogen content is high, in the range of 11.3-12.2 wt%; and heteroatom contents are low: 0.1- 0.3 wt% nitrogen, less than 0.1 wt% sulfur, and 1-2% oxygen [Lee et al. 1991]. Liquid products from lower-rank coals are characterized by more oxygen and higher paraffinicity than bituminous coal liquids. The subbituminous Black Thunder coal liquids have a greater concentration of normal paraffins, olefins, and phenols than Pittsburgh seam coal liquids [Robbins et al. 1992].

As complex mixtures of hydrocarbons and hetero-compounds, coal liquids and petroleum exhibit many fundamental similarities; therefore, coal liquids can be refined into liquid transportation fuels by current petroleum refining technologies. Extensive research on coal-liquid refining done by Chevron, UOP, and Exxon demonstrated that environmentally clean, quality liquid fuels, can be produced from coal liquids. Modern TSL liquids, however, have a lower boiling range than petroleum, with an end point around 427°C, and are free of residual materials and metals. The H/C ratio of TSL liquids falls within the H/C range of crude oils, although at the lower end, reflecting the cyclic nature of coal liquids. Coal liquids have very low sulfur contents, moderate nitrogen contents, and relatively high oxygen contents. These unique features of coal liquids require somewhat different refining strategies than those conventionally used for the refining of petroleum.

Oxygen compounds in coal liquids are concentrated in the 175-315°C boiling range, with a peak at 230°C [Pauls et al. 1990]. For Black Thunder coal liquid, 3.6 wt% of the naphtha (IBP - 193°C) and 10 wt% of the 193-266°F fraction are phenolic compounds and can be extracted easily by caustic washing [Burke et al. 1991]. This naphtha phenolic extract contains phenol, cresols, xylenols, ethyl phenol, methylethyl-phenol and propyl-phenol [Robbins et al. 1992].

Some coal liquids produced recently at Wilsonville are characterized in Table 1. Tables 2 through 4 compare the properties of respective fractions of these coal liquids with corresponding specifications for gasoline, jet fuel, and diesel fuel.

HYDROPROCESSING -- THE MAJOR TOOL FOR COAL-LIQUID REFINING

Based on the characteristics of coal liquids, hydroprocessing is obviously the most important refining technology for coal-liquid upgrading. Coal liquefaction is a hydrogenation process, and coal-liquid refining can be envisioned as an extension of the coal-to-liquid fuel conversion process. The hydrogenation conditions in the liquefaction step determine the yield and properties of the coal liquids produced, which in turn dictate the extent of upgrading required for coal-liquid fuel production.

Current liquefaction practice is to recycle resids to extinction to produce a total distillate product with an end point in the range of 370-427°C. With improved liquefaction operation, it is possible to lower the end point further to around 350°C, as suggested by some authors [Zhou and Rao, 1992]. This is particularly advantageous to the downstream refining facility which may have limited cracking (either catalytic or hydrocracking) capacity, and provides the added benefit of confining the toxicologically active polycyclic aromatic hydrocarbons within the boundary of the liquefaction plant. In fact, Exxon's new liquefaction process is generating 350°C- coal liquids, which make a naphtha plus distillate product slate [Stuntz 1991].

Hydroprocessing, e.g. hydrotreating and hydrocracking, of coal liquids is highly versatile in that the extent of hydrogenation can be adjusted to produce different product slates (maximum gasoline or maximum distillate) as well as product quality (primarily aromatics content).

UTILIZATION OF EXISTING PETROLEUM REFINERY INFRASTRUCTURE

It appears to be more realistic to consider the co-refining of coal liquids with petroleum in an existing petroleum refinery rather than in a grass-roots, dedicated coal-liquid refinery.

