



Energieia

Production of Coal-Based Fuels and Value-Added Products: Coal to Liquids Using Petroleum Refinery Streams

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BACKGROUND

The rise in petroleum prices shows no sign of abating, and has led to much interest in alternative fuel sources. The focus in coal-to-liquids technology has mainly been on gasification coupled with Fischer-Tropsch (F-T) synthesis. However, F-T liquids normally have very low concentrations of aromatic and naphthenic compounds that may be necessary to improve some fuel properties, such as thermal stability, density, freeze point, seal swell, and lubricity.

An added issue is the time to implement F-T projects. The Sasol-II and -III complexes in South Africa took six years to build once given the go-ahead. A similar project in the US could take

eight to ten years. The F-T project in Gilberton, PA has been twelve years in gestation. Our concern is that, given major dislocation in world crude oil markets and availability to the US, what do we do in the eight years while F-T plants are coming on line? Transitioning crude-starved refineries to coal and/or biomass, while using most of the existing infrastructure, could effect a transition to alternative fuels much more quickly.

We are studying several processes that utilize coal, coal-derived materials, or biomass in existing refining facilities. A major emphasis is the production of a coal-based replacement for JP-8 jet fuel (a military fuel). This fuel is very similar to Jet A and Jet A-1 in commercial aviation, so this work has significant carry-over

into the private sector. We have been focusing on three processes that could be retrofitted into a refinery: 1) coal tar/refinery stream blending and hydro-treatment; 2) coal extraction using refinery streams followed by hydro-treatment; and 3) co-coking of coal blended with refinery streams.

COAL TAR BLENDING

Our initial objective was to create a jet fuel that could resist pyrolytic degradation for two hours at 480 °C. Our first pilot-plant campaign showed that the prototype fuel met or exceeded most JP-8 specifications. That finding, and the significant increases in fuel prices, changed our emphasis to a coal-based replacement for JP-8. The project has three major activities: fuel production, stability, and combustion. At first we needed a ready source of coal-derived liquids to use as a surrogate, to make fuel for the stability and combustion portions of the project while routes to coal liquids were being developed. Refined chemical oil (RCO), a product from coal tar from metallurgical coke ovens, fills this role nicely.

The pilot-scale work is done by Inter-tek-PARC, Harmarville, PA, to obtain multiple-drum quantities of prototype fuel. RCO (Koppers) was blended with light cycle oil, LCO (United Refining Co., Warren, PA) in a 1:1 ratio. The feeds were hydro-treated to remove sulfur and nitrogen. They were then hydrogenated to saturate ring compounds, with fractionation at various stages. The location of fractionation cut points will affect yield of products and

