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 InterTek-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...
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 cycloalkanes. The prototype fuel produced 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

<table>
<thead>
<tr>
<th>Coals used</th>
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<tbody>
<tr>
<td>Pittsburgh</td>
</tr>
<tr>
<td>Powelton</td>
</tr>
<tr>
<td>Blind Canyon</td>
</tr>
<tr>
<td>Illinois # 6</td>
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<tr>
<td>Upper Freeport</td>
</tr>
</tbody>
</table>

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

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, we need to demonstrate that the product could be fed directly into a hydro-treater. 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 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

<table>
<thead>
<tr>
<th>API Gravity @ 60°F</th>
<th>10.3</th>
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</thead>
<tbody>
<tr>
<td>Specific Gravity (gr/mL)</td>
<td>0.9979</td>
</tr>
<tr>
<td>Sulfur (wt %)</td>
<td>1.92</td>
</tr>
<tr>
<td>Nitrogen (ppm)</td>
<td>535</td>
</tr>
</tbody>
</table>

### Table 2: LCO characterization.

![Figure 2: Schematic of multi-stage reactor.](image)
Coal-Based Fuels (cont.)

The jet fuel is mainly paraffins and single-ring compounds. The gasoline contains paraffins and two-ring compounds. 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.

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

Figure 3: Laboratory-scale delayed coker.

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
Volatilite 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)
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 anashless material to meet the mineral specifications for anodes and electrodes.

### Table 4: Characterization of decant oil from United Refining

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>Pittsburgh Runs</th>
<th>Marfork Runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (dry wt %)</td>
<td>0.22</td>
<td>0.25</td>
<td>0.24</td>
</tr>
<tr>
<td>Carbon (daf wt %)</td>
<td>89.59</td>
<td>89.5</td>
<td>89.5</td>
</tr>
<tr>
<td>Hydrogen (daf wt %)</td>
<td>7.32</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>Nitrogen (daf wt %)</td>
<td>0.22</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulfur (daf wt %)</td>
<td>2.99</td>
<td>2.9</td>
<td>2.9</td>
</tr>
</tbody>
</table>

daf=dry, ash free

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

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Coker Runs #50 - #61</th>
<th>Marfork Runs EI-187</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Stock, hrs</td>
<td>5.86</td>
<td></td>
</tr>
<tr>
<td>Steam Stripping</td>
<td>0</td>
<td></td>
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<tr>
<td>Hold at 500°C, hrs</td>
<td>24</td>
<td></td>
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<tr>
<td>Feed Rate, g/min</td>
<td>16.76</td>
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<tr>
<td>Preheater inlet, °C</td>
<td>120.9</td>
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<tr>
<td>Preheater Outlet, °C</td>
<td>438.7</td>
<td></td>
</tr>
<tr>
<td>Coke Drum Inlet, °C</td>
<td>499.2</td>
<td></td>
</tr>
<tr>
<td>Coke Drum Low/Mid, °C</td>
<td>496.3</td>
<td></td>
</tr>
<tr>
<td>Coke Drum Top, °C</td>
<td>478.8</td>
<td></td>
</tr>
<tr>
<td>Material Fed, g</td>
<td>5750</td>
<td></td>
</tr>
</tbody>
</table>

### Figures

**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-extraction 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.

### ACKNOWLEDGEMENTS

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Energy Fair to Students

Marybeth McAlister
CAER

Last year when we began charting the course for the CAER’s 30th anniversary celebrations, I remember speaking up in a meeting to say, “Let’s put on an energy fair for elementary students.” I’m not sure from where my naïve enthusiasm sprang. It was reminiscent of the old musicals, where somebody inevitably decides to solve problems by yelling, “Hey gang, let’s put on a show.”

I suppose that along with the ‘important’ adults who would participate in the Kentucky Energy Summit, 30th anniversary dinner, short courses, and Distinguished Lecture, I wanted to see the future of energy represented through some of the kids in our community.

The outcome of my Polly Anna-ish outburst was that on January 23rd, fourth and fifth grade students from Johnson, Linlee, Mary Todd and Russell Cave elementary schools enjoyed a short coach bus ride to the University of Kentucky for a day-long fair, which featured displays by energy-related organizations from both inside and outside the university. Along the way, they watched an energy DVD we provided. Each bus was equipped with monitors above the seats. Pretty cool, huh!

Before touring the exhibits, each class got to see a 20 minute stage performance. The on-stage live action included: a demonstration by CAER researchers of combustion via an invisible ink experiment; The Kentucky Geological Survey explained carbon sequestration; and a representative from the Kentucky NEED program illustrated how electricity travels by using the students as conductors.

After watching the demos, we gave the students bags to hold the goodies they would collect at the individual stops and they were on their way. Among the more popular events were: the E.ON U.S. mini-city and Touchstone Energy’s kinetic energy demonstration using live reptiles. Some of the other stations included the Bluegrass Community and Technical College, whose station featured tornado tubes and a magnet board. Exhibitors from UK’s College of Engineering explained greenhouse gasses (Department of Chemical and Materials Engineering) and snap circuitry (Department of Electrical Engineering), while CAER scientists showed the students how to make batteries.

In my habitual compulsion to over-plan everything, I created tour routes and general time frames for each group to visit the 16 exhibitors. Although the classes arrived on a 30 minute staggered schedule in order not to overcrowd any one area, it became immediately apparent that we would have to be flexible and allow the groups to go where they wanted when they wanted. I have the greatest respect for elementary school teachers. They always have a plan B.

After touring the first half of the exhibits, the classes had lunch in an adjoining dining room. They then visited any exhibits that they missed on the early round.

As the kids gathered their coats and left, we gave each a small basketball. I intended them to be gifts. The teachers planned to use them in lessons on “forces in motion” by rolling their UK basketballs along the floor at different speeds. This is a different kind of plan B.
Out of the thousands of school children in Lexington, Kentucky, these kids were chosen from elementary schools whose science scores are among the lowest in town. We worked with the science-education experts in the county’s school system to ensure we were providing something that was actually needed. Bringing them on board at the beginning was an essential element in gathering the input that prevented this event from being a well-intentioned, but superfluous do-gooder’s exercise. Instead, we targeted the kids who needed it the most and worked within the curriculum that the state mandates.

I hear a lot about the sad state of public schools. But that hasn’t been my experience. I have worked with local teachers on several programs ranging from intensive one-day teacher workshops to long-range ‘scientist in the classroom’ programs. I have found intelligent, caring educators who serve multiple functions as teachers, social workers, part-time parents, budgeters, and cheerleaders.

I don’t think events like this one will solve our energy problems, but we have to find a way to get kids excited about working in math and science. We see our program as a spoke in the larger wheel that represents UK’s overall program aimed at increasing the number of students majoring in science, technology, engineering and math. This is a start.