Coal liquids can be introduced into a refinery either as a single feed or as previously fractionated individual cuts. The unique properties of coal liquids warrant a different refining strategy than that for petroleum. Mixing the total coal liquid with petroleum would eliminate many possible refining schemes suitable for each of these two feedstocks. More flexibility in processing can be achieved if coal liquids are distilled in the liquefaction plant and individual fractions are introduced into the refinery at points where their properties are most compatible with petroleum counterparts.

Much work has been done on the hydrotreatment of total coal liquids; however, evidence shows that hydrotreating the individual naphtha, kerosene, and diesel fractions is advantageous from a product-quality standpoint. For example, jet fuels with higher smoke points may be obtained by hydrotreating the respective fractions rather than the total coal liquid [Sullivan 1987b, Zhou and Rao 1992]. Depending on the coal liquid properties, the product slate, and the refinery infrastructure, coal liquid fractions may be hydroprocessed together with or separately from their petroleum counterparts.

REFINERY LINEAR PROGRAMMING

Linear programming (LP) techniques are used routinely within the refining industry to evaluate the economics of petroleum processing. Linear programming can also be applied to coal liquids to determine their value as refinery feedstocks. LP is potentially a very powerful tool since the products from most liquefaction processes are intermediates which must be further upgraded or blended with petroleum-derived intermediates to meet product specifications. Thus, LP allows the effects of variations in yields and quality between different liquefaction operations to be quantified, and can provide a benchmark for comparing and ranking different coal liquid products.

The effect of feeding coal-liquid fractions to a refinery is being studied with the linear programming technique and preliminary results are reported here. The LP model used in this study was developed by Bechtel, Inc. as part of the DOE-funded Direct Liquefaction Baseline Design project [Bechtel, work in progress]. It is a model of the typical midwestern U.S. refinery, producing the average U.S. midwest product slate. Incremental quantities of different coal-liquid cuts are introduced into the refinery model, which calculates the effect of each cut on refinery net profit. In general, liquids produced by direct liquefaction are found to be more valuable than crude petroleum. The results reported here are expressed as a coal liquid premium defined as the percentage difference between the value of the coal liquid and the price of crude oil.

GASOLINE PRODUCTION FROM COAL NAPHTHA

Coal-liquid naphthas are similar to the naphtha fraction from a naphthenic crude oil. Data in Table 2 show that the oxidation stability, caused by heteroatoms (mainly oxygen), and lack of light ends are the two major problems in the manufacture of gasoline from coal liquids. Coal naphtha, however, has a high octane number and low aromatics content and is an ideal source for gasoline production. The clear motor octane of coal naphthas is in the range of 76-83 [Zhou and Rao, 1992]. The aromatics content of coal naphthas from recent TSL runs, contrary to conventional views, are fairly low (7-13 vol%), and the naphthene content is very high (60-70 vol%), as shown in Table 2. It is an excellent reformer feedstock to make gasoline components with a research octane number above 105 [Sullivan 1987b], which is attractive at the present time. However, conversion of naphthenes to aromatics by catalytic reforming may no longer be advisable due to provisions in the U. S. Clean Air Act Admendment. A cost-effective means of gasoline production from coal naphthas is to maintain the current level of naphthenes, which have fairly high octane numbers, and improve the oxidation stability of the coal naphtha via mild hydrotreating to remove the heteroatoms. Isomerization of light coal naphtha is also a promising option. Volatility requirements can be easily remedied by blending.

LP studies show that for a refinery not deficient in high- octane gasoline blendstocks, this scheme results in a premium for coal naphtha of 12% over the price of crude oil. Under the assumptions used in the calculation, straight blending of the hydrotreated coal naphtha is preferable to catalytic reforming which has a premium of 6.5%. This difference is due primarily to the loss of volume which occurs during reforming. In this study, the refinery product slate was assumed to be unchanged. Further studies are planned to explore various scenarios in which the refinery infrastructure and product slate are modified to take best advantage of coal liquid potentials. Higher premiums are anticipated.

