SUBTASK 3.11 – PRODUCTION OF CBTL-BASED JET FUELS FROM BIOMASS-BASED FEEDSTOCKS AND MONTANA COAL

Final Report

(for the period February 1, 2013, through June 30, 2014)

Prepared for:

AAD Document Control

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2015-EERC-01-23 January 2015

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ACKNOWLEDGMENTS

This report was prepared with support of the Accelergy Corporation and the DOE National Energy Technology Laboratory (NETL) Cooperative Agreement No. DE-FC26-08NT43291. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of Accelergy Corporation and DOE.

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ABSTRACT

The Energy & Environmental Research Center (EERC), in partnership with the U.S. Department of Energy (DOE) and Accelergy Corporation, an advanced fuels developer with technologies exclusively licensed from Exxon Mobil, undertook Subtask 3.11 to use a recently installed bench-scale direct coal liquefaction (DCL) system capable of converting 45 pounds/hour of pulverized, dried coal to a liquid suitable for upgrading to fuels and/or chemicals. The process involves liquefaction of Rosebud mine coal (Montana coal) coupled with an upgrading scheme to produce a naphthenic fuel. The upgrading comprises catalytic hydrotreating and saturation to produce naphthenic fuel. A synthetic jet fuel was prepared by blending equal volumes of naphthenic fuel with similar aliphatic fuel derived from biomass and 11 volume % of aromatic hydrocarbons. The synthetic fuel was tested using standard ASTM International techniques to determine compliance with JP-8 fuel. The composite fuel thus produced not only meets but exceeds the military aviation fuel-screening criteria.

A 500-milliliter synthetic jet fuel sample which met internal screening criteria was submitted to the Air Force Research Laboratory (AFRL) at Wright–Patterson Air Force Base, Dayton, Ohio, for evaluation. The sample was confirmed by AFRL to be in compliance with U.S. Air Force-prescribed alternative aviation fuel initial screening criteria. The results show that this fuel meets or exceeds the key specification parameters for JP-8, a petroleum-based jet fuel widely used by the U.S. military. JP-8 specifications include parameters such as freeze point, density, flash point, and others; all of which were met by the EERC fuel sample. The fuel also exceeds the thermal stability specification of JP-8 fuel as determined by the quartz crystalline microbalance (QCM) test also performed at an independent laboratory as well as AFRL. This means that the EERC fuel looks and acts identically to petroleum-derived jet fuel and can be used interchangeably without any special requirements and thus provides a pathway to energy security to the U.S. military and the entire nation.

This subtask was funded through the EERC–DOE Joint Program on Research and Development for Fossil Energy-Related Resources Cooperative Agreement No. DE-FC26-08NT43291. Nonfederal funding was provided by Accelergy Corporation.

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EXECUTIVE SUMMARY

This Energy & Environmental Research Center (EERC) subtask is being conducted using cost share from Accelergy Corporation, an advanced fuels developer with technologies exclusively licensed from Exxon Mobil. The primary objectives of this subtask are to modify the recently fabricated direct coal liquefaction (DCL) system to make it more efficient and user-friendly and use this system to produce 3–5 gallons of middle distillate from a Montana coal (Rosebud mine coal) for submission to the Intertek PARC facility for upgrading. The fractional distillation of the upgraded middle distillate produced a naphthenic fraction with a boiling point distribution similar to petroleum-derived jet fuel.

Activities conducted by the EERC during the tenure of this project consisted of liquefaction of Rosebud mine coal to produce distillate fuel. The distillate derived from liquefaction of coal produces fuel that contains aromatics and naphthenes which do not have the key components to meet the key properties of aviation fuels. In order to overcome this problem, the coal-derived fuel was blended with a biomass-derived fuel primarily aliphatic in nature that was obtained from Accelergy Corporation, Inc. A blending study demonstrated that equal volumes of coal- and biomass-derived jet fuel along with 11 vol% aromatics needed to enhance its lubricity produced a synthetic fuel capable of compliance with JP-8 specifications. The complete characterization of the composite fuel was performed to determine its compliance with U.S. military specifications for JP-8 jet fuel. Following successful testing of the coal–biomass-to-liquid jet fuel, the fuel was delivered to the U.S. Air Force Research Laboratory at Wright–Patterson Air Force Base for analysis to assess compliance with MIL-DTL-83133F, the U.S. military specification for JP-8 jet fuel.

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SUBTASK 3.11 – PRODUCTION OF CBTL-BASED JET FUELS FROM BIOMASS-BASED FEEDSTOCKS AND MONTANA COAL

INTRODUCTION

This Energy & Environmental Research Center (EERC) modified the recently fabricated direct coal liquefaction (DCL) system to make it more efficient and user-friendly and used this system to produce 3–5 gallons of middle distillate from a Montana coal (Rosebud Mine coal) for submission to the Intertek PARC facility for upgrading. The fractional distillation of the upgraded middle distillate produced a naphthenic fraction with boiling point distribution similar to petroleum-derived jet fuel.

A coal-derived fuel was blended with a biomass-derived fuel primarily aliphatic in nature obtained from Accelergy Corporation, Inc. A blending study demonstrated that equal volumes of coal- and biomass-derived jet fuel along with 11 vol% aromatics needed to enhance its lubricity produced a synthetic fuel capable of compliance with JP-8 specifications. Complete characterization of the composite fuel was performed to determine its compliance with U.S. military specifications for JP-8 jet fuel. Following successful testing of the coal–biomass-to-liquid (CBTL) jet fuel, the fuel was delivered to the U.S. Air Force Research Laboratory at Wright–Patterson Air Force Base for analysis to assess compliance with MIL-DTL-83133F, the U.S. military specification for JP-8 jet fuel.

EXPERIMENTAL

Activity 1 – Production of Middle Distillate from Montana Coal

Activity 1.1 – Preparation and Procurement of Materials

- The coal was ground to pass through a 100-mesh sieve. The ground coal was vacuum-dried and analyzed for proximate and ultimate analyses. It was stored under nitrogen for further use.

- Anthracene oil was distilled using high-vacuum distillation to generate 8 gallons of vacuum gas oil (VGO) boiling at 650°–1000°F. The vacuum gas oil was saved in a dark, cold place for further use as a solvent in liquefaction testing.

