RENEWABLE OIL REFINERY DEVELOPMENT FOR COMMERCIALIZATION

Final Report

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RENEWABLE OIL REFINERY DEVELOPMENT FOR COMMERCIALIZATION

PROJECT BACKGROUND

In 2008, the United States consumed nearly 20 million barrels a day of petroleum hydrocarbon products, predominantly in the form of liquid fuels like gasoline, aviation fuel, and diesel fuel. Significant interest has developed around alternatives to petroleum-based products because of concern about petroleum sustainability and its impact on climate change and national security. Increasing worldwide demand has raised concerns about the availability and rising price of crude oil in the next few decades. Concern about the climatic impact of anthropogenic CO_2 has spurred interest in renewable liquid fuels with lower life cycle carbon emissions than fossil fuels. Lastly, increasing interest in reducing our reliance on foreign countries for greater than 60% of our petroleum has resulted in increased U.S. government funding for development of domestic alternatives to petroleum fuels.

The University of North Dakota Energy & Environmental Research Center (EERC), under contract to the Defense Advanced Research Projects Agency, developed a technology pathway for converting renewable triacylglycerides such as crop oil, algal oil, animal fats, and waste grease to jet fuel and other liquid fuels. These alternative fuels have chemical and physical properties identical to their petroleum-derived counterparts. Unique from traditional trans-esterification-based biodiesel technologies, the EERC's catalytic hydrodeoxygenation and isomerization (CHI) process yields an oxygen-free hydrocarbon mixture which, when distilled, produces renewable versions of naphtha, jet fuel, and diesel that can be fully integrated with current U.S. petroleum fuel infrastructure. In addition to being renewable and fungible, renewable oil-based fuel produced using the CHI technology contains very low levels of sulfur. Sulfur is increasingly being eliminated from petroleum-derived fuels in order to meet strict U.S. Environmental Protection Agency (EPA) limits. The sub-ppm levels of sulfur present in CHI-based fuels provide a significant advantage to petroleum refiners looking for alternatives to reducing sulfur content in fuel.

PROJECT DESCRIPTION

Research activities at the EERC have resulted in the production of hundreds of gallons of hydrocarbon samples from a variety of waste fats and oils and crop oils, including soybean, canola, coconut, cuphea, camelina, crambe, and corn. The primary end product generated via CHI from all of these feedstocks has been aviation fuel (JP-8) that complies with Appendix A of the military specification MIL-DTL-83133F. However, oxygen-free hydrocarbon produced from the CHI technology can readily be converted into any of several petrochemical intermediates used to produce surfactants or plastics in addition to gasoline, jet fuel, or diesel. A general block flow diagram outlining the CHI process is presented in Figure 1. The process's three major steps are 1) hydrodeoxygenation, 2) isomerization, and 3) distillation. The hydrodeoxygenation step feeds crop oil and hydrogen to a hot, pressurized reactor filled with catalyst. Oxygen is removed from the crop oil in this step resulting in an oxygen-free hydrocarbon product and produced carbon monoxide, carbon dioxide, and water. The hydrocarbon product from Step 1 contains

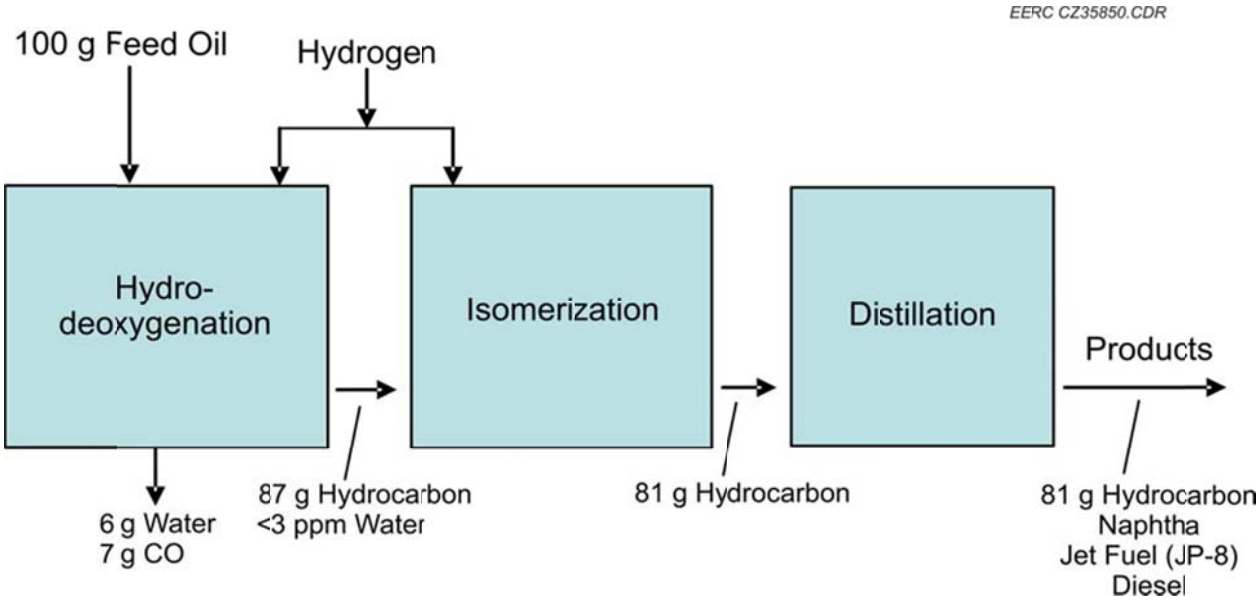

Figure 1. CHI process block flow.

predominantly normal alkanes. The second step, isomerization, functions to improve the fuel's cold-flow properties through isomerization and molecular weight reduction. Isomerization refers to the molecular rearrangement of normal alkanes to form branched isoalkanes. Branched alkanes have lower freezing points than normal alkanes. Cracking reactions also occur in the isomerization reactor. Cracking reactions broaden the chemical distribution of the fuel by breaking long-chain hydrocarbons into two or more shorter-chain hydrocarbons. The third step in the CHI process is distillation. Distillation separates the fuel components by boiling point. The end products leaving the distillation columns are naphtha, jet fuel, and diesel fuel.

In order to advance the technology and enable large-scale commercial production of renewable fuel in North Dakota, a pilot plant demonstration will be required. The goal of this project was to further optimize the CHI technology and to complete a pilot-scale renewable oil refinery design. The primary tasks conducted included 1) tailoring the CHI renewable oil refining technology for North Dakota feedstocks, 2) evaluating CHI economic viability, and 3) completing a renewable oil refinery pilot plant design.

Using existing EERC equipment and facilities, research was conducted to improve conversion and yield of hydrocarbon fuels from North Dakota feedstocks such as canola and crambe. Additionally, the EERC worked closely with Tesoro Mandan to design a process with the capability of being integrated into a petroleum refinery, using conventional processing conditions and strategies.

Each research task supported the process design package. In Task 1, experiments were conducted with North Dakota-grown feedstocks to assess the possibility of operating with a partially refined crop oil feedstock. In Task 2, a Microsoft Excel-based economic model was developed to calculate yearly cash flows as a function of user-defined inputs. Task 3 included hydrodeoxygenation (HDO) and isomerization (ISOM) reactor scale-up and balance-of-plant

design. Together, these three tasks ensure that the CHI pilot plant will produce specification-compliant fuels from North Dakota feedstocks, will have predictable plant economics, and will operate similarly to laboratory-scale equipment. The process design package delivered by WorleyParsons provides process flow diagrams, an equipment list, a total installed cost estimate, and other information required for a contractor to bid on construction of the pilot plant. This information is included in a separate report being submitted by the EERC to NDIC.

Task 1 – Technology Tailoring for North Dakota Feedstocks

CHI Process Summary

Crop oils differ from one another in the type and amount of triglycerides that they contain. The term triglyceride refers to the molecular structure of vegetable oils and animal fats. Vegetable oils differ from each other because of differences in the carbon number of their inherent triglycerides and also because of the degree of carbon–carbon bond saturation. A triglyceride with all of its carbon–carbon bonds saturated is referred to as a saturated fat. The carbon number and degree of carbon–carbon bond saturation in a vegetable oil feedstock affect reactor performance and composition of HDO product. A vegetable oil with a large percentage of unsaturated carbon–carbon bonds will require a higher hydrogen treat rate and will produce more heat inside of the reactor. Additionally, the carbon number of the vegetable oil feedstock is directly related to the carbon number of the hydrocarbon product. In other words, a vegetable oil feedstock with a high carbon number will produce an HDO product with a high carbon number, and a vegetable oil feedstock with a low carbon number will produce an HDO product with a low carbon number. Researchers recognized this fact and hypothesized that vegetable oils with a higher carbon number would be better suited for producing fuels with higher carbon numbers, for example diesel fuel.

A stepwise illustration of the chemical changes that occur during the CHI process is shown in Figures 2 through 4. Canola oil contains C16 and C18 fatty acids, as shown in Figure 2. During the HDO step, oxygen is removed. If oxygen is removed via reduction, the resulting hydrocarbon has the same number of carbons as the parent fatty acid. If oxygen is removed via decarboxylation or decarbonylation, the resulting hydrocarbon has one carbon less than the parent fatty acid. The HDO product from canola oil contains pentadecane (C15), hexadecane (C16), heptadecane (C17), and octadecane (C18), as shown in the gas chromatograph (GC) chromatogram labeled Figure 3. The HDO product is then isomerized to improve cold-flow properties through isomerization and cracking reactions. The final isomerized product is shown in Figure 4.

Feedstock Opportunities

A comparison of the fatty acid characteristics including carbon chain composition, distribution, and saturation levels for several oils is summarized in Table 1 and illustrates the range of oil chemistry that exists in renewable oils. Canola oil, soy oil, and corn oil all contain primarily 18-carbon fatty acids. When deoxygenated, these compounds produce straight-chain hydrocarbons that fall in the lower middle of a typical diesel fuel carbon distribution, which ranges from C10 to C22. Canola oil, soybean oil, and corn oil differ primarily in the extent of

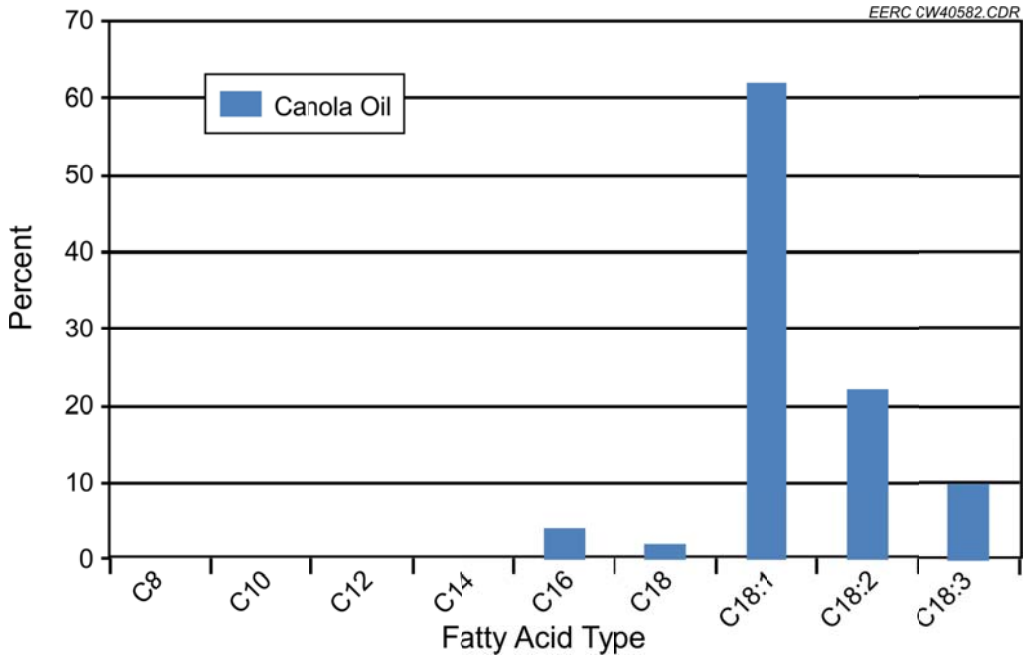

Figure 2. Fatty acid composition of canola oil.