PHENOLICS EXTRACTION

Since oxygen is the major heteroatom found in coal liquids, hydrogen used for oxygen removal during hydrotreating accounts for the major part of hydrogen consumption. The oxygen compounds in the 232°C- fraction are mostly single-ring phenolics, which can be easily extracted by caustic washing.

A promising approach is, therefore, to extract these phenolics before hydrotreating as chemicals by-product. Preliminary work indicated that this has good potential for raising the coal-liquid premium for the naphtha fraction.

JET FUEL PRODUCTION

As illustrated in Table 4, the coal-derived kerosene fractions have lower hydrogen contents than do naphthas from the same source. This follows the general trend that hydrogen content decreases with increasing boiling point. The hydrogen level of the coal-derived kerosene fraction is low compared with that of petroleum-derived jet fuels (H 13.5-14.0 wt%), and is a reflection of its high aromatics content, typically around 50%. As a result, the API gravity and smoke point, two major properties for jet fuels, are much lower than specifications.

The jet fuel fraction obtained from an EDS distillate by hydrotreating do not meet gravity and smoke point specifications [Erwin and Sefer 1989]. It was reported, however, that through appropriate hydrotreatment smoke points of at least 20 mm can be obtained for jet fuels from Illinois No. 6 coal liquids (aromatics content 10 vol% or lower) and for jet fuels from Wyodak coal liquids (aromatics content about 15 vol%) [Sullivan 1987a]. Hydrocracking appears to be a more efficient way of making specification jet fuels from coal liquids [Sullivan and O'Rear 1981]. In essence, this is a matter of the depth of hydrogenation. Jet fuels with no aromatics and no sulfur can be produced and meet all of the current ASTM specifications for jet fuel [Stuntz 1991].

Due to the compositional uniqueness, traditional density specification is more difficult to meet than smoke point for coal-derived jet fuel fractions, which comprise largely two-ring cycloparaffins. However, the high naphthene content of coal liquids makes them a remarkable feedstock for manufacturing high-density, high-energy jet fuels, a range-extender for high-mach aircrafts. More work is required in this area.

DIESEL FUEL PRODUCTION

With an even lower hydrogen content than the kerosene fraction, the coal-derived middle distillates have low cetane numbers, usually in the twenties. Upgrading of the middle distillates is necessary to increase the hydrogen content and remove hetero-compounds. However, saturation of a large part of the aromatics in the diesel fuel fractions may not be justified economically, and the use of multi-purpose additives may be advisable [Sefer and Erwin 1989]. The coal-derived diesel fuel does show good susceptibility to ignition improvers [Sullivan et al. 1981].

With all the aromatic hydrocarbons in coal diesel fractions saturated, a zero-aromatics, zero-sulfur diesel fuel is made by Exxon, which has a cetane value in the 42-53 range and considerably reduced particulate emissions relative to a typical petroleum diesel fuel [Stuntz 1991].

Initial LP work indicates that low-severity hydrotreating results in a diesel blendstock with a premium of about 4% over crude oil. A better premium may be possible by adjusting the cut points of this fraction.

CRACKING

Coal-derived middle and heavy distillates can be cracked, either by catalytic cracking or hydrocracking, to boost yields of gasoline or light distillate fuels. In order to be a good cat-cracker feedstock comparable to petroleum feedstocks, coal distillates must be hydrogenated to a 11.5-12.0 wt% hydrogen content [Riedl and deRosset 1980].

A decision on whether the hydrotreated middle distillate should be used as a diesel fuel blending stock or subjected to catalytic cracking should be based largely on economic considerations. Product slate constraints, however, will probably dictate that a certain part of the middle distillate should be blended to diesel fuel and the rest cracked to generate gasoline blending components. Heavy distillate or vacuum gas oil, if produced by the liquefaction plant, should be cracked. Hydrocracking of coal-derived heavy distillates can produce quality gasoline, jet, and diesel fuels. The choice between catalytic cracking and hydrocracking depends on the refinery infrastructure. The mode of operation for the hydrocracker, all-gasoline mode or maximum-jet-fuel mode, depends on refinery economics. Further LP work is under way to study this and other related options.