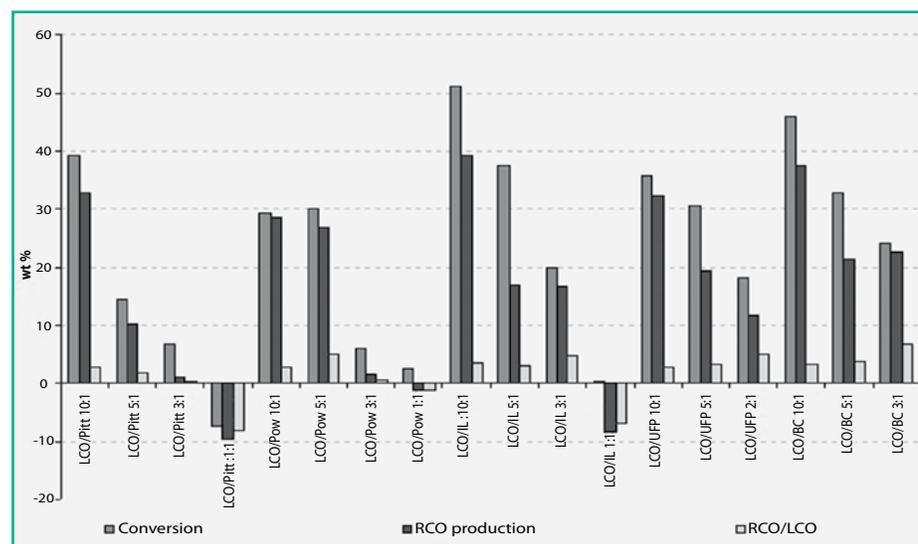


Figure 1: Yield data for small scale stirred autoclave extractions using LCO in various solvent ratios (10:1, 5:1, 3:1, 1:1) for the following coals: Pittsburgh (Pitt), Powellton (Pow), Illinois #6 (Ill), Upper Freeport (UFP), and Blind Canyon (BC).

(continued, page 2)

Coal-Based Fuels (cont.)

the interaction of the inputs with the catalytic treatments. Fractionation after both hydro-treatments gives a product distribution of 6% gasoline, 80% jet fuel, 10% diesel and 4% fuel oil.

The jet fuel fraction contains mainly two-ring hydro-aromatics and cyclo-alkanes. The prototype fuel produced

Coals used
Pittsburgh
Powellton
Blind Canyon
Illinois # 6
Upper Freeport

Table 1: Coals used in extractions using LCO as solvent.

from this process was successfully tested by the Air Force in a turbo shaft engine and performed similarly to a control sample of JP-8, both in terms of engine operation and emissions.

Jet fuel represents only a small portion of refinery output, about 10%. To convince a refiner to convert the jet fuel section of a refinery to produce coal-based jet fuel by this or other processes requires information on the impact of this change on quality and quantity of the other products: gasoline, diesel, fuel oil, and coke. The gasoline and diesel fractions from coal tar blending were analyzed and tested in engines. For gasoline, prominent coal-derived species were methylcyclohexane and decalin, with a small amount of tetralin. These components lowered the octane number, but for the most part would not affect the gasoline pool when used as blend stocks. In the diesel cut, prominent coal-derived species were fluorene, phenanthrene, and their derivatives. Blends of up to 5% of these compounds with conventional diesel fuel did not alter its properties significantly. Co-processed fuel oil was similar to No. 5 and No. 6 fuel oil, with less sulfur and nitrogen; however, the trace metals in the co-processed fuel oil were more similar to those in coal than in petroleum. Work continues on the improvement of catalysts for hydro-treatment and hydrogenation processes. The focus for desulfurization and denitrogenation has been on adsorption catalysts to remove heavy sulfur and nitrogen compounds and unsupported dispersed Ni/Mo and Co/Mo hydro desulfurization catalysts.

SOLVENT EXTRACTION

Despite the success with coal tar blending, large-scale commercialization

API Gravity @ 60°F	10.3	
Specific Gravity (gr/mL)	0.9979	
Sulfur (wt %)	1.92	
Nitrogen (ppm)	535	
Distillation	ASTM D-86	ASTM D-2887
IBP	220	146
10	266	249
30	286	279
50	296	301
70	313	324
90	336	359
FBP	354	396

Table 2: LCO characterization.

will be limited by current and future supplies of RCO. Use of electric-furnace technology in steelmaking, and improvements in the coke rate in blast furnaces, have reduced demand for coke, consequently reducing production of by-products. Environmental issues make it unlikely that another coke-oven battery will ever be built in the US. Therefore, we have been working to develop low-cost routes to the chemical equivalent of RCO, but ones that do not require a coke oven. For retrofitting into an existing oil refinery, solvent extraction is attractive, particularly if some refinery stream might prove to be a good solvent.