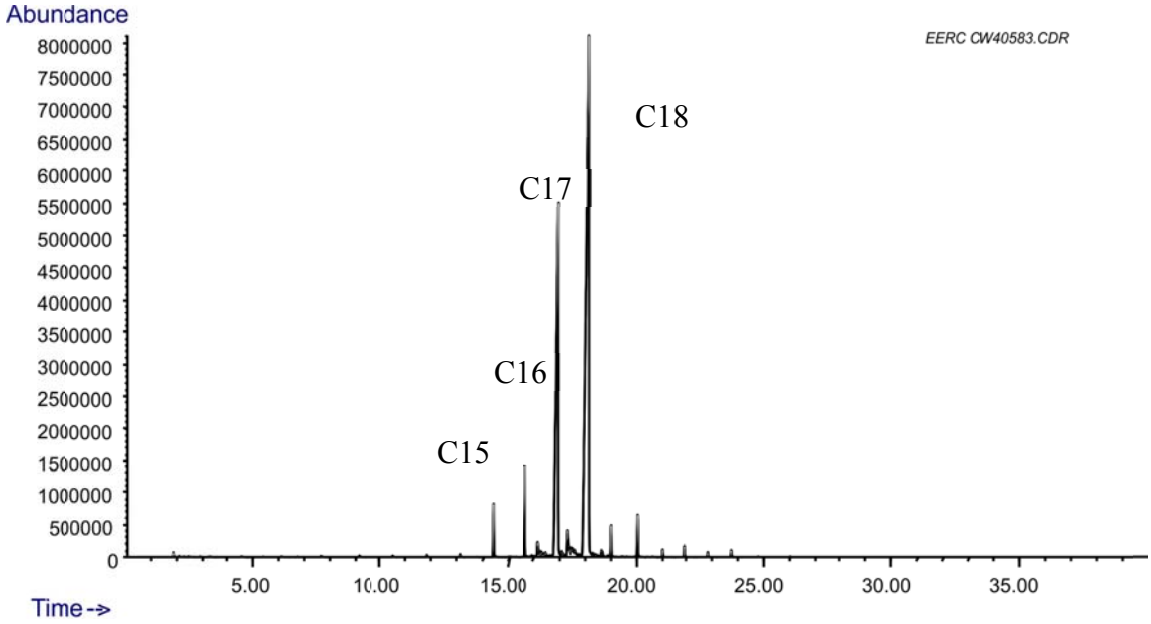

Figure 3. Hydrodeoxygenated canola oil.

unsaturated bonds. Camelina and crambe oil are unique among many crop oils because of their longer-chain (20- and 22-carbon) fatty acids. Since processing these oils into oxygen-free fuel typically results in molecule chain shortening and a broader distribution of carbon chain length, oils from camelina and crambe have the potential to produce more diesel range fuel per unit of vegetable oil feed compared to canola and soy which are better suited for jet fuel production.

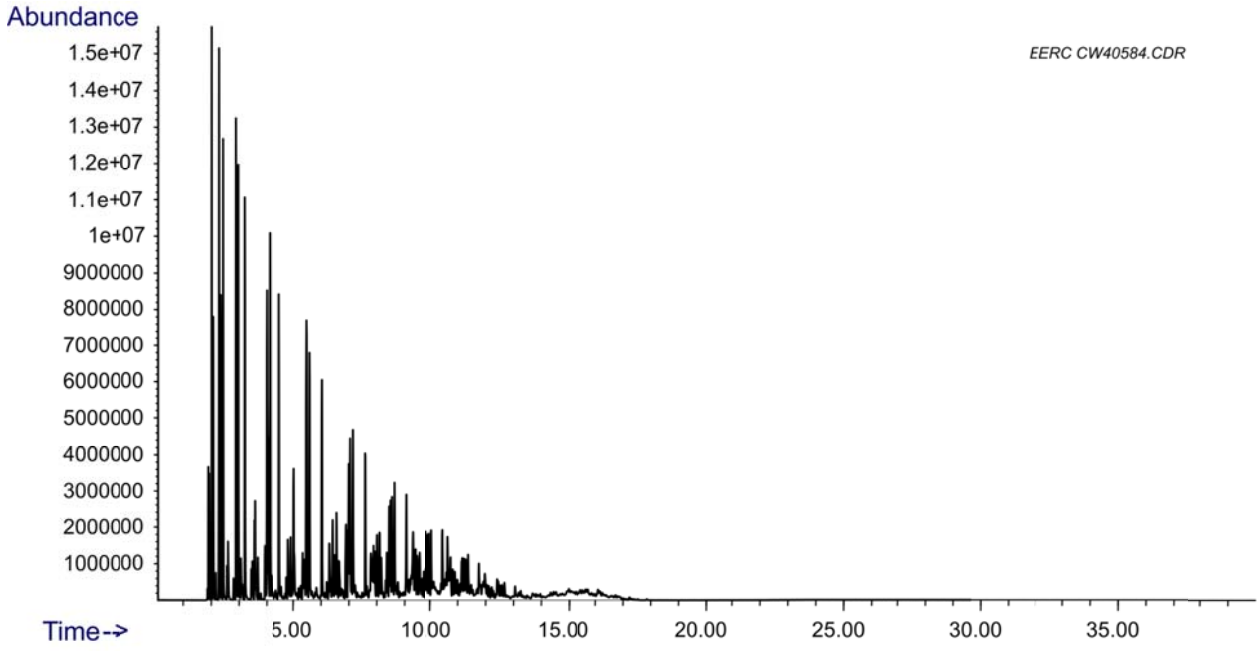

Figure 4. Isomerized canola HDO product.

This project focused on two vegetable oils from Table 1: crambe and canola oil. These two vegetable oils were selected because they are both North Dakota-grown crops. Canola is a widely planted crop in North Dakota. According to the U.S. Department of Agriculture (USDA), 1,270,000 acres of canola were planted in North Dakota in 2010.[1] North Dakota is among the leading states for canola production.[2]

North Dakota farmers do not typically plant crambe today; however, it was grown extensively in the 1990s as an industrial oil for the European Union. Crambe was studied within this project because of its prior success in North Dakota as a cool-season crop, being well adapted to the environment, and the properties of its oil which make it a good candidate for greater diesel fuel production as compared to canola.

Figure 5 shows the fatty acid composition of crambe oil and canola oil. Crambe oil has a high concentration, 56%, of erucic acid denoted as C22:1 (C22:1 denotes a 22-carbon molecule possessing one unsaturated bond), and canola oil has a high concentration of oleic acid denoted as C18:1 fatty acid. Jet fuel contains a blend of hydrocarbons concentrated around C12 and ranges in carbon number from C8 to C16, as shown in Figure 6. Diesel fuel contains a blend of hydrocarbons concentrated around C18 and ranges in carbon number from C10 to C26, as shown in Figure 7.

[1] 2010 State Agriculture Overview – North Dakota. www.nass.usda.gov/Statistics_by_State/Ag_Overview /AgOverview_ND.pdf (accessed 2011)
[2] North Dakota Economy – Crops. www.netstate.com/economy/nd_economy.htm (accessed 2011).

Table 1. Renewable Oil Feedstock Fatty Acid Composition

Feedstock, %	C14	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Eicosanoic C20:1	Behenic C22:0	Erucic C22:1	C24:0	C24:1	Source
Beef Tallow	3	24	19	43	3	1						www.scientificpsychic.com /fitness/fattyacids1.html
Camelina		5	3	19	16	38	12		3			www.cyberlipid.org/glycer/ glyc0064.htm#top
Canola		4	2	62	22	10						www.scientificpsychic.com /fitness/fattyacids1.html
Corn		11	2	28	58	1						www.scientificpsychic.com /fitness/fattyacids1.html
Crambe		2	1	17	9	5	3	2	56	1	2	Industrial Crops and Products 7 (1998) 231–238
Waste Oil		31	7	40	19		1		1			
Soy		11	4	24	54	7						www.scientificpsychic.com /fitness/fattyacids1.html

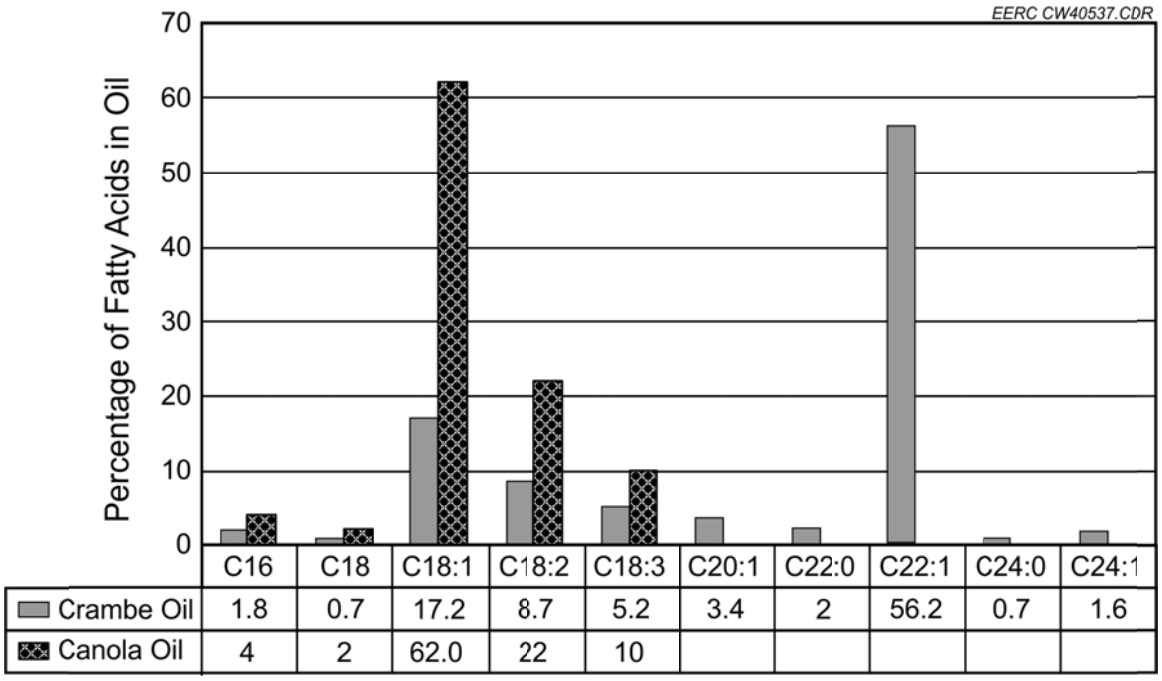

Figure 5. Fatty acid profile of crambe and canola oil.