- A commercial catalyst Moly-Van (Co-Moly) was used as a catalyst for liquefaction testing.

Activity 1.2 – Modifications and Shakedown of the Continuous DCL System

The DCL system was fabricated under a recently completed U.S. Department of Energy (DOE)–Accelergy joint project and installed in the EERC National Center for Hydrogen Technology$^{®}$ (NCHT$^{®}$) building. The initial shakedown of the system identified several issues that needed to be addressed to ensure continuous operation of the system. The modifications included the addition of fluidized-bed sand bath heaters, larger collection pots, and flowmeters to overcome operational difficulties encountered during initial system shakedown. The following changes were made to the system to address these concerns:

- In response to concerns regarding potentially inadequate heating capacity, additional heaters were added to the sand bath.

- All tubing lines and connections were heat-traced and insulated.

- In response to concerns regarding frequent product collections, larger bottoms stripper accumulator (BSA) pots were installed and attached to a vent line.

- The DCL reactor tube inside diameter and length were adjusted to accommodate Accelergy-specified slurry linear velocity and residence time requirements of 0.40 feet/second and 1 hour, respectively.

The photographs of the two-level reactor system are provided as Figures 1 and 2.

Activity 1.3 – Liquefaction Test

The direct liquefaction of coal was performed in two stages described as follows.

Stage 1 – "Once-Through operation": Preparation of VGO

The purpose of the once-through operation is to generate enough test coal-derived vacuum bottoms and VGO to start the liquefaction process; thereafter, the process will be self-sustaining and generate bottoms and VGO on a continuous basis. After sufficient amounts of vacuum bottoms and VGO needed to initiate the liquefaction process are produced, further processing is conducted to produce test coal-derived raw middle distillate for upgrading to jet fuel blendstock.

Initially, a start-up slurry consisting of coal, catalyst (1000 ppm in coal–catalyst mix), and hydrogenated anthracene oil (1.6 solvent/coal mass ratio) was premixed in a slurry mixing tank (feed mixing tank, Figure 1) and then transferred to a slurry feed tank with the help of a pump. The start-up slurry was then fed into the tubular reactor housed in a fluidized-bed sand bath at a predetermined rate using a high-pressure pump (Figure 1). The liquefaction was carried out under following conditions:

- Temperature = 450°C
- Residence time = 60 minutes
- Pressure = 2500 psi

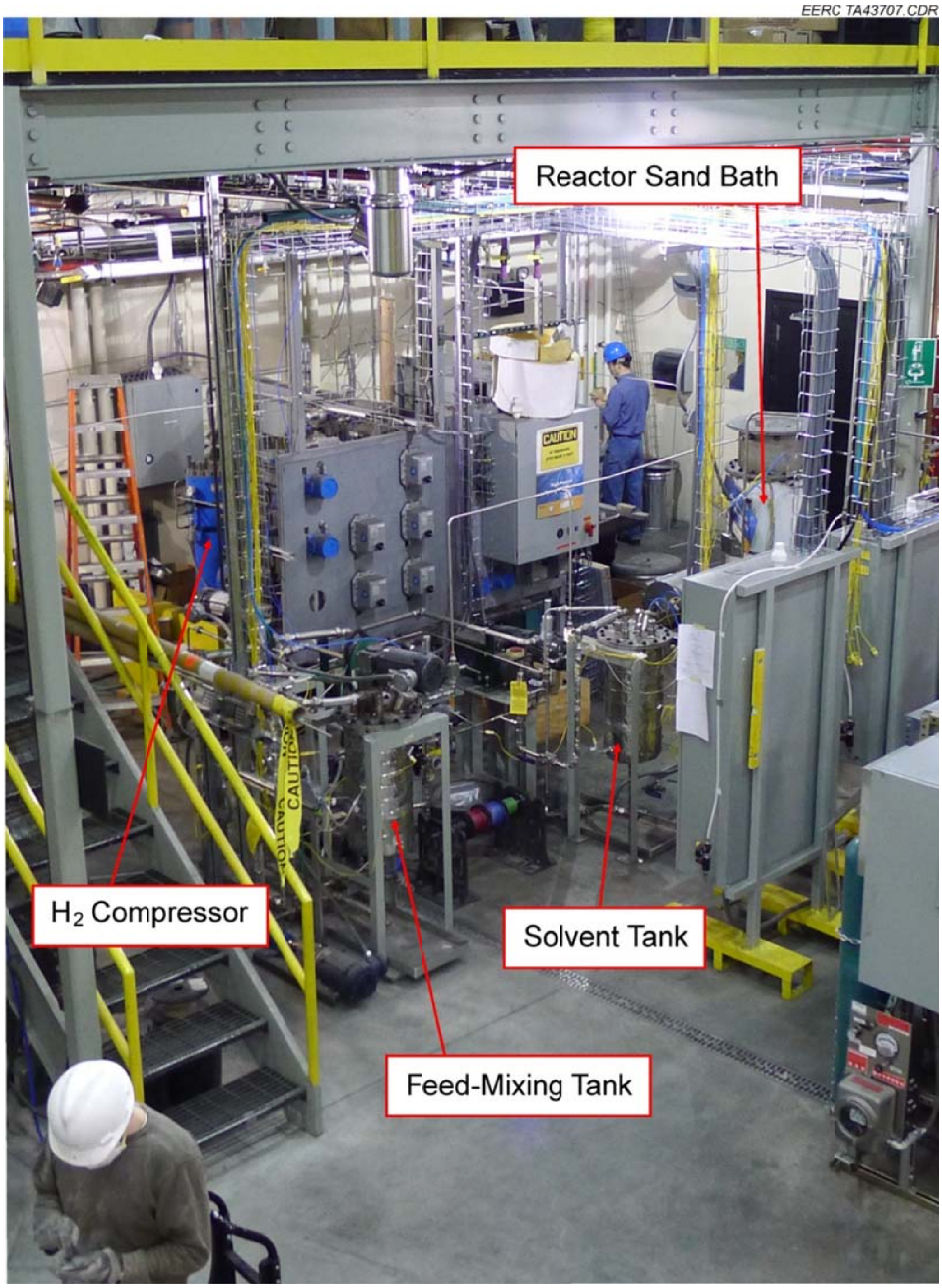

Figure 1. First-floor view of the DCL reactor system.