We are developing a process for extraction using LCO, since no separation of the liquids would be necessary and the product could be fed directly into a hydro-treater. Tables 1 and 2 show the coals and solvent used for extraction in a stirred autoclave. Figure 1 shows the

yield data for various LCO:coal ratios. The best yields were obtained with Pittsburgh, Illinois, and Blind Canyon coals. With a 10:1 ratio of LCO and coal at 360 °C, ~40-50% conversion of the coal was obtained. In a laboratory-scale multistage reactor (Figure 2), the yield from Pittsburgh coal increased to ~73% in the third stage. Current research focuses on reducing the amount of solvent needed, with the goal of making a 1:1 LCO/coal liquid for further hydro-treatment. We will also investigate other prospective solvents and possible uses for the residue.

CO-COKING

This process blends coal with decant oil as feed to a delayed coker, to produce a high-quality carbon material and liquids that could be upgraded to jet fuel. We have a unique, large laboratory-scale delayed coker to do this, shown in Figure 3. The addition of coal to coker feed streams may produce value-added

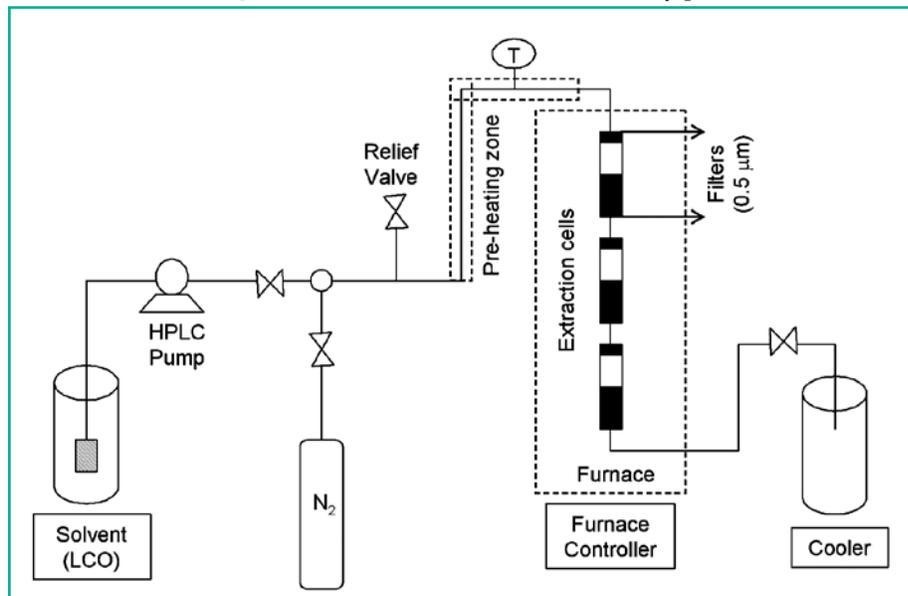
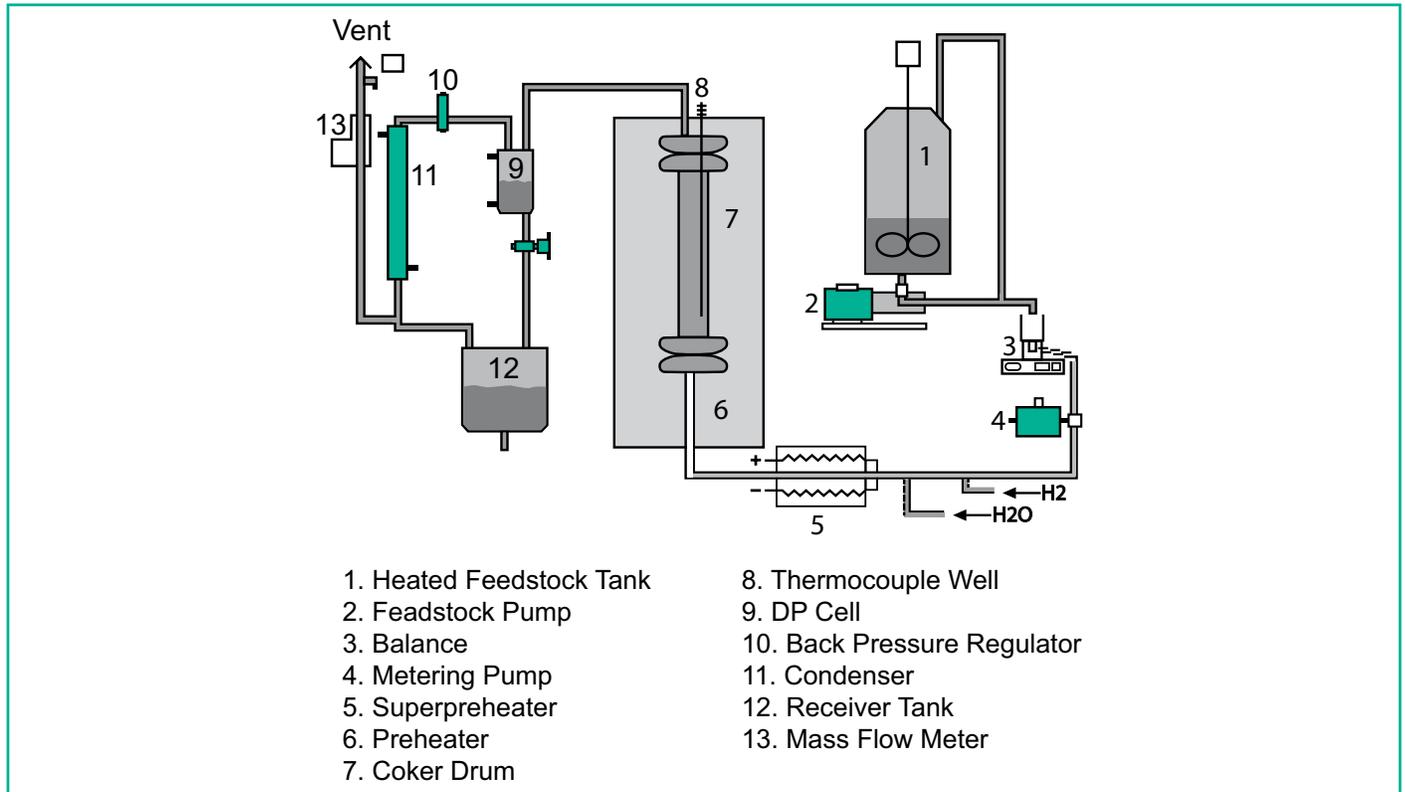