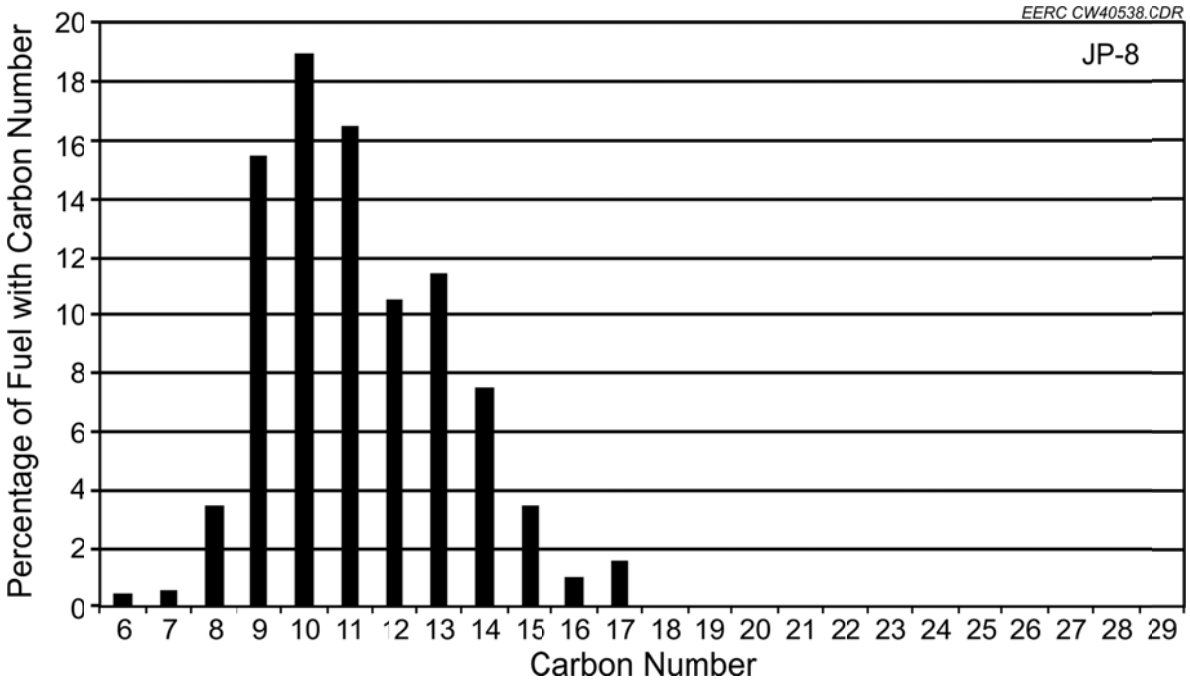

Figure 6. Hydrocarbon distribution of JP-8 jet fuel.

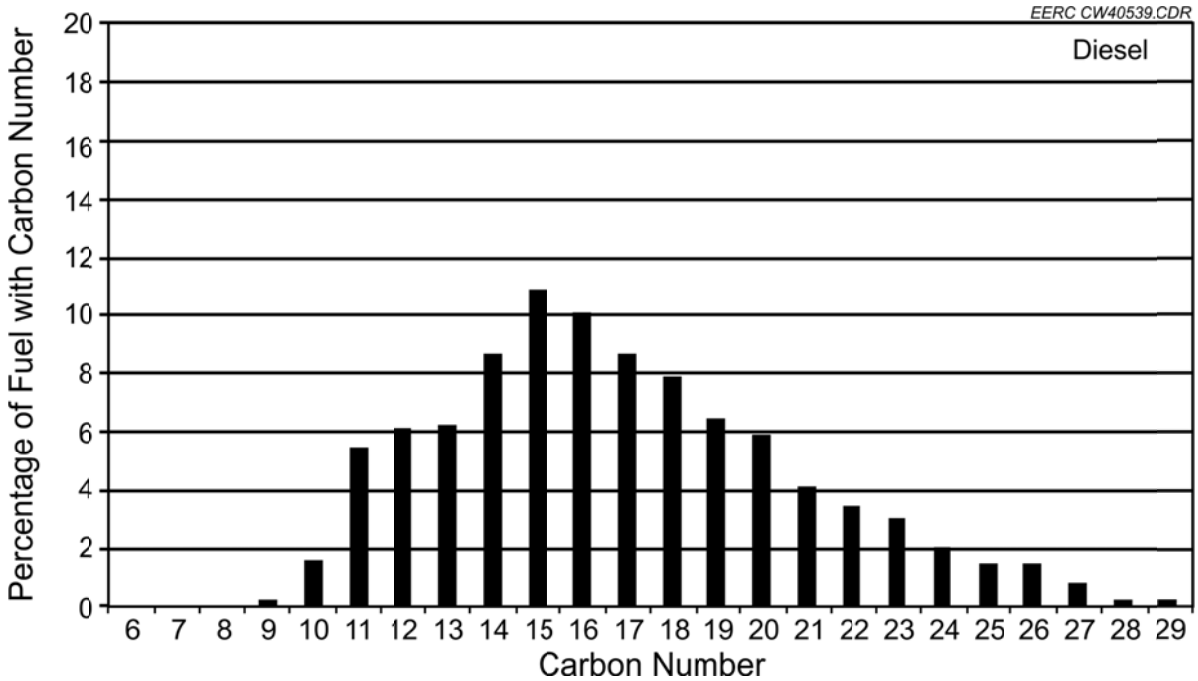

Figure 7. Hydrocarbon distribution of diesel fuel.

Evaluation of Crambe Seed Oil Extraction and Processing

Since crambe oil is not commercially available, the EERC contacted North Dakota State University Carrington Research Extension Office (NDSU CREC), which graciously provided oil seed from its 2009 test plots. These oil seeds were processed by USDA to extract and refine the oil used in the EERC's subsequent process optimization and fuel sample production. In order to gain additional information about the quality of oil achieved during the crop oil-refining process, the EERC worked with USDA to collect oil samples and data on oil characteristics after each step of the process. A more detailed description of the refining process is included in USDA's summary report located in Appendix A. The primary objective of this effort was to assess the extent of oil preprocessing required to remove contaminants from the crop oil. For typical vegetable oil-refining applications, oils are treated by three processes, including degumming, bleaching, and deodorizing. This investigation indicates that degumming would likely be sufficient to achieve the feedstock quality required for commercial-scale fuel production.

Oil seed and oil properties including oil content, free fatty acid content, moisture, and color were analyzed at the USDA facility at the time of processing. Additional analyses of the crambe oil, including CHN, sulfur, and oil density, were obtained from an independent analytical laboratory and are included in Table 2. The data suggest that the degumming process removed nearly all of the phosphorus and small amounts of metals or other constituents present in the crude oil. Carbon, hydrogen, oxygen, and nitrogen content, along with most of the other parameters, remained fairly constant across the various stages of refining. Sulfur was the only constituent that was not entirely removed in the degumming process. Instead, sulfur content decreased gradually throughout the refining process. The initial sulfur concentration in the crude

Table 2. Analyses of Crude, Degummed, Bleached, and Deodorized Crambe Oils

Parameter	Crude	Degummed	Bleached	Deodorized[a]	Deodorized[b]
Free Fatty Acid, % (as oleic)	0.39	0.49	0.38	0.20	0.19
Peroxide, meq/kg	0.03	0.02	0.00	0.00	0.00
Color: Gardner (10 mm)	11.0	10.9	3.1	3.6	4.1
L* (0=black, 100=white)	75.99	74.63	92.95	90.68	89.41
A* (-) green, (+) red	13.42	11.14	−2.83	−1.85	−1.47
B* (-) blue, (+) yellow	124.87	122.70	15.72	19.48	23.72
Density (ASTM D4052)	0.9117	0.9111	0.9108	NA[c]	0.9112
Water Content, ppm	447	296	736	NA	155
Total Chloride, ppm	<1	<1	<1	NA	<1
Carbon, wt%	78.62	78.57	78.64	NA	78.74
Hydrogen, wt%	12.13	12.16	12.24	NA	12.21
Nitrogen, wt%	<0.75	<0.75	<0.75	NA	<0.75
Oxygen, wt% by diff.	8.50	8.52	8.37	NA	8.30
Sulfur, ppm	24.7	17.4	10.2	NA	5.86
Aluminum, ppm	<1	NA	NA	NA	<1
Arsenic, ppm	<1	NA	NA	NA	<1
Barium, ppm	<1	NA	NA	NA	<1
Beryllium, ppm	<1	NA	NA	NA	<1
Bismuth, ppm	<1	NA	NA	NA	<1
Boron, ppm	<1	NA	NA	NA	<1
Cadmium, ppm	<1	NA	NA	NA	<1
Calcium, ppm	43	0.6	<0.1	NA	1
Chromium, ppm	<1	NA	NA	NA	<1
Cobalt, ppm	<1	NA	NA	NA	<1
Copper, ppm	<1	0.4	<0.1	NA	<1
Iron, ppm	1	0.2	<0.1	NA	1
Lead, ppm	<1	NA	NA	NA	<1
Magnesium, ppm	<1	0.4	<0.1	NA	<1
Manganese, ppm	30	NA	NA	NA	<1
Mercury, ppm	<1	NA	NA	NA	<1
Molybdenum, ppm	<1	NA	NA	NA	<1
Nickel, ppm	<1	NA	NA	NA	<1
Phosphorus, ppm	78	1.2	<0.1	NA	1
Potassium, ppm	9	NA	NA	NA	<1
Silicon, ppm	<1	NA	NA	NA	<1
Silver, ppm	1	NA	NA	NA	<1
Sodium, ppm	3	0.2	<0.1	NA	<1
Tin, ppm	<1	NA	NA	NA	<1
Antimony, ppm	<1	NA	NA	NA	<1
Titanium, ppm	<1	NA	NA	NA	<1
Vanadium, ppm	<1	NA	NA	NA	<1
Zinc, ppm	<1	NA	NA	NA	<1
Zirconium, ppm	<1	NA	NA	NA	<1
Strontium, ppm	<1	NA	NA	NA	<1
Platinum, ppm	<1	NA	NA	NA	<1
Gallium, ppm	<1	NA	NA	NA	<1
Rhodium, ppm	<1	NA	NA	NA	<1

[a] 100-gallon deodorizer.
[b] 1.5-gallon deodorizer.
[c] Not analyzed.

oil was 25 ppm and was reduced incrementally to 17, 10, and 6 ppm in the degumming, bleaching, and deodorizing processes, respectively. The results from the two different batches of deodorized oil indicate that the temperature achieved in the larger unit, although not at the maximum desired temperature, was still sufficient to complete the deodorizing process. From a fuel-upgrading perspective, the degumming process appears to be the only necessary step in achieving a feedstock oil that is suitable for catalytic conversion to hydrocarbon fuels.

After receiving the refined crambe oil from USDA, approximately 55 gallons of fully refined crambe seed oil was passed through the EERC's catalytic process to convert the triglyceride-rich oil to HDO hydrocarbon components, and the product was analyzed using a GC/mass spectrometer (MS). The crambe oil feedstock produced a hydrocarbon with chain lengths ranging from C5 (pentane) to C24 (tetracosane), with an abundance of the material in the C17 (heptadecane) to the C22 (docosane) range. Figure 8 illustrates the range of hydrocarbons produced from the crambe feedstock, containing two peak hydrocarbon concentrations in the C18 (octadecane) and C22 range. By comparison, a typical HDO produced from canola oil feedstock, as shown in Figure 9, comprises mainly C17 (heptadecane) and 18 (octadecane) hydrocarbons. The hydrocarbon product derived from crambe oil feedstock exhibits properties consistent with other hydrocarbon products that have been successfully processed to naphtha- (gasoline), jet-, and diesel-range fuels. Although crambe oil could be utilized to derive any of these hydrocarbon products, it may be preferred for the production of diesel-range hydrocarbons because of its natural abundance of longer-carbon-chain-length hydrocarbons.

