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Refinery Integration of By-Products from Coal-Derived Jet Fuels

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Abstract
This report summarizes the accomplishments toward project goals during the first six months of the project to assess the properties and performance of coal based products. These products are in the gasoline, diesel and fuel oil range and result from coal based jet fuel production from an Air Force funded program. Specific areas of progress include generation of coal based material that has been fractionated into the desired refinery cuts, acquisition and installation of a research gasoline engine, and modification of diesel engines for use in evaluating diesel produced in the project. The desulfurization of sulfur containing components of coal and petroleum is being studied so that effective conversion of blended coal and petroleum streams can be efficiently converted to useful refinery products. Equipment is now in place to begin fuel oil evaluations to assess the quality of coal based fuel oil. Coal samples have procured and are being assessed for cleaning prior to use in coking studies.

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Introduction

This program is investigating the fate of each major product from a refinery complex, except jet fuel, resulting from the refinery integration of coal-derived jet fuel production via a combined RCO/LCO strategy by studying the physical and chemical nature of all products that are perturbed by introduction of coal components into the refinery.

The impact of the proposed research is to provide the scientific and fundamental engineering basis to integrate the production of coal-based jet fuel into existing refinery operations in a time frame consistent with availability and economic forecasts related to petroleum-derived as opposed to coal-based feedstocks. The results of these studies lead to the integration of all non-jet-fuel streams into current refinery operations in concert with desired production of coal-based jet fuel engine testing toward the end of the first decade of the new century. For successful utilization of coal-based jet fuels all non-jet-fuel components must fit existing and future product stream specifications.

Executive Summary

Penn State has been working for more than a decade on the development of an advanced, thermally stable, coal-based jet fuel, JP-900. Two process routes to JP-900 have been identified, one involving the hydrotreating of blends of refined chemical oil (a by-product of the coal tar industry) with light cycle oil, and the other involving the addition of coal to delayed cokers. However, no refinery is operated for the primary purpose of making jet fuel. The conversion of the jet fuel section of a refinery to production of coal-based JP-900 would necessarily impact the quantity and quality of the other refinery products, such as gasoline, diesel fuel, fuel oil, and coke. The overall objective of this project is to examine the characteristics and quality of the streams *other than the jet fuel*, and to determine the effect those materials would have on other unit operations in the refinery.

The present report documents the activities of the first six months of what is envisioned to be a four-year program. Our collateral work on jet fuel, funded by the Air Force Office of Scientific Research, is focused exclusively on that product. Thus as we branch out into the study of the other refinery streams, under this present contract, much of the initial effort has necessarily been devoted to equipment acquisition and installation, and to the first experiments.

The overall project involves pilot-scale production of materials at PARC Technical Services (Harmarville, PA). The coal-based gasoline and diesel fuel will be evaluated in appropriate internal combustion engines. Desulfurization, denitrogenation, and saturation of aromatics will be tested. The coal-based fuel oil will be tested in a research boiler. The pitch and coke produced will also be characterized. These interrelated activities are designed to evaluate the full range of products from coal-based thermally stable jet fuel production and to lead toward process integration in existing refineries.

The hydrotreatment of blends of refined chemical oil and light cycle oil, followed by fractionation of the total product, has been performed at PARC. The various distillation cuts have been provided to the researchers at Penn State for analytical characterization and for use in the appropriate evaluation tests. In addition, decant oil was hydrotreated at several levels of severity for use in the co-coking work.

For evaluation of gasoline quality and performance, we have acquired and installed a Ricardo Hydra single-cylinder research engine. Work is continuing on instrumentation and facilities hook-up to the engine test stand.

To assess the impact on diesel fuel quality and performance, two existing engine test stands, using Navistar and DCC turbodiesel engines were enhanced. In addition, new instrumentation for testing ignition quality was purchased and is being installed. The ignition quality test has recently become an ASTM method; we will participate in a round-robin evaluation of this test, which will provide a useful external comparison of data on the coal-based fuels at no additional cost to the project.