CONCLUSION

Coal liquids can be refined by modern refining technologies, primarily hydroprocessing, into specification transportation fuels. Mild hydrotreatment of coal naphtha to produce a gasoline blendstock is preferred over catalytic reforming in the long run. The middle distillate can be hydro-upgraded into high-density jet fuel or diesel fuel with the use of an appropriate additive package. Heavy distillates may be cracked to boost gasoline yield. By adjusting the depth of hydrogenation, zero-aromatics liquid fuels can be obtained with high quality. A high degree of product slate flexibility is possible with coal-liquid refining. Suitable refining strategies will result in a considerable premium for coal liquids over the price of crude oils. More research is recommended on coal-liquid characterization, including detailed analysis and development of correlations for property prediction; and on coal-liquid processing, including experimental and LP studies.

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TABLE 1
PROPERTIES OF WILSONVILLE TWO-STAGE LIQUIDS

Coal	Spring Creek	Pittsburgh Seam	Black Thunder	Illinois No. 6
Gravity, ^a API @15°C	16.2-18.3	27.7	23.9	24.5
Elemental				
Carbon, wt%	86.2-86.9	86.9	87.4	87.2
Hydrogen, wt%	10.9-11.3	11.55	11.2	11.8
Sulfur, wt%	0.05-0.10	0.05	0.05	0.02
Nitrogen, wt%	0.40-0.52	0.1	0.3	0.22
Oxygen, wt% (diff)	1.36-2.21	1.4	1.10	0.76
H/C Atom Ratio	1.51-1.58	1.59	1.54	1.62
V, Ni, Fe, Cu, ppm	-	<4.5	<25.0	-
Characterization Factor	-	10.9	10.9	-
Ash, wt%	-	0.002	0.01	-
Conradson Carbon, wt%	-	0	0	-
Pour Point, °C	-	-59	-26	-
Bromine Number, g/100g	-	8	14	-
Aniline Point, °C	-	23.8	-	-
Kin. Viscosity, cSt, @38°C	-	2.1	3.1	-
Phenolic-OH Conc., meq/g	-	0.18	-	-
Acidity, meq/g	-	-	0.38	-
GC Simulated Dist., °C				
IBP	36-57	-	-	-
10%	118-180	85	80.5	-
50%	277-331	253	270	-
95%	363-417	362	379	-

Data Source for Tables 1 through 4:

Burke et al. 1991.
Kramer 1991.
Visalchand et al. 1991.
Winschel, Burke, and Zhou 1991.

Kowalski and Basu 1984.
SEI 1991.
Winschel and Zhou 1991.
Zhou and Rao 1992.

TABLE 2
PROPERTIES OF WILSONVILLE COAL-DERIVED NAPHTHAS

Coal	Illinois No. 6 ^a	Pittsburgh Seam	Black Thunder	gasoline Specs
Cut, °C	IBP-182	IBP-193	IBP-193	
Gravity, ^a API @15°C	43.1	48.9	50.9	
DBS Distillation, °C				
10%	74 ^b	91	80 ^b	70 max
50%	121	126	116	77-121
90%	173	172	171	190 max
EP	197	187	204	225 max
RVP, kPa	-	19.3	21.4	62 max ^c
Elemental, wt%				
C	85.2	85.3	84.3	
H	12.9	13.3	13.6	
N	0.008	<0.1	0.1	
S	0.36	0.05	0.08	0.10 max
O (diff)	1.56	1.25	1.92	
Group Analysis, vol%				
Paraffins	15.9	19.3	38.0	
Naphthenes	60.7	67.5	7.0	
Aromatics	23.4	13.2	5.0	
Olefins	5.5	-	-	
Acidity, mg KOH/g	-	-	0.38	
Phenolic-OH, meq/g	-	0.18	0.40	
Motor Octane	73.4	86.5 ^d	87.1 ^d	
Existent Gum, mg/g	-	7.6	40.2	5 max
Copper Corrosion	-	1A	1A	1 max
Oxidation Stability, min	-	Pass	Fail	240 min
Yield, wt%				
on Total Coal Liquid	18.4	26.7	23.7	
on maf Coal	-	19.7	-	

^a Wilsonville Run 244.
^b Class A.