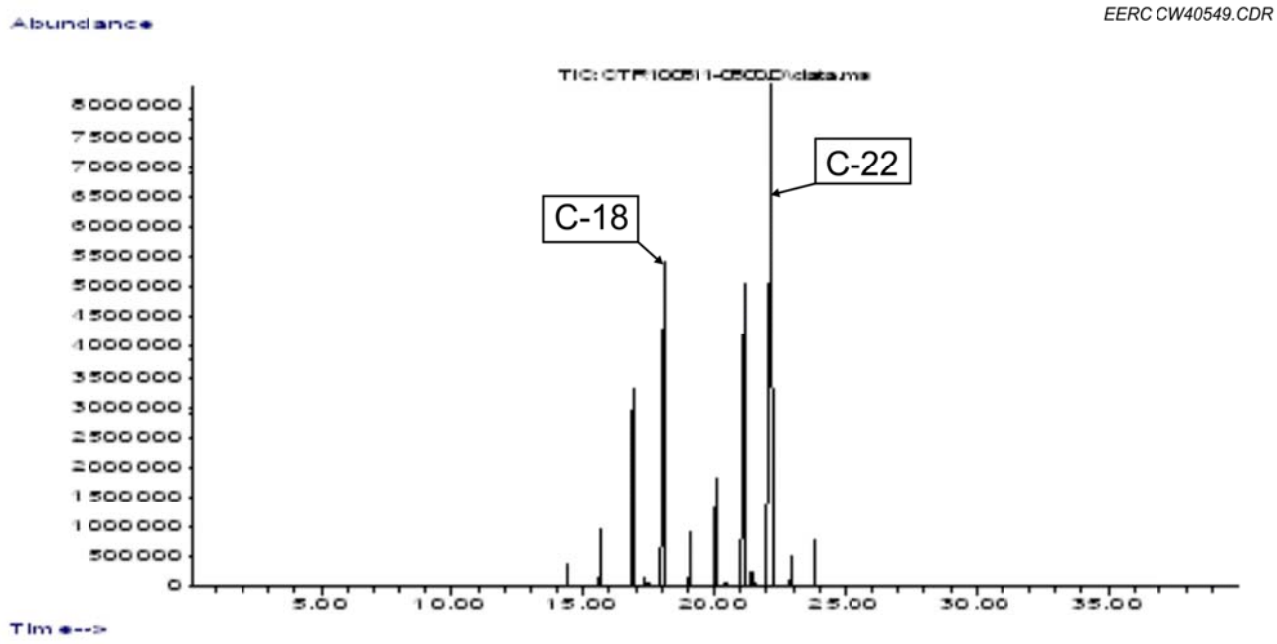

Figure 8. GC illustrating hydrocarbon distribution of crambe-derived product.

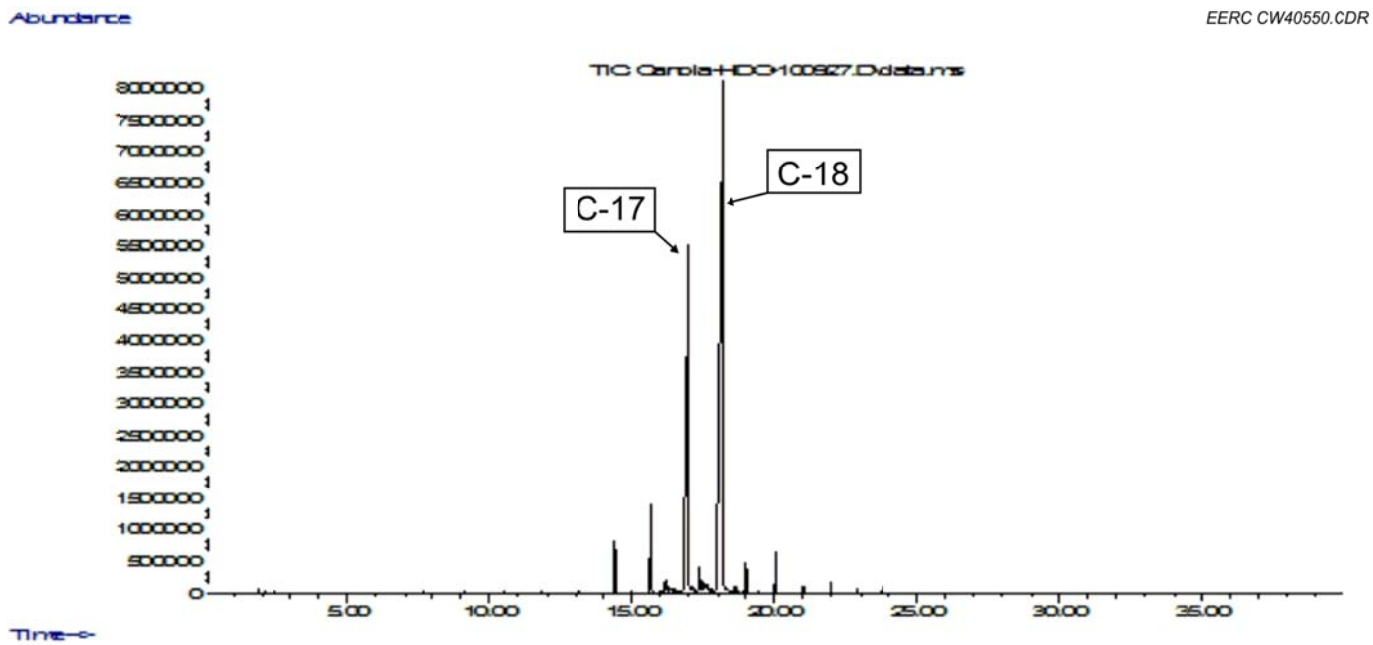

Figure 9. GC illustrating hydrocarbon distribution of canola-derived product.

Fuel Production from North Dakota Crops

Two jet fuel and two diesel fuel samples were produced from canola- and crambe-derived seed oil utilizing optimized conditions developed during the design effort. Both jet fuel samples, one canola-based and one crambe-based, were submitted to the Air Force Research Laboratory (AFRL) for evaluation of military JP-8 fuel specification compliance. EERC measurements indicate that both jet fuel samples met the specifications for freeze point and flash point, as shown in Table 3. Complete AFRL test results for these two jet fuel samples will be submitted to the North Dakota Industrial Commission (NDIC) as an addendum to this report once the results are received by the EERC. The two diesel fuel samples, one each from canola and crambe oil, were submitted to a contract laboratory in Texas for diesel fuel specification compliance. The data from the diesel fuel specification testing are shown in Table 4. The seed-derived diesel samples are very similar to the petroleum-derived diesel fuel in most chemical and physical aspects. However, the cetane index is much higher for the renewable diesel samples, and the sulfur content is virtually nonexistent. Both of these attributes are excellent properties for diesel transportation fuel.

A bulk (8-gallon) sample of the crambe-derived diesel was also shipped to Mankato State University for static engine performance and emission evaluation. The static engine testing was performed on a four-cycle, three-cylinder, in-line, liquid-cooled diesel engine (Figure 10), which was mounted to an engine dynamometer with automated controls and a data acquisition system. Mankato State University's report is included as Appendix C.

Table 3. Preliminary Data on Jet Fuel Samples Submitted by the EERC to AFRL

	Flash, °C	Flash, °C	Freeze, °C	Freeze, °C
		JP-8 Specification		JP-8 Specification
Canola Jet	42	>38	−53.6	<−47
Crambe Jet	39	>38	−53.5	<−47

Table 4. Test Results of a Canola- and Crambe-Derived Diesel in Comparison with a Typical Winter Diesel

Test	Typical No. 2 Diesel (winter blend)	EERC Canola-Derived Diesel	EERC Crambe-Derived Diesel
Appearance	Clear and Bright	Clear and Bright	Clear and Bright
Density, kg/m^3	845	772	778
API[1] Gravity	35.9	51.7	50.5
Cetane Index	43.8	75.3	76.8
Cloud Point, °F	0	−38	−20
Pour Point, °F	−35	−75	−30
Distillation (D86), °F			
IBP[2]	331	327	335
T10	386	389	402
T20	412	417	434
T30	435	441	463
T40	456	464	490
T50	476	484	515
T60	496	502	536
T70	520	516	554
T80	547	528	573
T90	584	547	596
FBP[3]	653	552	622
Flash Point, °F (TCC®)[4]	146	139	146
Sulfur, ppm	9.8	<3	<3
Viscosity	2.4	2.0	2.4
Ash, wt%		<0.001	0.001
Copper Strip, (3 h at 122°F)		1a	1a
Water and Sediment		0	0

[1] American Petroleum Institute.
[2] Initial boiling point.
[3] Final boiling point.
[4] Tag closed cup.

The dynamometer control and data acquisition system enable the engine to be operated and evaluated at specific load and rpm set points corresponding to an EPA testing protocol. Along with the engine performance data, gaseous emission data including particulate emissions were also measured at varying stages of operation. All gaseous emission measurements were performed with California analytical instruments emission equipment shown in Figures 11 and 12.

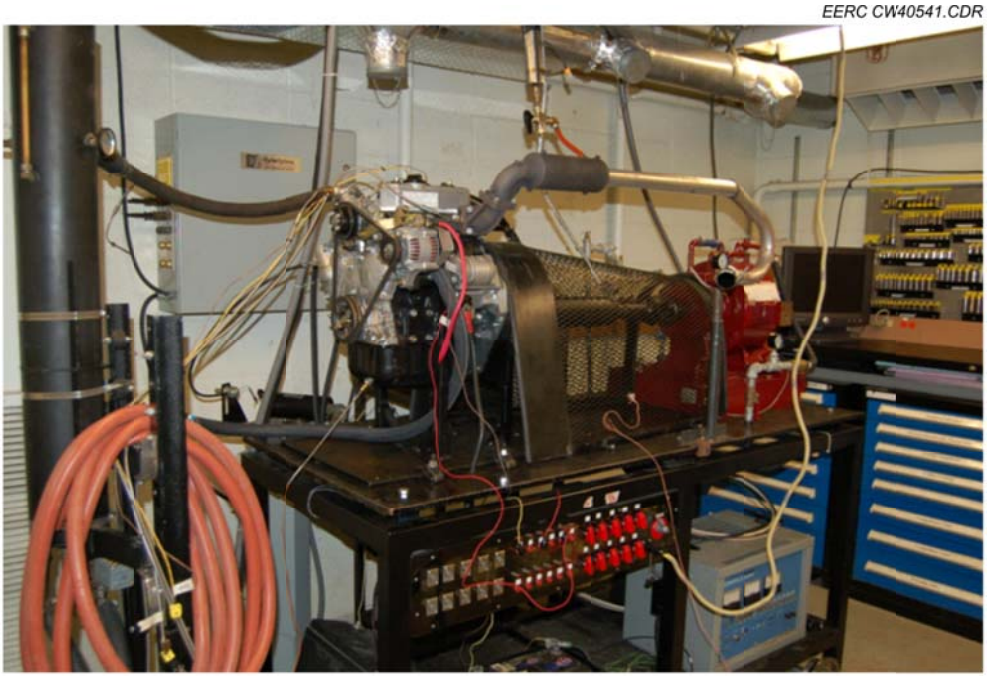

Figure 10. Static engine testing system at Mankato State University.

Figure 11. California analytical instruments emission equipment data acquisition system.

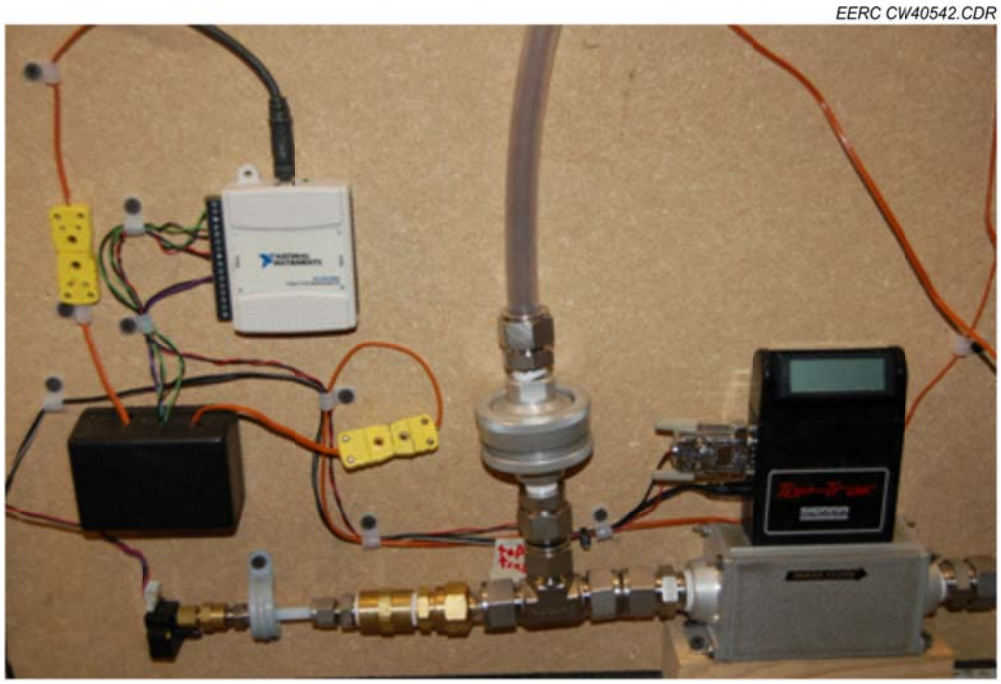

Figure 12. Emission testing particulate trap and sample probe setup.