Figure 2: Schematic of multi-stage reactor.



- 1. Heated Feedstock Tank
- 2. Feedstock Pump
- 3. Balance
- 4. Metering Pump
- 5. Superpreheater
- 6. Preheater
- 7. Coker Drum
- 8. Thermocouple Well
- 9. DP Cell
- 10. Back Pressure Regulator
- 11. Condenser
- 12. Receiver Tank
- 13. Mass Flow Meter

Figure 3: Laboratory-scale delayed coker.

carbon products with properties different from those typically generated from delayed coking of resids. Consequently, we are also investigating whether coal introduced into the coker can result in carbon materials of potentially high value, along with streams for clean liquid fuels and binder pitch.

Most work has been on Pittsburgh seam coal blended with decant oil from United Refining. We are now evaluating coal from the Marfork mine in West Virginia. The properties of both coals and the beneficiated coals (Pittsburgh FCE and Marfork JCE) are shown in Table 3. The ultimate analysis for the decant oil is shown in Table 4.

With Pittsburgh coal, twelve duplicate runs were completed (Table 5). Using 4:1 decant oil to ultra-clean Pittsburgh seam coal at ~465 °C and 25 psig, the products are 27% coke, 10% gas, and 63% liquid. The liquids, analyzed by simulated distillation and GC/MS, were: 1) gasoline, IBP-180°C, 2.3%; 2) jet, 180-270°C, 4.6%; 3) diesel, 270-332°C, 6.0%; and fuel oil/pitch, 332 °C-FBP, 86%. The liquids were not hydro-treated. Hydro-treatment and hydrocracking will make the product distribution lighter. The compositions of the gasoline, jet fuel, and diesel are shown in Figure 4. The gasoline contains paraffins and single-ring compounds. The jet fuel is mainly paraffins and two-ring compounds; and the diesel

Analytical Procedure	Pittsburgh Seam DECS-34	Pittsburgh FCE 1.280 Float EI-186	Marfork Product DECS-36	Marfork JCE 1.268 Float EI-187
Proximate Analysis: (dry)				
Fixed Carbon, %	54.3	63.4	58.3	nd
Volatile Matter, %	38.4	35.6	34.5	nd
Ash, %	7.4	1.0	7.2	1.2
Ultimate Analysis: (dry)				
Carbon, %	78.2	84.6	80.8	nd
Hydrogen, %	5.2	5.3	5.1	nd
Nitrogen, %	1.6	1.6	1.5	nd
Sulfur, %	1.6	1.1	1.0	nd
Oxygen, % (diff.)	6.0	6.4	4.4	nd
Gieseler Plastometer:				
Softening Temperature, °C	381	385	384	375
Fluid Temperature Range, °C	91	93	108	121
Maximum Fluidity (ddpm)	16,418	29,527	30,000	29,516
Temperature at Maximum, °C	435	436	448	439
Ash Mineral Composition:				
Silicon Dioxide, %	48.47	41.8	57.38	nd
Aluminum Oxide, %	23.15	27.3	25.60	nd
Ferric Oxide, %	14.84	13.6	11.36	nd
Titanium Oxide, %	1.00	nd	1.44	nd
Phosphorus Pentoxide, %	0.53	0.61	0.23	nd
Calcium Oxide, %	2.49	5.65	1.21	nd
Magnesium Oxide, %	0.76	0.74	0.93	nd
Sodium Oxide, %	0.69	0.72	0.72	nd
Potassium Oxide, %	1.87	1.64	1.87	nd
Sulfur Trioxide, %	1.95	nd	0.47	nd
Organic Petrography: (volume %)				
Total Vitrinite	82.8	96.2	73.8	91.4
Total Liptinite	4.0	1.5	5.3	3.9
Total Inertinite	13.2	2.3	20.9	4.7

Table 3: Comparison of Coal Properties of Run-of-Mine and Clean Coal Samples for the Pittsburgh Seam FCE (EI-186) and Marfork JCE (EI-187)

	Decant Oil
Ash (dry wt %)	0.22
Carbon (daf wt %)	89.59
Hydrogen (daf wt %)	7.32
Nitrogen (daf wt %)	0.22
Sulfur (daf wt %)	2.99
daf=dry, ash free	

Table 4: Characterization of decant oil from United Refining

mostly polycyclic aromatic hydrocarbons, primarily three-ring compounds. The fuel-oil fraction will contain the heaviest components, and has been fractionated to produce pitch.

of the decant oil improves the liquid composition and the coke. Another approach is to test other coals. Testing of Marfork is in progress. The data for the first two runs are in Table 5. While the coke yield is similar to the Pittsburgh runs, the liquid yields are significantly higher (~70%)

and gas yields are lower (~3%). The products have not yet been characterized. Another approach has been to extract coal with decant oil in order to feed an ashless material to meet the mineral specifications for anodes and electrodes.

tion process that eliminates dependence on the coke industry for RCO, and produces a blend of coal liquids with LCO for further upgrading. In co-coking, the value-added coke may have applications as an electrode carbon, activated carbon, or other commercial uses. The advantages to utilizing refinery liquids and coal or coal tar in processes existing within a refinery to produce particular fuels and value-added materials are that the time to implementation could be much faster than projected for commercial gasification/F-T plants in the US and the possible production of fuels and carbon materials with specific uses for which F-T liquids may not be suitable.