The desulfurization of 4,6-dimethyldibenzothiophene and of dibenzothiophene in decalin was studied over commercial cobalt-molybdenum and nickel-molybdenum catalysts. Quinoline was used as a model compound to investigate the effect of the presence of nitrogen compounds of the desulfurization process. The desulfurization can be explained by pseudo-first-order kinetics, and is strongly inhibited by the presence of quinoline. A flow reactor was designed and constructed for saturation of aromatics. The first series of experiments involved palladium on various supports as the catalysts for saturation. Selective methylation of 2-methylnaphthalene with methanol has been studied for the production of 2.6-dimethylnaphthalene, which would be a value-added coal-based by-product for the petrochemical industry.

For fuel-oil evaluation, a high-temperature in-furnace camera was procured and installed in a water-tube research boiler. Shakedown tests of the camera are underway.

Samples of as-mined coal and of froth flotation products from a Consol mine in Washington County. Pennsylvania were obtained. These materials will be used in co-coking experiments. Some of the froth flotation products still have significant ash yield, suggesting that secondary cleaning processes may be necessary to have a low-ash feed to the coker.

Experimental

The respective experimental details for each of the tasks of this project are described within the individual Tasks I – V detailed later in this report.

Results and Discussion

The results of each task of this project are documented and discussed within the appropriate Task I – V detailed later in this report.

Conclusions

Each of the individual tasks of this project has progressed as proposed or to a greater extent than originally proposed. Each task individually contributes to the ultimate goal of refinery integration. This first semiannual report describes the procurement of equipment into the appropriate laboratories, the establishment of experimental procedures and the generation of early results that indicate the relevance and feasibility of the proposed work. Progress has been made to produce hydrotreated products, differing from conventional refinery products but also compatible with conventional materials. A new approach has generated similar materials not having the added cost of hydrotreating. These materials will be evaluated in the next reporting period and be compared with extensively hydrotreated gasoline, diesel and fuel oil fractions. Engines have been installed which will provide detailed performance measurements on both the gasoline and diesel components in this process. Equipment to provide detailed understanding of the quality of fuel oil has been procured as has equipment needed to study the heavy components available through the process of generating the desired jet fuels within a conventional petroleum refinery complex.

Technical Discussion

Background

Penn State has been involved in a multi-phase fifteen-year program to develop an advanced thermally stable jet fuel for the Air Force [1-4]. This fuel would resist breaking down at high temperatures (900°F), so it could be used for cooling sensitive parts on high-performance aircraft, as well as providing the propulsion. It is provisionally called JP-900.

At its inception, the JP-900 program presumed that this new fuel would be made entirely or substantially from coal. There are three reasons for this.

Scientific validity. Penn State's researchers have shown clearly that the kinds of chemicals in the fuel that make it stable at 900°F (hydroaromatics and naphthenes) can be derived in abundant amounts from coal. This has been demonstrated in numerous peer-reviewed publications [5-10].

Long-term security. Unlike petroleum, coal is a secure, domestic energy resource for which centuries' worth of reserves remain in the U.S.

Stable procurement. Both petroleum and natural gas are vulnerable to significant price spikes. In contrast, coal companies are willing to write twenty-year delivery contracts at a guaranteed stable price. In turn, this would help stabilize the price of military fuel for decades to come.

To ultimately produce an advanced thermally stable coal-based jet fuel a practical and economically viable process, compatible with current refinery practice, is necessary. The evaluation of this scenario is the subject of this proposal. No refinery is operated for the specific purpose of making jet fuel. Furthermore, refineries are highly integrated, in that many of the individual operations are dependent on, or use streams from, other operations. Therefore, in order to insure that the production of coal-based JP-900 in the jet fuel section of a refinery is acceptable to refinery operators, it is crucial to have data showing the effect of the by-products from coal-based JP-900 production (i.e., the $<180^{o}C$ and the $>270^{o}C$ fractions) on the quantity and quality of the other refinery products: gasoline, diesel, fuel oil, pitch, and coke.