The static engine testing was performed on both the EERC renewable diesel and an ultralow-sulfur diesel (ULSD) certification fuel for comparison. The engine was operated on each fuel at a variety of steady-state conditions (modes) and monitored for power output and emission characteristics. Specific data collected on each fuel during each steady-state condition included the following:

- Hydrocarbon concentration
- Carbon monoxide concentration
- NO_x concentration
- Oxygen and carbon dioxide concentration
- Particulate concentration
- Engine rpm
- Engine torque
- Fuel consumption

The testing sequence was repeated three times on each fuel, and an average value for each data point was calculated. The raw data were then used to determine brake-specific emission and fuel economy data. Particulate matter concentration was determined by measuring deposition on a filter paper during a specific amount of time (300 seconds of steady-state operation).

Static Engine Testing Results

Emissions

Federal regulations for emissions have set requirements on the maximum levels of output for specifically measured constituents such as non-methane hydrocarbons (NMHC) + NO_x, carbon monoxide (CO), and particulate matter (PM). Table 5 and corresponding Figure 13 illustrate the federal emission requirements compared to those of the EERC diesel fuel and the ULSD certification fuel.

Both the certification fuel and the EERC renewable diesel fuel yielded emission levels well below the maximum allowable levels. The EERC fuel had slightly lower NMHC and NO_x concentrations and slightly higher carbon monoxide levels than the certification fuel; however, both fuels had similar PM output concentrations.

Table 5. Specific Emission Concentrations for Evaluated Fuels

	Weighted Specific Emissions Averages (g/kWh)		
	NMHC+NO_x	CO	PM
Federal Regulation Emission Requirements (Tier 1)	9.5	6.6	0.80
2007 ULSD Certification Fuel	5.5	2.2	0.27
EERC Renewable Diesel	3.9	4	0.30

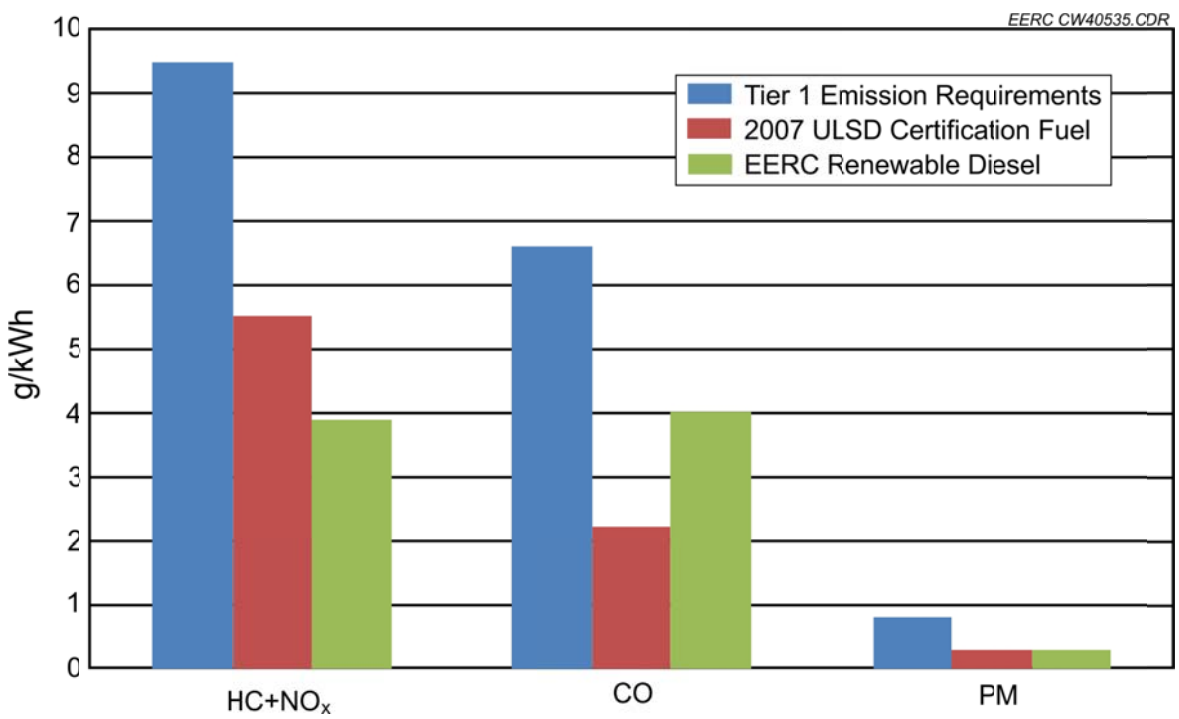

Figure 13. Graph of emission data for the tested fuels and the federally required levels.

Engine Performance

The measure of fuel efficiency and engine performance used in this testing was brake-specific fuel consumption (BSFC). The BSFC is determined by measuring the amount of fuel consumed by the engine to generate power equivalent to 1 horsepower for 1 hour. The specific unit of measure for BSFC is pounds of fuel used per horsepower hour (lb/hp-hr or g/kW-hr). Therefore, a lower BSFC value indicates that less fuel was consumed, corresponding to more fuel-efficient operation.

Both fuels were evaluated during eight separate modes of operation with varying operating conditions, such as torque speed and rpm. During each mode of engine operation, a BSFC value was calculated for each fuel type for comparison. As shown in Table 6 and corresponding Figure 14, BSFC values indicate the engine utilized slightly more of the EERC fuel to produce

Table 6. BSFC Averages for Each Mode on Both the Certification and EERC Fuels (BSFC units of g/kWh)

	BSFC Mode Averages							
	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Mode 6	Mode 7	Mode 8
2007 ULSD Certification Fuel	313.4	324.1	373.9	1255.9	293.5	315.6	374.1	idle
EERC Renewable Diesel	336.8	355.0	454.7	1395.3	327.4	327.7	387.2	
% Difference	6.95%	8.69%	17.78%	9.99%	10.37%	3.69%	3.40%	

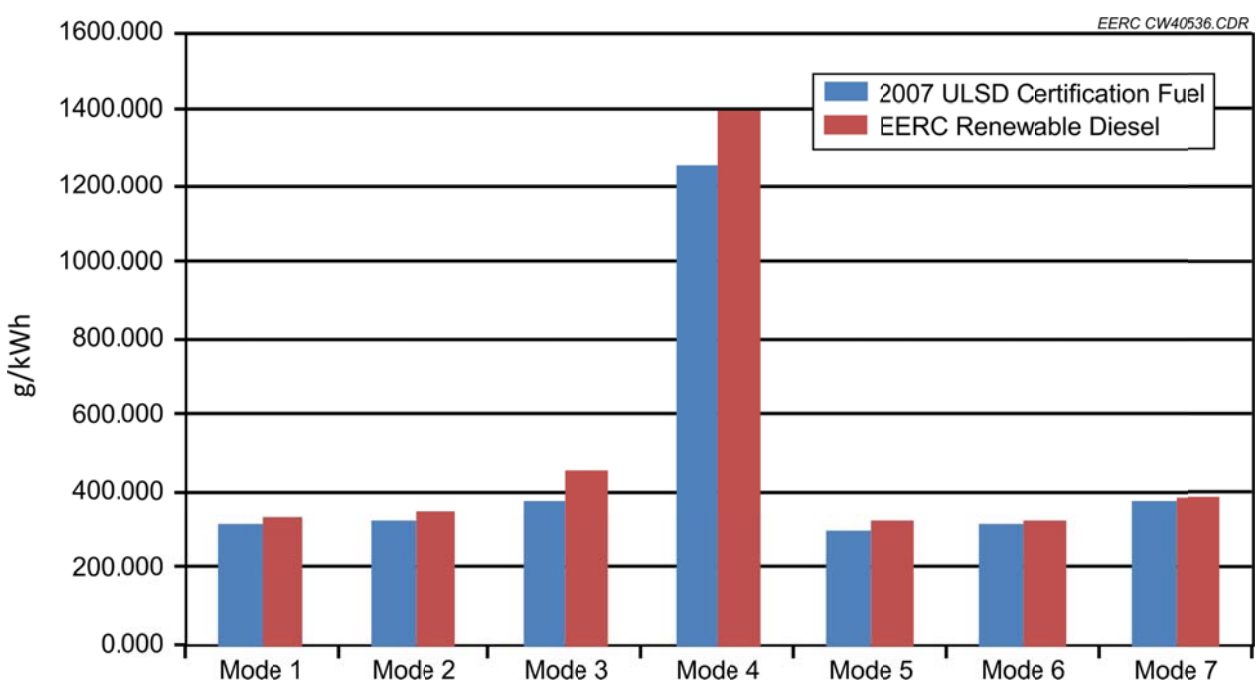

Figure 14. Graph of BSFC for both the certification and EERC fuels.

the same amount of power as did the ULSD certification fuel. Overall, the performance of the EERC diesel is very similar to that of an ultralow-sulfur diesel certification fuel.

Task 2 – Renewable Oil Refinery Economic Assessment

The EERC conducted a preliminary economic assessment which was submitted to NDIC as a special report on November 1, 2010. Inputs to this economic model have been revised based on the completed process design package and associated total installed cost estimate. Specifically, capital cost, power requirements, and water requirements have been adjusted to reflect a more realistic cost estimate to build and operate a commercial renewable oil refinery.

The economic model takes into account feedstock cost, capital equipment costs, operating and maintenance costs, and financing scenarios. The model was developed using Microsoft Excel and calculates plant economics based on user-defined inputs. Model inputs and user defined assumptions included the following:

- Annual capacity (58 Mgpy)
- Crude oil price ($85/bbl)
- ULSD (ultralow-sulfur diesel) rack price ($2.94/gal)
- Blend ratio of lower-value fuel component (0–2.37 gal per gal CHI)
- Value of blending component ($2.18/gal)
- Feedstock cost ($560/ton–$835/ton)
- Hydrogen cost ($1.75/kg)
- Power cost ($0.05/kWh)
- Heating cost ($10.37/MMBtu)
- Water cost ($0.067/1000 kg)
- Catalyst cost ($0.12/bbl)
- RIN (renewable identification number) value ($1.38/gal)[3]
- U.S. inflation rate
- Labor, maintenance, overhead, insurance costs
- Financing costs (amount, interest rate, payback time, depreciation rate)
- Income tax rate

The capital equipment cost for the 2.9-Mgpy pilot plant design was used to estimate the capital equipment cost for a 58-Mgpy commercial plant. The six-tenths rule[4] was used for this estimation and is commonly used for scaling up equipment costs to a different capacity. The six-tenths rule is shown in Equation 1 and takes into account the nonlinear relationship between increasing capacity and increasing cost.

$$\frac{C_a}{C_b}=\left(\frac{A_a}{A_b}\right)^n \qquad \text{[Eq. 1]}$$

[3] The 2011 RINs are trading from $1.36 to $1.40 a gallon. *The Jacobsen Biodiesel Bulletin*, June 8, 2011.
[4] Turton. *Analysis, Synthesis, and Design of Chemical Processes*; Prentice Halls: Upper Saddle River, NJ, 2003: p. 148, 155.

Where: A = Equipment cost attribute (in this case, annual volumetric capacity)
C = Purchased cost
n = Cost exponent (0.6 on average for process plant equipment)
a = refers to equipment with the required attribute (58 Mgpy)
b = refers to equipment with the base attribute (2.9 Mgpy)

The scaled capital equipment cost for the 58-Mgpy plant was used in a spreadsheet provided by WorleyParsons to calculate additional direct costs, indirect costs, and engineering and management costs. The sum of these costs equaled the total installed cost ($211 M) and was entered into the economic model as the amount of financing required to construct a 58-Mgpy plant.