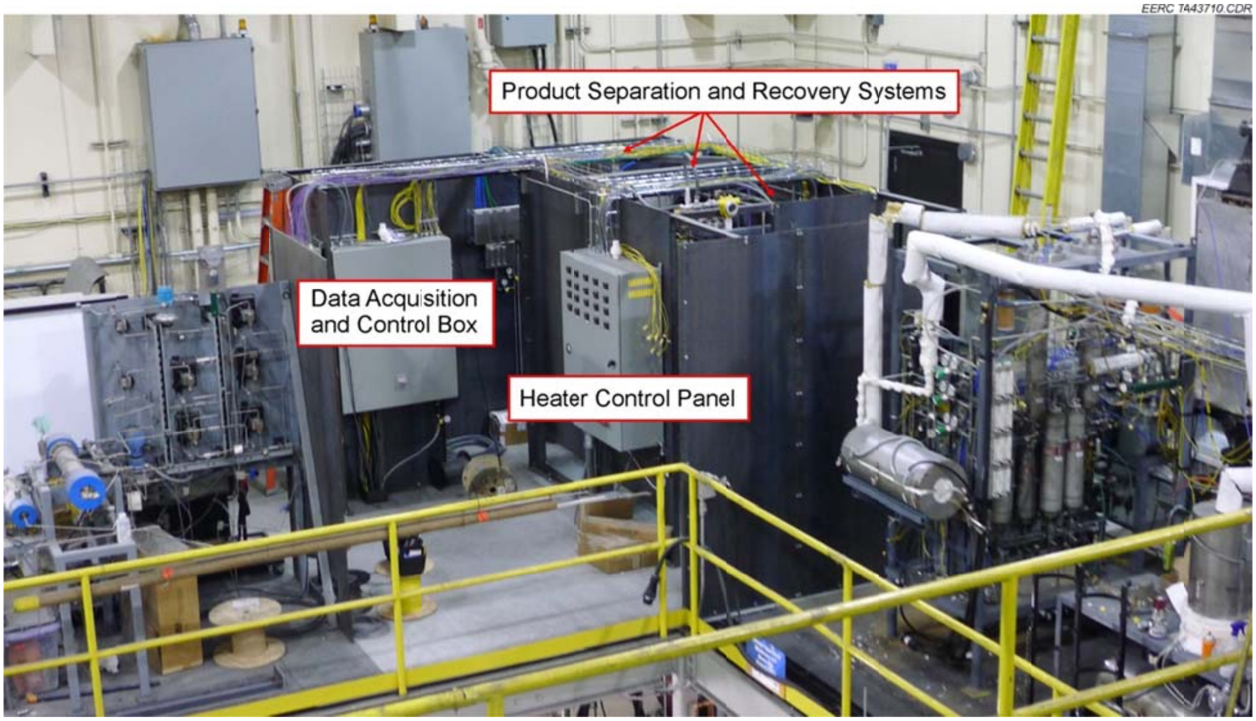

Figure 2. Second-floor view of the DCL reactor system.

The volatile products were condensed to form a liquid using a series of condensers, and the remaining slurry (vacuum bottoms) was collected and transferred to a freezer for storage. The frozen slurry was pulverized and transferred into the mixing tank for recycle. The uncondensed gas was passed through a scrubber for removal of acidic gases, and the remaining gas was sent to the flare system. The condensed liquid was collected every 6 hours, transferred to a distillation unit located near the DCL system (Figure 3), and batch-distilled to yield about 4.2 liters of VGO and 3 liters of distillate comprising naphtha, water, and a "middle distillate cut" (which may necessarily contain a significant amount of start-up anthracene oil-derived compounds). The VGO obtained from distillation (along with previously collected vacuum bottoms) was recycled until a test coal-derived VGO was generated.

Stage 2 – Bottom Recycle Operation

After generating sufficient quantities of a Montana coal-derived solvent VGO and vacuum bottoms, the liquefaction of predried Montana coal was conducted to generate distillate fuel referred to as middle distillate for upgrading to produce synthetic fuels.

Figure 3. P9600 spinning band distillation system.

For liquefaction processing of test coal, coal and vacuum bottoms ground to –100 mesh were mixed with VGO and catalyst and were transferred to the slurry tank. The overall process involved feeding slurry consisting of an approximate 1/1/1 mixture of dried coal (2 pounds), coal-derived solvent/VGO (2 pounds), vacuum bottoms (2 pounds), and 100-ppm catalyst per hour to the reactor. A constant pressure of 2500 psig was maintained through use of a pressure control valve and constant flow of hydrogen. The "bottom recycle VGO operation" utilized the same procedures as described above. The vacuum bottoms and liquid products were collected every 6 hours. The liquid product was distilled to generate water, naphtha, middle distillate and heavy oil (VGO).

- Naphtha (<300°F)
- Middle distillate (300–650°F)
- VGO (>650°F)

The vacuum bottoms and VGO generated every 6 hour using a distillation system (Figure 3) to produce VGO which was recycled until 5 gallons of middle of middle distillate was produced. The overall liquefaction process is shown in the flow diagram (Figure 4).