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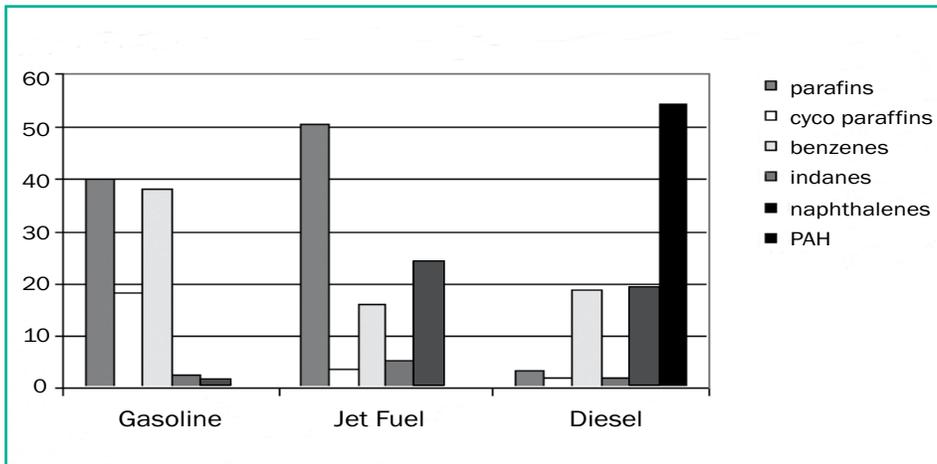


Figure 4: Composition of typical fractionated liquids for Pittsburgh co-coking runs.

Coke from ultra-clean coal was of good quality for aluminum-smelting anodes, though the iron and silicon in the carbon did not meet specifications. Testing at Alcoa indicated the carbon product had superior electrical resistivity. Therefore, we are considering further coal-cleaning strategies and characterizing the coke in more detail to determine other uses. Optical microscopy, XRD and density measurements show the cokes to be sponge coke. Preliminary data suggest that activated carbon could be produced by chemical activation, and that the coke is also graphitizable. Other developing markets may be attainable, e.g., substitution for blast furnace coke or in other solid carbon-based direct reduction processes.

We have examined modifications to improve liquid composition and reduce minerals in the coke. One aspect has been to hydro-treat the decant oil before co-coking. Prior hydro-treating

SUMMARY

We have shown potential for making a coal-based replacement for JP-8 (and thus Jet A) by blending and hydro-treating RCO and LCO. Clean diesel is co-produced with the jet fuel. A turboshaft engine has operated successfully with performance and emissions comparable to JP-8. We have developed a solvent-extrac-

Conditions	Coker Runs #50 - #61 Pittsburgh FCE EI-186			Marfork Runs EI-187	
	Average	Range	Condition Desired	#84	#85
Feed Stock, hrs	5.86	5.6 – 6.0	6.0	6.0	6.0
Steam Stripping	0	0	0	0	0
Hold at 500°C, hrs	24	-	24	24	24
Feed Rate, g/min	16.76	16.7 – 16.8	16.8	16.7	16.7
Preheater inlet, °C	120.9	119 – 124	120	118	115
Preheater Outlet, °C	438.7	432 – 443	440	432	426
Coke Drum Inlet, °C	499.2	483 – 512	500	504	509
Coke Drum Low/Mid, °C	496.3	487 – 505	500	486	502
Coke Drum Top, °C	478.8	468 – 499	475	475	473
Material Fed, g	5750	5206 – 6054	6000	5938	5898
Products:					
% Coke	27.42	-	-	26.29	27.20
% Liquid Products	62.82	-	-	70.24	70.14
% Gas (diff.)	9.76	-	-	3.47	2.66

Table 5: Run conditions used for Pittsburgh Seam FCE (EI-186) compared with Marfork Clean Coal Product (EI-187)