The utility requirements from the pilot plant design were directly scaled on a per-gallon basis to estimate the utility requirements of the 58-Mgpy commercial plant. These updated values were entered into the economic model.

Based on these user-defined inputs, the economic model calculated operating revenues, fixed and variable operating costs, annual capital cost payments, assets depreciation, net income taxes, tax incentives, and yearly cash flow.

A promising strategy to maximize CHI plant profitability is to upgrade a lower-value refinery product through direct blending with CHI fuel. Because of CHI fuel's extremely low sulfur content (<3 ppm), low aromatic content (<1.8 vol%), and high cetane value (green diesel typically ranges from 70 to 90), it can theoretically be blended with lower-value products that do not meet ULSD specifications and result in a blended fuel that meets ULSD specs. As a result, the profit made by selling the blended fuel is greater than what would be made by selling each fuel individually.

Sensitivity Analysis

A sensitivity analysis was conducted to study the effects of blend ratio, capital cost, and hydrogen cost on yearly cash flow. Because feedstock cost has an overwhelming effect on yearly cash flow, sensitivity analyses were conducted for two cases. Case 1 represented a low-feedstock-cost scenario and assumed that yellow grease was the feedstock and was available at $560/ton.[5] Case 2 represented a high-feedstock-cost scenario and assumed that soybean oil was the feedstock and was available at $835/ton.[6] The price of vegetable oils and waste grease is volatile and trends up and down with the price of petroleum. The vegetable oil and petroleum values used in this economic assessment were recorded at a common point in time during the last year.

[5] 2010 Yellow Grease Price Look-up. www.ams.usda.gov/mnreports/sj_gr210.txt (accessed Oct 2010).
[6] 2010 Soy Oil Price Look-up. www.indexmundi.com/commodities/?commodity=soybean-oil&months=60 (accessed June 2011).

Blend Ratio

When the impact of blend ratio on yearly cash flow was assessed, it was assumed that a low-value refinery stream was available that would have otherwise been blended and sold as home heating oil. This stream was assumed to have a composition similar to a refinery's light cycle oil stream. Specifically, the stream was assumed to have a cetane index of 23 and an aromatics content of 80%.[7] ULSD specifications require a cetane value greater than 40 and an aromatic concentration less than 35%. Calculations showed that 0.73 gallons of this low-value fuel could be blended with CHI fuel before reaching the specified upper limit on aromatics. Similarly, 2.37 gallons of the low-value fuel could be blended with CHI fuel before reaching the specified lower limit on cetane. These blend limits provided the points at which to evaluate the effect of blend ratio on yearly cash flow. Results are shown in Figures 15 and 16. Asterisk in the legend identifies the base-case scenario. Figure 15 suggests that a low-cost feedstock results in positive cash flow, even in the absence of blending. This assumes a $1.38 RIN credit. The plant is much more profitable as the blend ratio of low-value fuel to CHI fuel is increased. As shown in Figure 16, more expensive feedstocks, such as soybean oil, require blending with a lower-value fuel to result in a profitable plant, even with a $1.38 RIN credit.

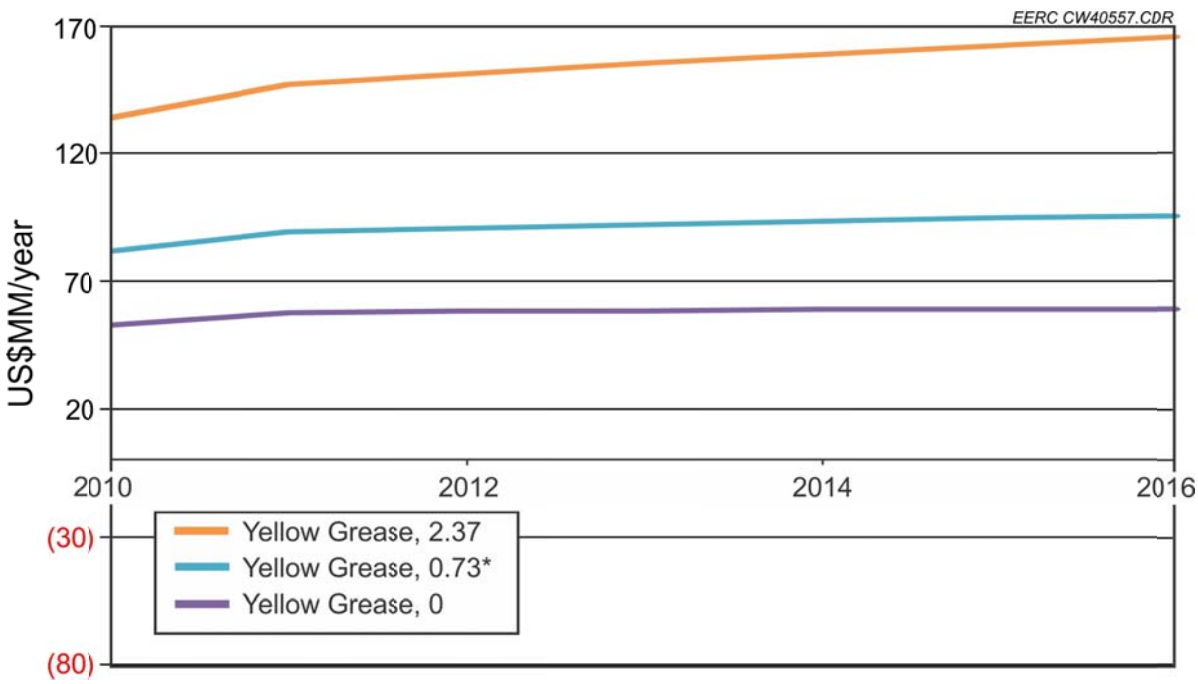

Figure 15. Yearly cash flow as a function of the blend ratio of low-value fuel to CHI fuel when yellow grease is used as feedstock.

[7] Thakkar, V. et al. LCO Upgrading – A Novel Approach for Greater Added Value and Improved Returns. UOP LLC, 2005.

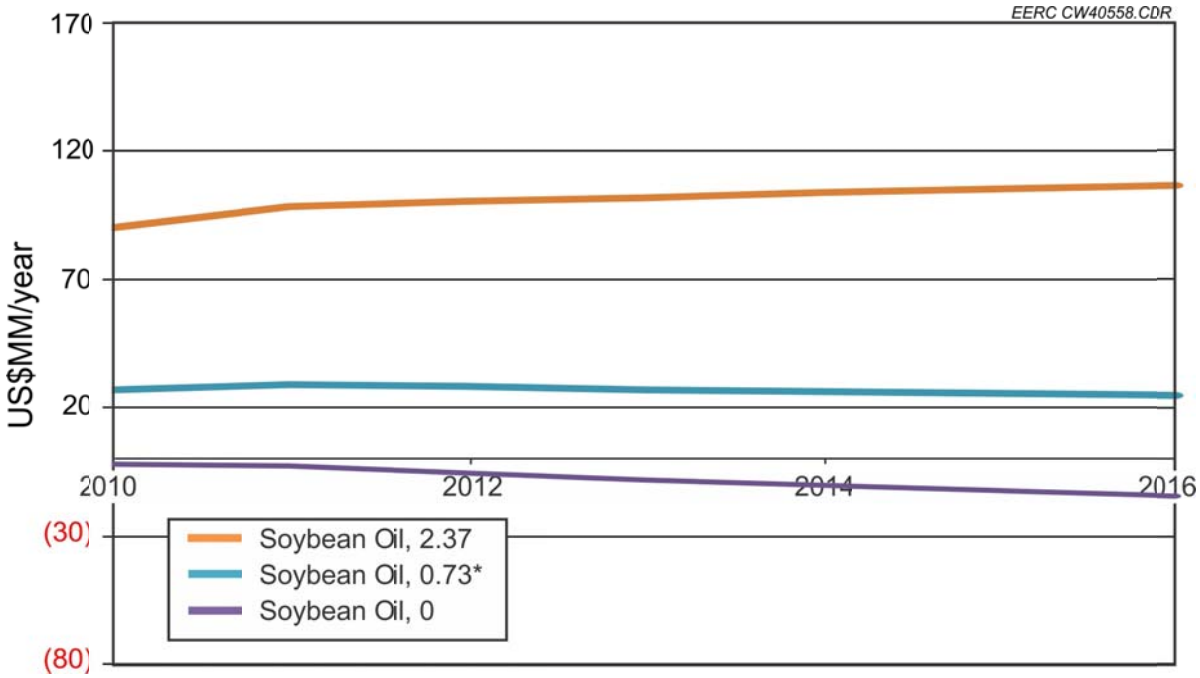

Figure 16. Yearly cash flow as a function of the blend ratio of low-value fuel to CHI fuel when soybean oil is used as feedstock

Capital Cost

To assess the sensitivity of plant profitability to capital cost, the estimated capital cost was varied ±80%. The baseline assumption was a capital cost of $210.8 M for a 58-Mgpy CHI plant. The effect of capital cost variation on yearly cash flow when a $560/ton yellow grease feedstock and an $835/ton soybean oil feedstock are processed is shown in Figures 17 and 18, respectively. For this analysis, the selected blend ratio was set to 0.73 gallons of low-value fuel per gallon of CHI fuel.

Hydrogen

The CHI process consumes hydrogen during the conversion of triacylglyceride to hydrocarbon. To access the sensitivity of plant profitability to hydrogen cost, the estimated hydrogen cost was varied ±80%. The baseline assumption was a hydrogen cost of $1.75/kg. The effect of hydrogen cost variation on yearly cash flow when a $560/ton yellow grease feedstock and an $835/ton soybean oil feedstock are processed is shown in Figures 19 and 20, respectively. For this analysis, the selected blend ratio was 0.73 gallons of low-value fuel per gallon of CHI fuel.

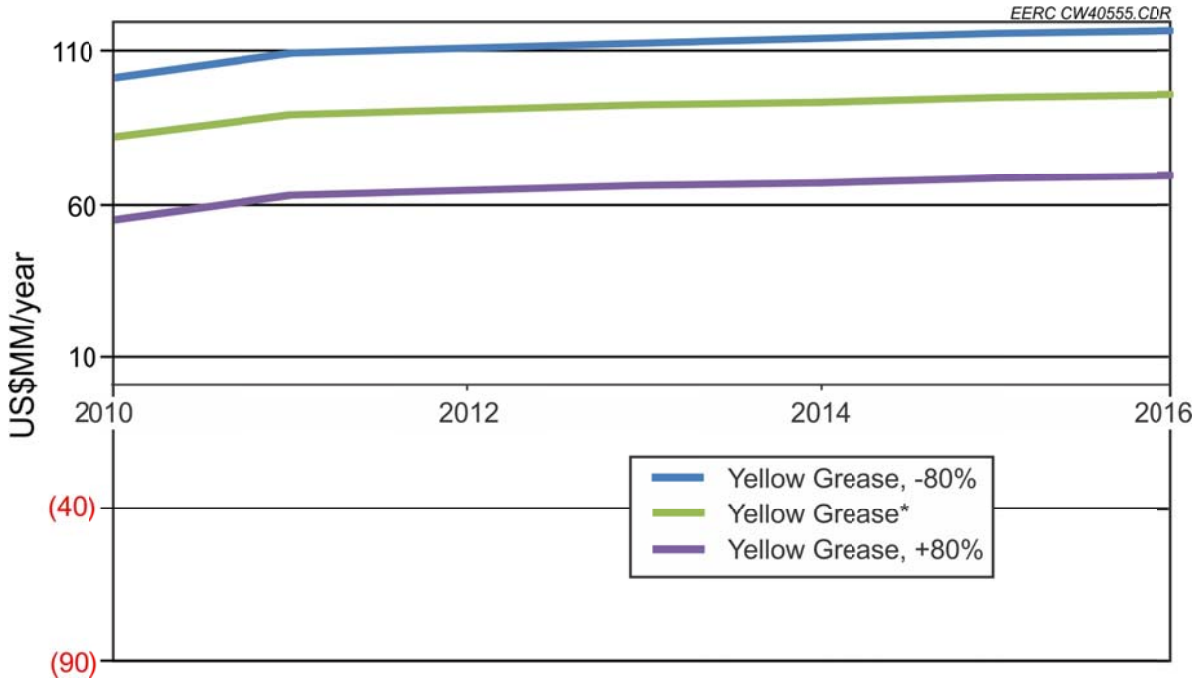

Figure 17. Yearly cash flow as a function of capital cost when a $560/ton yellow grease feedstock is processed.