Options for integrating coal, or a coal liquid product that is currently available commercially (a by-product coal tar distillate from the metallurgical coke industry) into existing refineries are illustrated in **Figure 1**. With respect to the first two options, coal can either be added to the coker directly or be co-processed with the resid. Of these, addition of the coal to coker has been selected – in consultation with our refinery partner – as the better option to produce sufficient quantities of coal-based fuel for thermal stability and combustion testing. Each of these approaches has a unique set of technical challenges in terms of specifying the proper feedstocks (for both petroleum- and coal-based components), process conditions (temperature and pressure) and processing approaches.

Previous work at Penn State has resulted in significant progress in identifying the remaining critical barriers to realization of coal-based fuels [11-20].

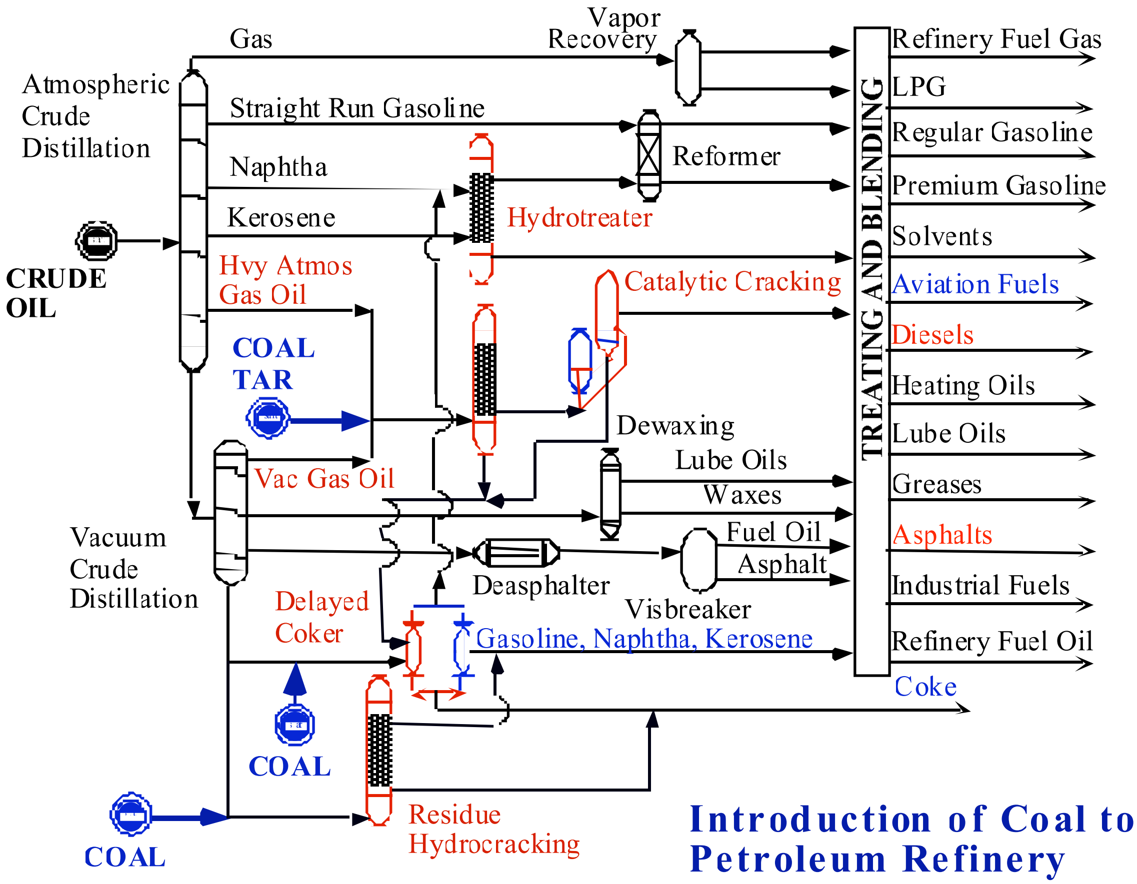

Figure 1. Possible integration of coal into existing refineries.

Objectives

A number of potential JP-900-type jet fuels have been produced by Pennsylvania Applied Research Corporation (PARC) from the hydrotreatment of a coal-derived refined chemical oil (RCO) and its mixture with a petroleum-derived light cycle oil (LCO).