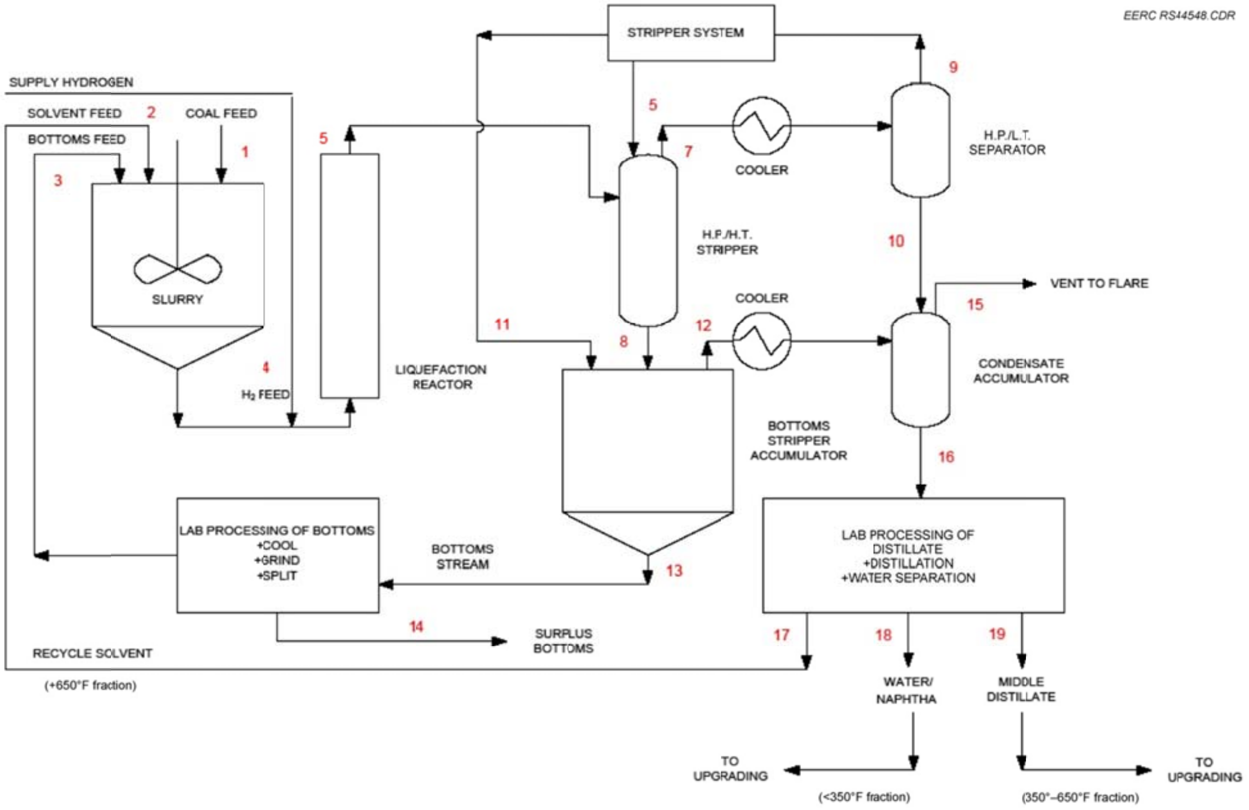

Figure 4. DCL process flow diagram (HP/LT stands for high pressure/low temperature).

The middle distillate and naphtha fractions were analyzed by specific gravity, elemental analysis, hydrocarbon type analysis, and boiling point distribution to determine the type of upgrading needed to make it suitable for preparing synthetic jet fuels (CBTL [coal–biomass-to-liquid]). The analytical details are discussed later in Results and Discussion.

Activity 1.4 – Upgrading of Middle Distillate

The analytical data show that hydroprocessing of the middle distillate is needed to remove heteroatoms, saturation of the aromatic rings, and moderate hydrocracking. Therefore, a 5-gallon middle distillate sample was sent to the Intertec PARC facility for upgrading. The catalytic hydrotreatment of the middle distillate (350°–650°F) was carried out at the Intertec PARC facility, located at the University of Pittsburgh in Pennsylvania.

The upgrading was carried out in two stages of hydroprocessing. In the Stage 1 hydrotreating step, coal distillate is passed through a tubular bed reactor packed with hydtrotreating catalyst to ensure removal of heteroatoms along with moderate hydrocracking to maximize the jet-fuel-range hydrocarbons. The upgraded product was further treated with a saturation catalyst to hydrogenate the aromatic and olefinic compounds and remove any residual heteroatoms.

Activity 2 – Preparation of CBTL Jet Fuel

Activity 2.1 – Preparation of Coal-Derived Blendstock

The upgraded middle distillate received from Intertec PARC was fractionally distilled to generate fraction distilling at 250°−475°F. This fraction was selected on the basis of simulated gas chromatographic distillation (GCD) to obtain a fuel with a boiling range closer to the petroleum-derived jet fuel and more likely to produce a JP-8-compliant fuel upon blending with biomass-derived fuel.

Activity 2.2 – Preparation of Biomass-Derived Blendstock

Hydrocarbons derived from biomass are needed for blending with coal-derived blendstock to meet the key properties of petroleum-derived aviation fuel. The soy-derived bio-oil supplied by Accelergy Corporation and the crambe-derived bio-oil produced at the EERC under a previous program were tested for blending with coal-derived fuel to produce JP-8-compliant fuel. Both of these oils were fractionally distilled to generate biomass-derived blendstocks with a similar boiling range as petroleum-derived jet fuel. The jet fuel blendstocks were analyzed by GCD, gas chromatography (GC)–mass spectroscopy (MS), and other relevant physical properties to determine the key properties of petroleum-derived jet fuels as discussed later in Results and Discussion.

Activity 2.3 – Preparation of Aromatic Blendstock

Aromatic hydrocarbons are needed to meet the desired lubricity of the aviation fuels. Although not an official specification, 8% aromatic hydrocarbons are recommended by AFRL as an unofficial guideline to ensure the optimal fit-for-purpose aviation fuel. An aromatic stream (A-150) was used to produce the aromatic blendstock for addition to the synthetic jet fuel (CBTL). The A-150 was distilled to remove BTX (benzene, toluene, xylene) and 2-ring aromatic hydrocarbons.

Activity 2.4 – Preparation of CBTL Jet Fuel

The blendstocks derived from coal and biomass were mixed together along with 10 vol% of an aromatic blendstock to produce synthetic jet fuels (CBTL). The ratio of the coal and biomass blendstocks was varied to produce several CBTL fuels. These fuels were tested by the following ASTM International (ASTM) standard techniques as follows:

- Distillation ([GC] or 15/5 TBP [true boiling point] – as appropriate)
- Specific gravity determination
- Elemental analysis (C, H, S, N, O)
- Total aromatic, naphthenes, and paraffin determinations
- Freeze point
- Flash point

RESULTS AND DISCUSSION

The current state of the art in the conversion of coal to liquid fuels is gasification, followed by syngas cleanup, CO and H_2 separation, and conversion to liquid fuels via Fischer–Tropsch (FT) technology at very high pressures. Extensive process equipment and operating labor are required to purify the syngas and condition it to the CO-to-H_2 ratio needed for the FT process to work.