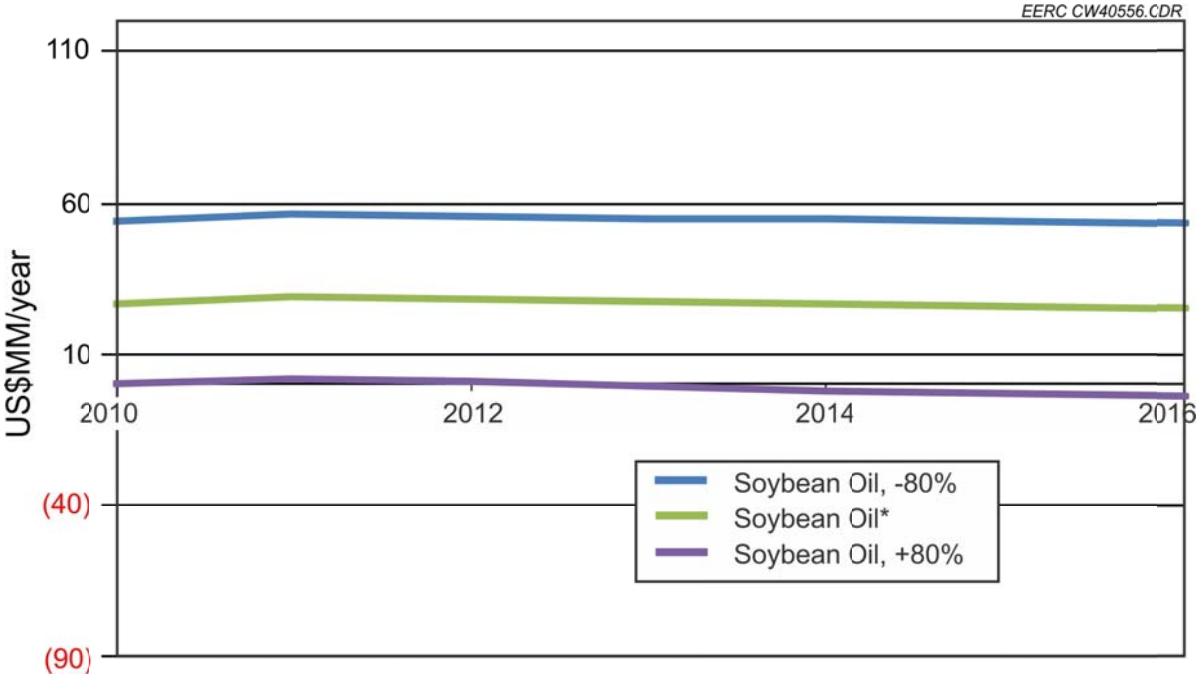

Figure 18. Yearly cash flow as a function of capital cost when an $835/ton soybean oil feedstock is processed.

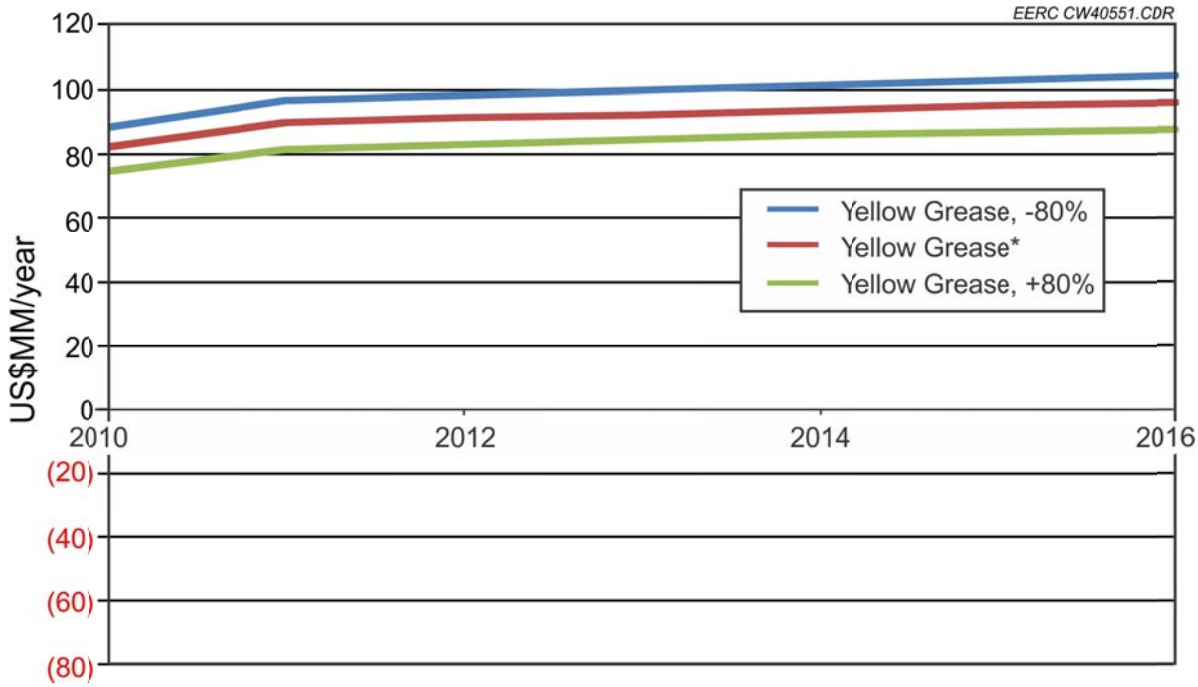

Figure 19. Yearly cash flow as a function of hydrogen cost when a $560/ton yellow grease feedstock is processed.

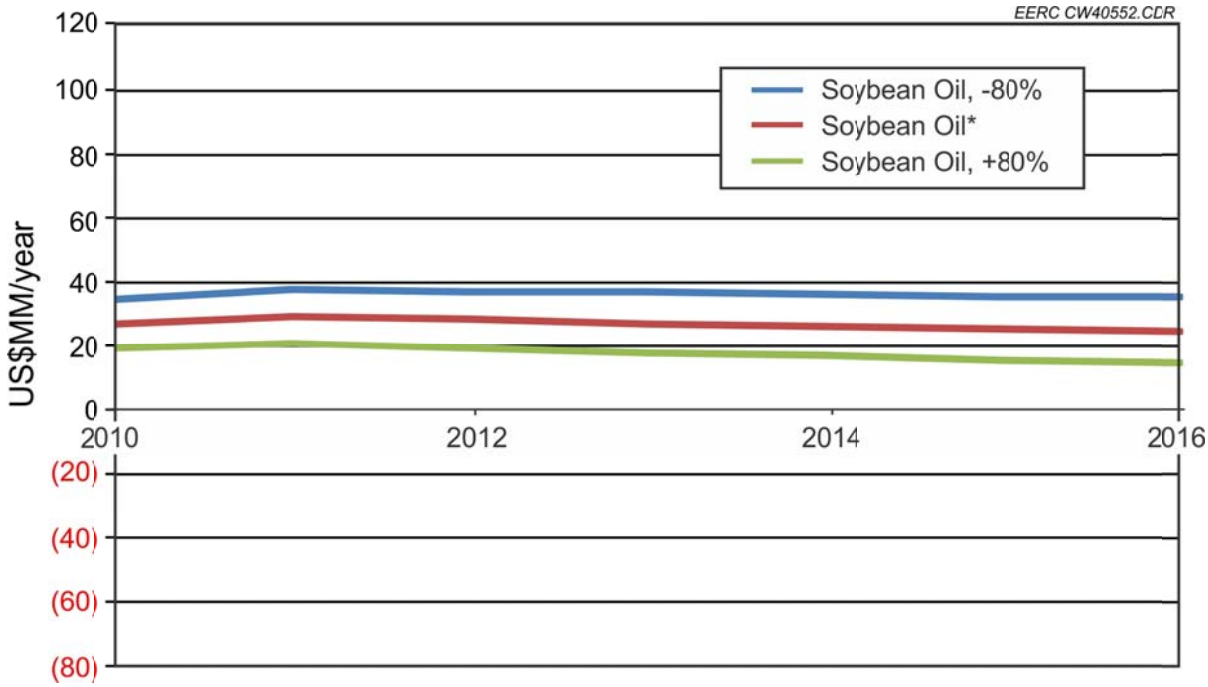

Figure 20. Yearly cash flow as a function of hydrogen cost when an $835/ton soybean oil feedstock is processed.

RIN Credit

The Energy Independence and Security Act (EISA) of 2007 increased the required volume of renewable fuel to be blended into transportation fuels from 9 to 36 billion gallons a year over the time period from 2008 to 2022.[8] The program created to help achieve the renewable fuel increase is the Renewable Fuel Standard 2 (RFS2). The RFS2 requires that multiple types of RINs be generated or purchased by obligated parties to ensure the mandated quota of renewable fuel is blended into the fuel pool. The supply and demand of RIN credits determine their value. As of June 8, 2011, The *Jacobsen Biodiesel Bulletin* reported that 2011 RINs are trading from $1.36 to $1.40 a gallon. Figure 21 shows cash flow for a CHI facility using yellow grease as a feedstock, when RIN value is zero and when RIN value is $1.38 per gallon. As the figure shows, yellow grease, when blended with 0.73 gallons of low-value fuel per gallon of CHI, is a profitable feedstock even in the absence of credits.

A more expensive feedstock, such as soybean oil, requires a RIN credit for plant profitability. Figure 22 shows the effect of RIN credits on the cash flow of a CHI facility using soybean oil to produce fuel. Again, for this analysis, the blend ratio was set at 0.73 gallons of low-value fuel per gallon of CHI fuel.

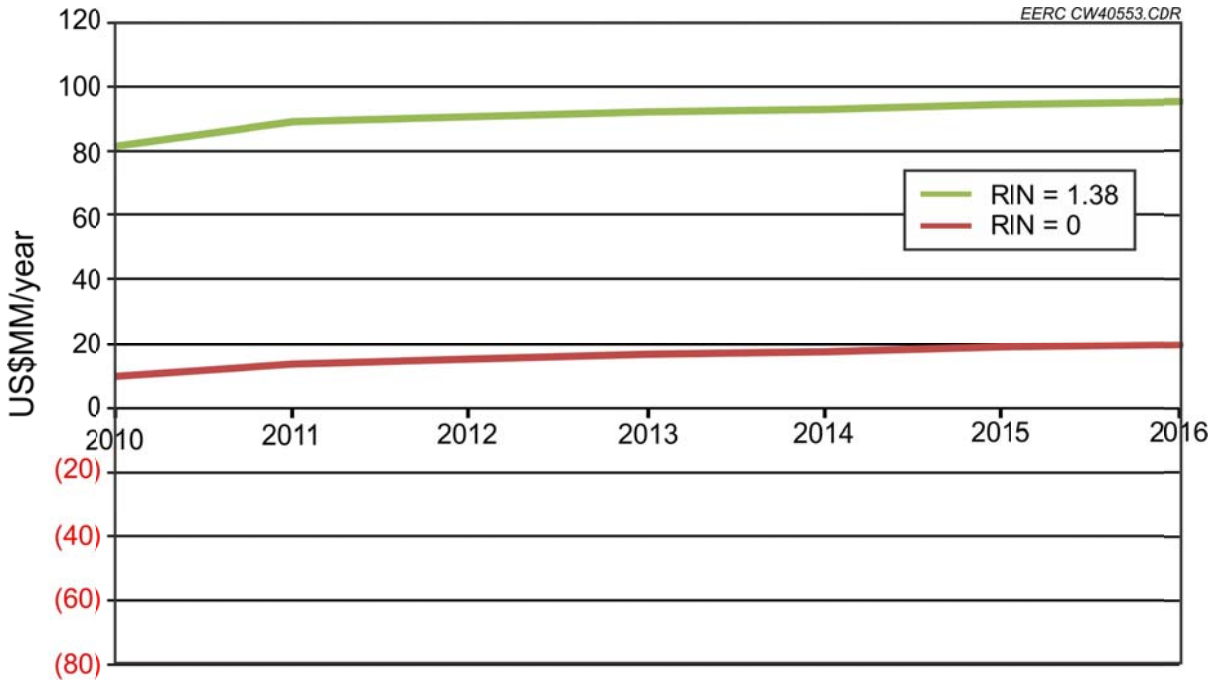

Figure 21. Yearly cash flow as a function of RIN credit value when a $560/ton yellow grease feedstock is processed.