^c GC Simulated.
^d by GC method.

TABLE 3
PROPERTIES OF WILSONVILLE KERSENE FRACTIONS

Coal	Illinois No. 6	Pittsburgh Seam	Black Thunder	Jet A-1 Specs
Cut, °C	182-232	193-266	193-266	
Gravity, °API @15°C	22.9	25.9	21.3	37-51
DBG Distillation, °C				
10%	178 ¹	220	2121	205 max
50%	200	227	242	
90%	222	244	259	
EP	379	263	346	300 max
RVP, kPa	-	9.6	-	20.7 max
Flash Point, °C	-	76.1	86.7	38 min
Freezing Point, °C	-	-53.5	dark	-47 max
Elemental, wt%				
C	84.4	87.0	85.8	
H	10.9	11.5	10.6	
N	0.22	<0.1	0.3	
S	0.23	0.04	0.04	0.30 max
Mercaptan S	-	0.003	0.009	0.003 max
O (diff)	4.26	1.36	3.26	
Group Analysis, vol%				
Paraffins	-	-	-	
Naphthenes	-	-	-	
Aromatics	-	44.0	50.0	25 max
Olefins	-	3.0	3.0	5 max ²
Naphthalene	-	-	4.94	
Smoke Point, mm	-	10.8	9.8	25 min
Acidity, mg KOH/g	-	0.05	0.92	0.1 max
Phenolic-OH, meq/g	-	0.25		
Kin. Viscosity, cSt				
@ -20°C	-	1.75	18.94	8 max
Existent Gum, mg/g	-	69.0	90.8	7 max
Copper Corrosion	-	1A	1A	1 max
JFTOT	-	Fail	-	25/3 Min.
Net Heat Value, MJ/kg	-	42.1	42.0	42.8 min
Yield, wt%				
on Total Liquid	11.0	31.4	19.0	
on maf Coal	-	23.1	-	

¹ GC Simulated.

² applicable to Jet B.

TABLE 4
PROPERTIES OF WILSONVILLE COAL-DERIVED MIDDLE DISTILLATES

Coal	Illinois No. 6	Pittsburgh Seam	Black Thunder	No. 1 Diesel
Cut, °C	182-343	266 ⁺	266-343	
Gravity, °API	18.6	16.3	17.7	
GC Simulated Dist., °C				
10%	193	-	256	
50%	250	-	289	
90%	317	365	321	288 max
EP	379	-	346	
Flash Point, °C	-	-	124	38 min
Elemental, wt%				
C	86.3	88.4	87.0	
H	10.7	10.5	10.7	
N	0.23	0.1	0.3	
S	0.22	0.04	0.03	0.50 max
O (diff)	2.48	0.96	1.75	
H/C Atom Ratio	1.49	1.43	1.48	
Aromatic Carbon, %	34.0	-	-	
Bromine No. g/100g	-	7.4	17	
Viscosity, cSt, @40°C	-	8.97	6.2	1.3-2.4
Ramsbottom Carbon, %	0.15	-	-	0.15 max
Hot C. Insolubles, %	0.48	-	-	
Ash, wt%	-	0.02	0.00	0.01 max
Copper corrosion	-	1A	1A	3 max
Cetane Index	21	26.5	27.7	40 min ¹
Yield, wt% on Total Liquid	45.7	41.9	22.9	

¹ Cetane number.