Exxon Research Center extensively studied an alternative process using coal liquefaction in a continuous process unit to produce transportation fuels. An exhaustive pilot study did not produce fuels that had all of the desired properties. Similar coal liquefaction studies were conducted at the EERC using a simulated coal bottoms recycle operation that produced a JP-8 specification-compliant fuel. However, only a narrow distillate cut met the desired set of properties, and a large portion of the distillate was either too light or too heavy. One way to ensure a coal-based specification-compliant fuel that utilizes a large portion of the coal distillate product is to blend the coal distillate with an appropriate bio-based renewable-derived blendstock.

Since 1987, the EERC has been involved in the development of catalysts and processes for the conversion of coals and renewable and waste materials into liquid fuels. This work has generated numerous reports, presentations, publications, and provisional patents.

Military and commercial specification-compliant petroleum-derived aviation fuels consist of paraffinic/isoparaffinic, aromatic, and naphthenic hydrocarbons. In order to obtain a similar composition for coal- and renewable-derived synthetic fuels, a series of steps are needed (1–2). The hydrocarbons derived from plants (biomass) are primarily paraffins (3–4) and from coal are mainly aromatics and naphthenes (5–6). Therefore, it is hypothesized that a suitable combination of coal and plants or animal-derived material may be appropriate for producing key constituents of the aviation fuel. During preliminary EERC investigations, it has been shown that direct liquefaction of coal–biomass feedstocks produced liquids, which upon subsequent upgrading generated synthetic fuels similar to petroleum-derived aviation fuels (7). The bituminous coals, and especially Illinois No. 6 coal, indicated great potential in outperforming many other coals in terms of yield and distillate quality.

The current project utilized EERC's technology to produce JP-8 specification-compliant aviation fuel from coal and biomass. Since the coal-derived fuels are highly naphthenic, they need to be mixed with biomass-derived paraffinic fuel to meet the key property requirements of JP-8 and other jet fuels. The bio-oils derived from soy and crambe were selected for blending with coal liquid to produce synthetic jet fuel while reducing the carbon footprint of the overall process.

Activity 1 – Production of Middle Distillate from Montana Coal

The middle distillate generated from the liquefaction of coal was analyzed using GC, GC–MS, simulated GCD, and elemental analyses. The analysis of the middle distillate shows significant quantities of sulfur, nitrogen, and oxygen compounds and aromatics, especially 2–4-ring aromatic compounds. Also, the density of the product is ca. 1; that is significantly higher than allowed by JP-8 specifications. Therefore, catalytic hydrotreating and saturation are needed for this fuel to be used for producing aviation fuels. To bring these undesirable properties to an acceptable level, the middle distillate was sent to Intertec PARC for further hydroprocessing.

The upgraded coal-derived middle distillate received from Intertec PARC was analyzed by GC–MS and elemental analysis. The upgraded fuel was then evaluated based on the following:

- Distillation ([GC] or 15/5 TBP – as appropriate)
- Specific gravity determination
- Elemental analysis (C, H, S, N, O)
- Total aromatic, naphthenes, and paraffin determinations
- Freeze point
- Flash point

The results of the raw and upgraded coal liquids are described below (Tables 1 and 2 and Figure 5).

Preparation of Coal-Derived Blendstock

The results of coal-derived fuels produced via coal liquefaction and upgrading at Intertek PARC contain significant quantities of the materials with boiling points outside the range for the petroleum-derived jet fuels and, therefore, do not qualify as blendstock for the production of JP-8-compliant aviation fuel. These materials were removed by fractional distillation to generate a

Table 1. **Hydrocarbon Type Analysis of Raw and Hydroprocessed Montana Coal-Derived Coal liquids**

Composition wt% by GC–MS	Raw Middle Distillate	Upgraded Middle Distillate
n-Paraffins	3.29	4.50
i-Paraffins	3.76	5.90
Total Paraffins	6.65	10.40
1-R Naphthenes	3.8	7.97
2-R Naphthenes	0	32.34
3-R Naphthenes	0	46.29
4-R Naphthenes	0	0.82
Total Naphthenes	3.80	87.42
1-R Aromatics	36.41	0
2-R Aromatics	41.23	0
3-R Aromatics	11.90	0
4-R Aromatics	0.00	0
Total Aromatics	89.54	0
Oxygenates/Others	*	2.18
Total	100	100

* The raw coal liquids contain phenols, naphthols, ketones, benzo and dibenzo furans and some sulfur and nitrogen compounds.

Table 2. Distillation Data for Coal-Derived Fuels

Sample Identification	Raw Middle Distillate	Upgraded Middle Distillate
wt% Off at °F		
100	0	0
150	0	0
200	0.02	0.13
250	0.08	1.08
300	0.78	4.74
350	4.71	9.39
400	11.60	19.83
450	22.15	33.25
500	38.94	62.36
550	67.92	89.42
600	89.86	95.02
650	100	99.39
650+	0	0.61
wt% Off		
300°F–	0.78	4.74
400°F–	11.60	19.83
450°F–	22.15	33.25
650°F+	0	0.61