The overall objective of this project is to examine the characteristics and quality of the streams other than the jet fuel, and what effect those materials would have on the other unit operations in the refinery, the quality and value of the other products. Broadly, these additional by-products are the liquids lighter and heavier than jet fuel itself, i.e., the <180°C and the >270°C fractions produced after hydrotreating the RCO/LCO blend and fractionating to recover the jet fuel and other refinery streams.

Prior to the beginning of this project, virtually all work was focused on the jet fuel. However, as we have noted above, no refinery is run for the specific purpose of making jet fuel. Therefore, to make these processes acceptable for adoption in refineries, it is vital to assess their impact on the other major operations and products in a refinery. The acquisition of that knowledge is the basis of this project.

These studies will impact all of the major product streams in a conventional petroleum-based refinery. Therefore, replacing petroleum feedstock with domestic coal, gasoline, diesel, fuel oil and pitch components will favorably impact reducing dependence on, and security of supply of, foreign petroleum resources.

The objectives of the project are to:

- Investigate and develop an understanding of the most promising refinery integration of all process streams resulting from the production of coal-based jet fuel.

- Demonstrate the quality of each of the process streams in terms of refinery requirements to maintain a stable, profitable refinery operation.

- Demonstrate the performance of key process streams in practical testing used for application of these streams.

This fundamental research was proposed as a four-year program. In this document we report activities and accomplishments for the first six months of the contract year. The approach chosen draws on previous work that has now successfully produced a coal-based JP-900 fuel at pilot-plant scale for initial investigations in the fuel stabilization and combustion studies [21-23]. In that work, it has been shown that hydrotreated blends of light cycle oil and refined chemical oil (a coal-derived liquid) resulted in the most thermally stable product to date.

This program is investigating the fate of each major product from a refinery complex, except jet fuel, resulting from the refinery integration of coal-derived jet fuel production via a combined RCO/LCO strategy by studying the physical and chemical nature of all products that are perturbed by introduction of coal components into the refinery.

The impact of the proposed research is to provide the scientific and fundamental engineering basis to integrate the production of coal-based jet fuel into existing refinery operations in a time frame consistent with availability and economic forecasts related to petroleum-derived as opposed to coal-based feedstocks. The results of these studies lead to the integration of all non-jet-fuel streams into current refinery operations in concert with desired production of coal-based jet fuel engine testing toward the end of the first decade of the new century. For successful utilization of coal-based jet fuels all non-jet-fuel components must fit existing and future product stream specifications.

Coal tar fractions have been successfully demonstrated to be suitable feedstocks for the production of jet fuels for high-speed aircraft [22-23]. The jet fuel, as prepared and evaluated in our Air Force project, is a 180-270^{o}C product cut from a mixture of RCO/LCO total liquid product. Of this product the $<$180^{o}C cut represents ~4% of the total product and the $>$270^{o}C fraction represents just over 40% of the total liquid product [24]. These streams must either be blended as is, chemically converted and then blended, converted to chemicals, or used as feed to the coker.

Scope Of Work For Year 1

The technical approach consists of five carefully planned goals whose successful completion will lead to the achievement of the project objectives. These goals include:

- pilot-scale fuel production at PARC,
- evaluation of coal-based gasoline and diesel products in internal combustion engines,
- desulfurization, and denitrogenation of coal-based fuels, the saturation of aromatics to improve stability and the development of chemicals from coal,

- evaluation of coal-based fuel oil, and

- evaluation of pitch and coke materials from coal-based fuel production.

These interrelated goals are designed to evaluate the full utilization of products from coal-based thermally stable jet fuel production and lead toward process integration into existing refineries.

Tasks To Be Performed

We are critically analyzing the performance and value of the streams produced from combination of coal-derived components and normal refinery process streams.

The critical analyses include:

- evaluation of gasoline range material in spark-ignited gasoline engines

- evaluation of diesel-range product for use in compression-ignited diesel engines

- evaluation of heavier range materials as heating oils and boiler fuels

- evaluation of products from co-coking strategies as precursors to higher value cokes and carbons.