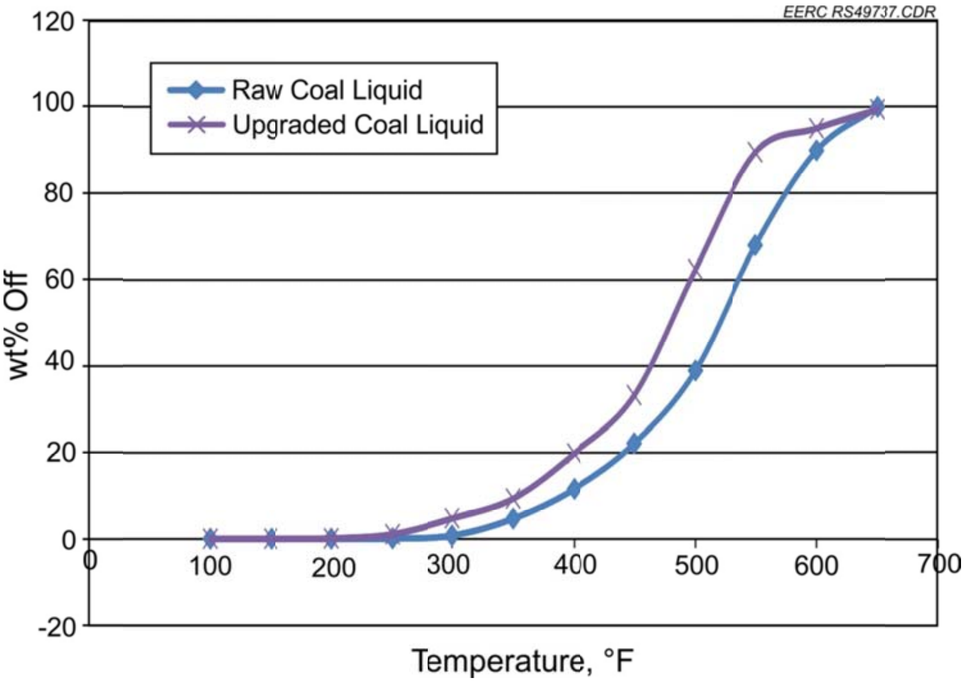

Figure 5. Distillation of the raw and upgraded middle distillates.

blendstock with a boiling range similar to petroleum-derived jet fuel. Fractional distillation produced the following cuts:

- Naphtha: <250°F
- Middle distillate: <250–475°F
- Heavy oil: >475°F

The middle distillate was fully characterized according to the follow ASTM standard:

- Distillation ([GC] or 15/5 TBP – as appropriate)
- Specific gravity determination
- Elemental analysis (C, H, S, N, O)
- Total aromatic, naphthenes, and paraffin determinations
- Freeze point
- Flash point

The physical properties of the coal-derived fuels such as density, flash point, energy contents, and freeze points are all outside the permissible range for the petroleum-derived fuels; therefore these fuels can, at best, be regarded as blendstocks and require additional blending with suitable fuels to bring these properties within the range in order to qualify for military and commercial use. This will not only reduce energy dependence but also add to energy security for the country.

Preparation of Biomass-Derived Blendstocks

Previous research at the EERC has demonstrated that the physical properties of jet-range fuels derived from plant and animal fat are appropriate for adding to coal-derived jet-range material to produce JP-8-compliant fuels. Therefore a bio-oil (HEFA) supplied by Accelergy Corporation and crambe-derived bio-oil produced at the EERC were evaluated as blendstocks for blending with coal-derived blendstocks to produce fuels that can meet the key requirements of aviation fuel.

Initial studies involved determining the suitability of bio-oil (HEFA) produced from catalytic processing of Soy or Soy-derived oil as a blendstock for mixing with coal-derived blendstock for produced JP-d compliant fuel. The HEFA was analyzed by GC, GC–MS and simulated-GCD to determine its composition and boiling point distribution. Based on the GCD, the HEFA was fractionally distilled to produce a product with boiling range similar to petroleum-derived jet fuel. Similar fraction was also generated from the Crambe-derived hydrocarbons. The complete characterization of HEFA and Crambe-derived blendstocks was carried out according to ASTM standards described as follows:

- Specific gravity
- Elemental analyses
- Freeze point
- Flash point
- Total aromatic, naphthenes and paraffins

The specific gravity of these blendstocks was determined in triplicate. The result shows the specific gravities of HEFA and crambe-derived blendstocks were 0.7557 and 0.7523, respectively, which do meet JP8 specifications on their own. The data also indicate that these products consist of straight chain and branched paraffins. The results for these two blendstocks are presented in Tables 3–5. The distillation profile of the product shows considerable similarity with the petroleum-derived jet fuel. The boiling profile is shown in Figure 6.

Preparation of Aromatic Blendstock

The aviation fuels need aromatic compounds to produce desired lubricity. A minimum 8 volume/vol% (v/v%) of aromatic compounds are recommended by AFRL for the optimal fit-for-purpose aviation fuels. In order to generate lubricity, a petroleum-derived aromatic liquid (A-150) consisting primarily of alkyl benzenes, naphthalene, and alkyl naphthalenes was tested for blending with coal- and bio-oil-derived blendstocks. Although alkyl benzenes enhance the lubricity of the aviation fuels, the excess of naphthalenes is not desired. In fact >3 vol% naphthane leads to disqualification of the fuel for civil or military use. Therefore, the aromatic liquid was fractionally distilled to remove benzene, xylenes, and naphthalenes to produce a fraction that can enhance the lubricity of the synthetic jet fuel. This fraction was analyzed to determine its composition and distillation profile. The analytical data for the blendstocks derived from coal, bio-oil, and A-150 are given in Tables 3 and 4 and Figure 6.

The bio-oil blendstock from crambe oil was previously used to produce SPK (synthetic paraffinic kerosene)-type fuel. This fuel met key properties of the SPK type of fuels currently in use for civil and military aviation purposes. This blendstock was kept as a backup option in case HEFA-derived blendstock failed to produce synthetic jet fuel (CBTL) upon blending with coal-derived fuel.

Table 3. Hydrocarbon Type of Blendstocks

Composition wt% by MS	Coal – Jet	HEFA – Jet	Crambe – Jet	Aromatic – Jet
n-Paraffins	4.50	16.21	12.89	0
i-Paraffins	5.90	83.14	85.82	0
Total Paraffins	10.40	99.35	98.71	0
1-R Naphthenes	7.97	0.35	1.29	0
2-R Naphthenes	32.34	0	0	3.48
3-R Naphthenes	46.29	0	0	0
4-R Naphthenes	0.82	0	0	0
Total Naphthenes	87.42	0.35	1.29	3.48
1-R Aromatics	0	0	0	88.85
2-R Aromatics	0	0	0	7.67
3-R Aromatics	0	0	0	0
4-R Aromatics	0	0	0	0
Total Aromatics	0	0	0	96.52
Oxygenates	2.18	0	0	0
Total	100	100	100	100

Table 4. Distillation Data for the Blendstocks

Sample Identification	Coal – Jet	HEFA – Jet	Crambe – Jet	Aromatic – Jet
wt% Off at °F				0
100	0	0	0	0
150	0	0	0	0
200	0.13	0.42	0.23	0
250	1.08	1.58	2.22	0
300	4.74	12.88	8.01	0
350	9.39	26.35	20.59	5.38
400	19.83	38.73	39.02	49.16
450	33.25	54.11	62.68	97.22
500	62.36	64.59	88.82	100
550	89.42	86.25	92.80	0
600	95.02	100	100	0
650	99.39	100	0	0
650+	0.61	0	0	0
wt% Off				
300°F–	4.74	12.88	8.01	0
400°F–	19.83	38.73	39.02	49.16
450°F–	33.25	54.11	62.68	97.22
650°F+	0.61	0	0	0

Table 5. Blending Data for CB Jet Fuels

Blendstock	Density, g/cm^3 at 15°C	Flash Point, °C	Freeze Point, °C
HJ[1]	0.751	37	–73.4
MJ[2]	0.843	50	–68.1
AJ	0.899	62	–9.2
MJ (45%)+ HJ(45%) + AJ[3](10%)	0.803	44.8	–47.8
MJ (50%) + HJ(50%) + AJ(0%)	0.798	44	–49.2
MJ (42.5%) + HJ(42.5%) + AJ(15%)	0.805	45	–46
MJ (43.75%) + HJ(43.75%) + AJ(12.5%)	0.804	44	–49.1
MJ (33.34%) + HJ (55.66%) + AJ(11.12%)	0.799	43.2	–49
MJ (55.56%) + HJ(33.34%) + AJ(11.12%)	0.819	45.5	–46.5
MJ (44.4) + CRJ[4](44.4) + AJ(11.2)	0.804	49	––71.9
MJ (44.4 + CJ[5](44.4) + AJ(11.2)	0.818	47	–72.7
MJ (44.4 + CJ(22.2) + HJ(22.2) +AJ(11.2)	0.777	46	–46.9

[1] HJ (250° – 500°F) = HEFA jet blendstock.

[2] MJ (250° – 475°F) = Montana coal jet blendstock.

[3] AJ = Aromatic jet blendstock.

[4] CRJ (250° – 500°F) = crambe oil jet blendstock.

[5] CJ (250° – 500°F) = canola oil jet blendstock.

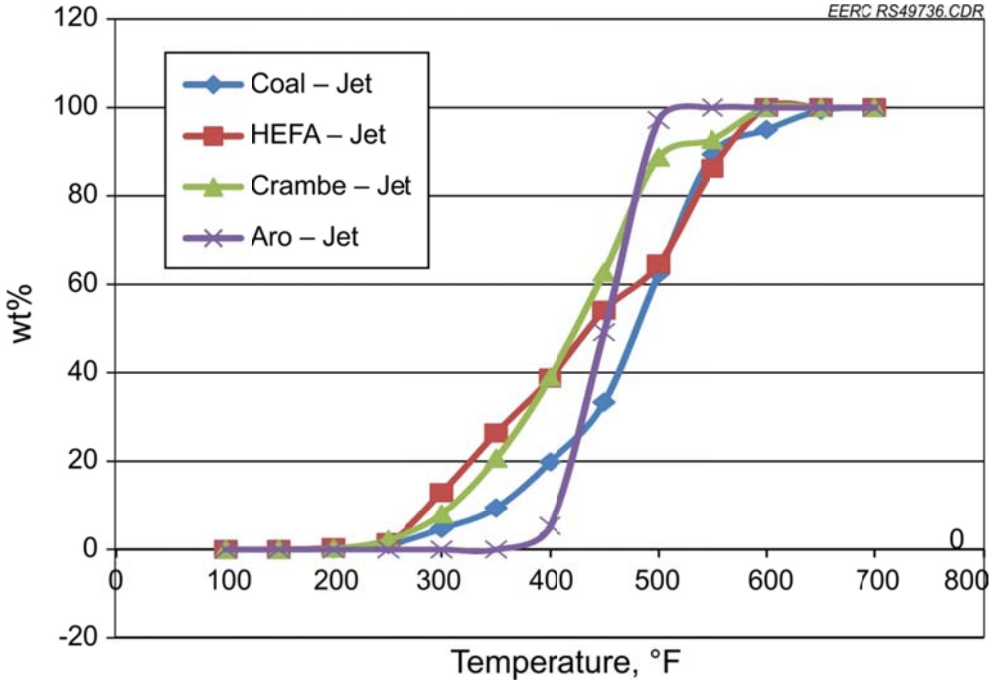

Figure 6. Distillation profile of blendstocks.

Activity 2 – Preparation of CBTL Jet Fuel

The analytical data for the coal- and bio-oil-derived blendstocks described above indicate that they, on their own, are unable to meet the key properties of jet fuels. A careful scrutiny of the analytical data suggested that combinations of these blendstocks may be able to generate composite fuels that can comply with U.S. military JP-8 specification (MIL-T-83133 Specifications). Several fuel samples were produced by mixing coal- and bio-oil blendstocks with a petroleum-derived aromatic blendstock. The addition of aromatic blendstock is necessary to impart lubricity to the jet fuel. The jet fractions obtained from the fractional distillations were fully characterized to determine their suitability for preparing coal-bio jet fuels:

- The specific gravity of the jet fractions obtained from the distillations of the upgraded middle distillate from Montana coal, HEFA 545°F – a bio-oil, and catalytic hydroprocessing of crambe oil was determined in triplicate. The result shows that the specific gravity of coal – jet is higher and bio – jets are lower than the density of JP-8. Also the freeze point, flash points, and hydrocarbon contents cannot be met by any of these blendstocks. This means that these products can only be used as a blendstocks or must be further hydrotreated to bring the density in line with JP-8 specifications.

- The simulated GC–MS analyses were performed to determine the composition of the blendstocks. The results of the simulated GC–MS distillations also suggest that none of these blendstocks contains specific compounds needed to meet the JP-8 specifications.

Initial blending tests were performed using blendstocks derived from coal (CJ), HEFA (HJ), and A-150 (AJ). Several fuel samples were prepared by blending 10 vol% of aromatic blendstock (AJ) with a mixture of coal-derived blendstock (coal – jet) and bio-oil derived blendstock (HEFA – jet). The ratio of the coal – jet and HEFA – jet were varied to optimize the ratios of the blendstocks that will meet the key properties of the petroleum-derived jet fuel. The composite fuels were analyzed to determine if they can meet the key properties for the JP-8 fuels. The composite fuels were tested according to the ASTM standards described as follows:

- Distillation ([GC] or 15/5 TBP – as appropriate)
- Specific gravity determination (API gravity)
- Elemental analysis (C, H, S, N, O)
- Hydrocarbon analysis (total aromatic, naphthenes, and paraffin determinations)
- Freeze point
- Flash point

The results of the specification testing show that most of the properties except freeze point not only meet but exceed the JP-8 specifications. All attempts to produce JP-8-compliant aviation fuel from coal- and HEFA-derived blendstocks were unsuccessful. Past research at the EERC has successfully prepared several JP-8-compliant aviation fuels from blendstocks derived from crop oils and coal. The crambe oil-derived blendstock prepared under a previous DOE-funded program was used to prepare synthetic fuel (CBTL). The fuel sample prepared by blending equal volumes of coal- and crambe-derived blendstocks with 11.11 vol% aromatic jet blendstock not only met but exceeded key properties of JP-8 fuel. The results of the blending studies are given in Table 5.

The successful coal- and crambe-derived blendstock along with 11.12 vol% was evaluated based on the following ASTM standards:

- Thermal stability (quartz crystal microbalance [QCM])
- Freeze point (phase technology automatic freeze point tester, ASTM D5972)
- Distillation (ASTM D2887) 10 mL
- Hydrocarbon range (GC–MS) (ASTM D6379 and D2425)
- Heat of combustion (ASTM D4809)
- Density, American Petroleum Institute gravity (ASTM D4052)
- Flash point (ASTM D93)
- Naphthalenes % (ASTM D1840)
- Aromatics and olefins % (ASTM D1319)
- Mercaptan sulfur % (ASTM D3227)
- Total sulfur (ASTM D4294)
- Hydrogen content (ASTM D3343)

The results of the ASTM testing are shown in Tables 6 and 7, and the distillation profile shown in Figure 7.

Table 6. Hydrocarbon Type Analysis of CB Jet

Composition, wt% by MS	CB Jet Fuel
n-Paraffins	8.2
i-Paraffins	40.0
Total Paraffins	48.2
1-R Naphthenes	13.1
2-R Naphthenes	19.9
3-R Naphthenes	7.9
4-R Naphthenes	0
Total Naphthenes	40.9
1-R Aromatics	10.3
2-R Aromatics	0.6
3-R Aromatics	0
4-R Aromatics	0
Total Aromatics	10.9
Oxygenates	0
Total	100

Table 7. Distillation Data for CB Jet

Sample Identification	CB Jet Fuel
wt% Off at °F	
100	0
150	0
200	0.03
250	1.66
300	6.65
350	17.66
400	42.30
450	70.83
500	91.52
550	100
600	
650	
650+	
wt% Off	
300°F–	6.65
400°F–	42.30
450°F–	70.83
650°F+	0

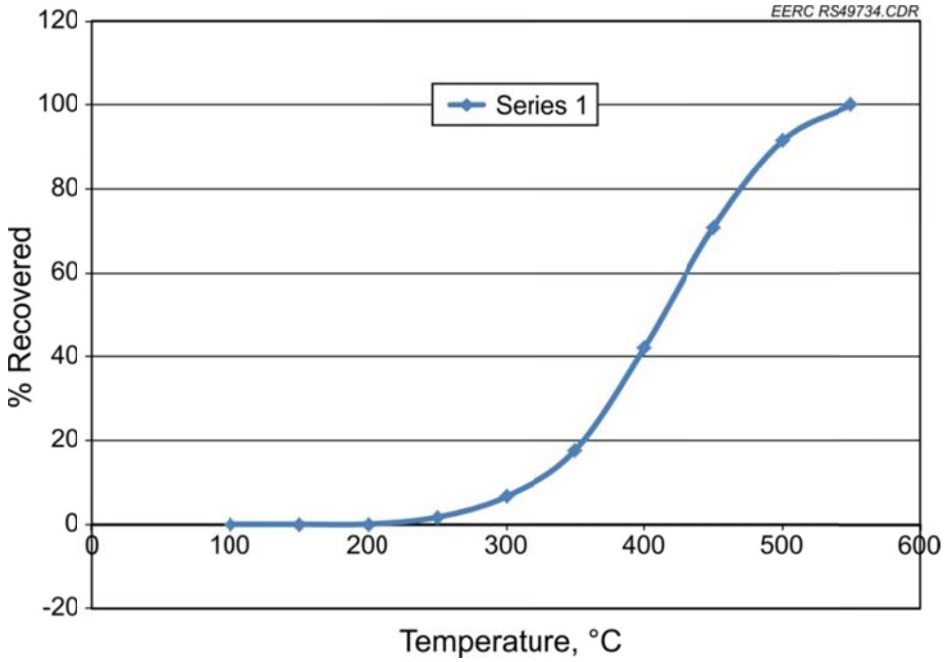

Figure 7. Distillation profile of the CB jet fuel.

The CB jet sample (CBTL) prepared by blending 44.4 vol% each of the MJ (Montana jet) and CJ (crambe jet) blendstocks with 11.2 vol% of AJ (aromatic jet) blendstock was found to meet JP-8 specifications (Table 8). This sample was submitted to Air Force Research Laboratory (AFRL) for further testing and evaluations. The aromatic blendstock was added to improve the lubricity of the CB jet fuel.

Table 8. EERC CB Jet vs. JP-8 Specifications

Grade: Specifications:	JP-8 MIL-DTL-83133F 11-Apr-2008	EERC CB Jet
Color, Saybolt	No limit	Clear, colorless
Aromatics, vol%	25.0 max	11.3
Sulfur, wppm	3000 max	0
Nitrogen, ppm	–	0
Density, g/cm3 at 15°C	0.775–0.840	0.804
Flash Point, °C	38 min	49
Freeze Point, °C	−47 max	–71.9
Naphthalene, vol%	3.0 max	0.53
Hydrogen Content, wt%	13.4 min	14.07

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