[8] Sissine, F. Energy Independence and Security Act of 2007: A Summary of Major Provisions. CRS Report for Congress, Dec 21, 2007.

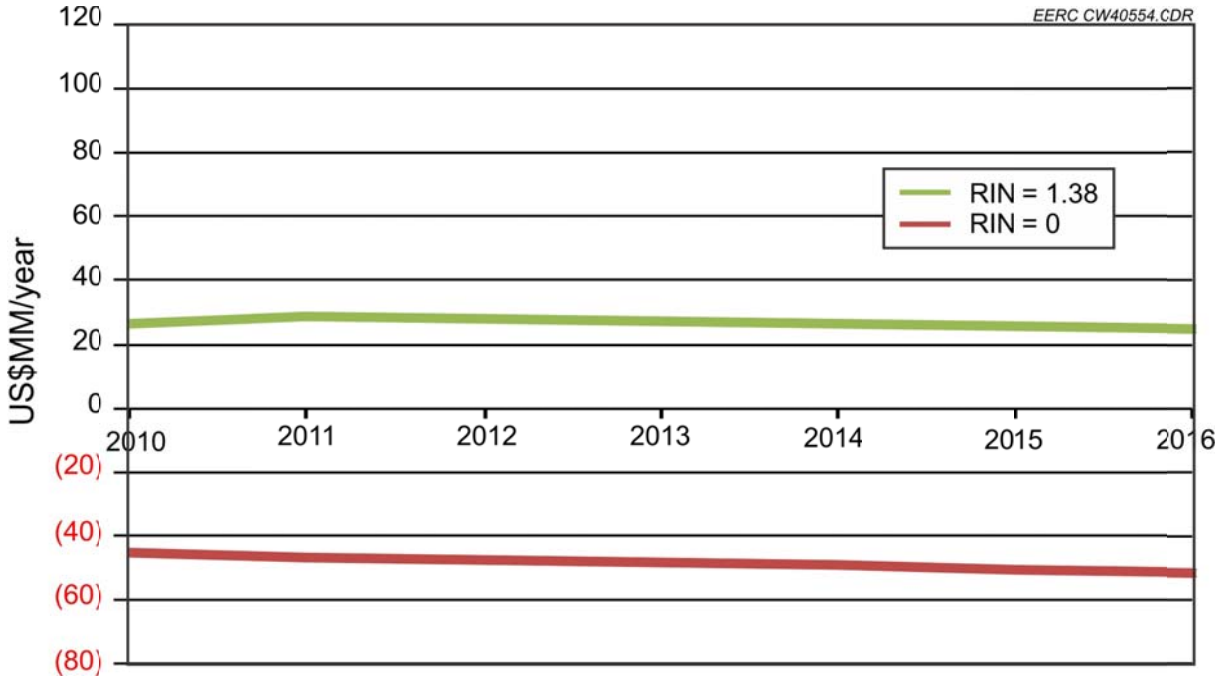

Figure 22. Yearly cash flow as a function of RIN credit value when an $835/ton soybean oil feedstock is processed.

Breakeven Feedstock Cost

The breakeven cost of feedstock was estimated at three different scenarios: 1) a blend level of zero gallons of light-cycle oil (LCO) per gallon of CHI and a RIN value of zero, 2) a blend level of zero and a RIN value of $1.38, and 3) a blend level of 0.73 and an RIN value of $1.38.

Scenario 1 assumed the worst case of no fuel blending and no RIN credit. In this case, a very inexpensive feedstock is required for plant profitability. Scenario 1 results in a breakeven feedstock cost of ~$485/ton. Scenario 2 assumed that there was no blending but that the RIN credit was valued at today's $1.38/gallon. Scenario 2 results in a breakeven feedstock cost of ~$800/ton. Scenario 3 assumed the best case of blending 0.73 gallons of LCO per gallon of CHI and a $1.38/gal RIN credit. Scenario 3 shows that a CHI facility could be profitable up to a feedstock cost of ~$955/ton, given the other assumptions made by the economic model. As an example of feedstock price variability, the average price of soybean oil in 2010 was $839/ton with a maximum trading price of $1096/ton and a minimum trading price of $745/ton.[9] Yellow grease is typically less expensive than soybean oil but is subject to similar price volatility.

Economic Assessment Conclusions

An economic model was developed and used to identify the key economic drivers for a CHI process plant that converts vegetable oils into hydrocarbon fuels. Feedstock cost, blend ratio

[9] www.indexmundi.com/commodities/?commodity=soybean-oil&months=60 (accessed 2011).

with low-value fuel, and RIN credit value had the greatest effect on plant economics. Capital cost and hydrogen costs had less of an effect. A breakeven analysis showed that a CHI facility can be profitable at low feedstock cost (~$485/ton) even if no fuel blending occurs and no value is assigned to the RIN credits generated along with fuel production. On the other hand, an expensive feedstock (~$955/ton) can result in profitable plant operation, given a sufficient blend strategy and a RIN value similar to today's RIN value.

Task 3 – Renewable Oil Refinery Pilot Plant Design

Reactor Design and Rate Data Experiments

Proper reactor design is critical to ensure that the 336-gph pilot plant reactors perform similarly to the 0.5-gph laboratory reactors. Heat and mass transfer have the potential to be very different when going from the lab scale to the pilot scale. In order to ensure successful scale-up, the EERC conducted extensive laboratory experiments and consulted with a reactor design firm, Impact Technology Development. Experimental data were analyzed and used to derive a mathematical model to predict conversion as a function of catalyst bed length. A kinetic model was especially important for designing the HDO reactor because the reactions that occur in this reactor are extremely exothermic. Predicting the extent of reaction as a function of catalyst length is critical to proper placement of quench zones and proper sizing of the reactor vessel. Catalyst life experiments were also conducted and showed that the HDO catalyst maintained its activity for >2000 hours, providing strong indication that the CHI process has the robustness to provide a commercially viable alternative fuel production pathway. Appendix B describes the work that was conducted to assess catalyst stability.

The EERC, in joint collaboration with WorleyParsons and Impact Technology Development, developed experimental designs to gather reaction rate data. The experimental apparatus consisted of a feed pump, a feed preheat section, a catalyst-filled reactor, a condenser, and a sample collection vessel. Temperature, pressure, flow rates, and catalyst weight were varied. Liquid product was analyzed by GC–MS and acid titration to determine conversion of triacylglyceride to hydrocarbon and conversion of triacylglyceride to fatty acid, an intermediate product.

The reactor used to collect kinetic rate data was carefully designed to control all manipulated variables. The feed for HDO experiments was a mixture of dodecane and canola oil. This allowed researchers to vary feed concentration during tests. In order to prevent canola oil breakdown to fatty acids at high temperatures, the dodecane was preheated over glass beads to a high temperature upstream of the catalyst bed. The canola oil was preheated to a lower temperature in a heat-traced feed line before separately entering the reactor. A mixing section, consisting of metal packing, was installed just upstream of the catalyst bed to ensure a homogeneous, isothermal mixture at the start of the catalyst bed. The entry point of the canola oil feed could be moved up or down in the reactor, depending on the size of the catalyst bed being tested. A schematic of the experimental reactor used to collect kinetic rate data is shown in Figure 23.

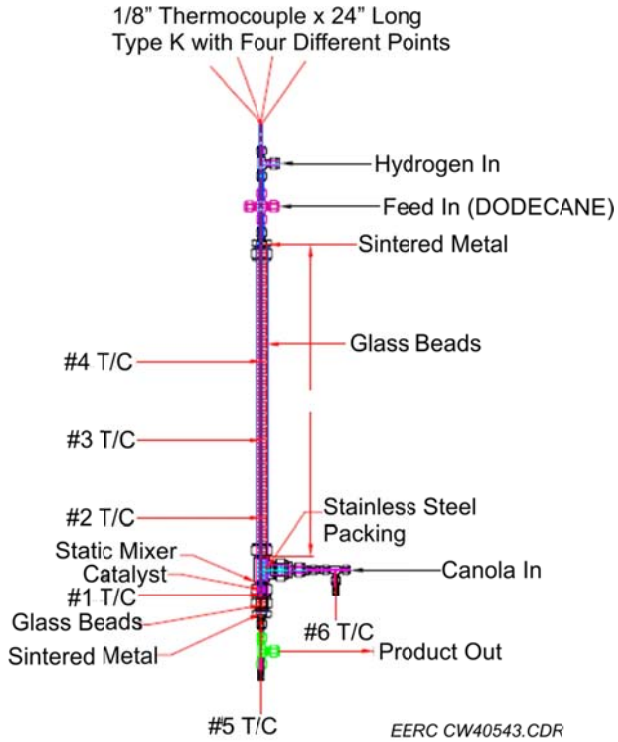

Figure 23. Experimental test reactor used to collect kinetic rate data.

Extensive laboratory testing was conducted to support the kinetic model. Chemical kinetics, mass diffusion, and heat management strategies were investigated. Experiments were first conducted at low conversions in a differential reactor in order to gather fundamental reaction rate data. Subsequent experiments were conducted at higher conversions using a longer catalyst bed. Gathering data at these two scales allowed the differential model to be refined and further developed. Primary variables that were investigated included temperature, liquid and gas flow rates, canola concentration, pressure, and catalyst size. Over 100 experimental runs were conducted to provide data for the HDO kinetic model. A kinetic expression was developed that fit all temperature studies, and an activation energy was determined. The final kinetic model was capable of calculating reaction rates and feedstock conversion as a function of catalyst bed volume and was utilized to design a scaled-up reactor to function similarly to the laboratory-scale reactor. Heat and mass balances were also calculated for the HDO reactor, allowing heat management strategies to be evaluated and selected. Useful plots were generated, based on the kinetic model, that predict conversion as a function of distance traveled down the reactor length. These plots will be helpful during pilot plant operation. The final deliverable for the HDO reactor design effort was a dimensioned reactor schematic, including reactor internals selection and insulation strategy. The HDO reactor schematic is shown in Figure 24.

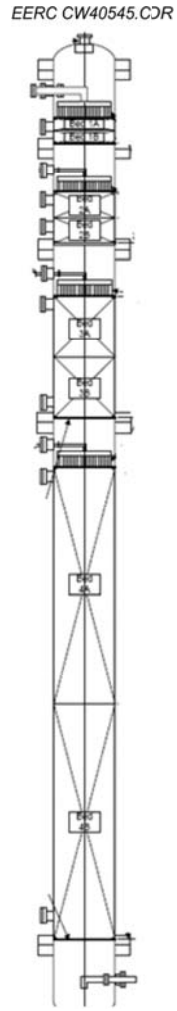

Figure 24. HDO reactor schematic.

A similar modeling effort was conducted for the scale-up of the isomerization reactor. A statistical design of experiments was formulated, and laboratory experiments were performed that gathered reaction rate data for the isomerization reaction. Isomerization testing was conducted at the EERC to support kinetic model development. Experiments fed a crop oil-derived, hydrocarbon feed into a 3-inch bed of catalyst. Temperature, pressure, liquid flow rate, and hydrogen flow rate were varied according to a statistical design of experiments. The conversion of normal paraffins in the feedstock to cracked products (<C8 hydrocarbons), jet range products (C8–C16 hydrocarbons), and diesel range products (C17–C18 hydrocarbons) were measured. The experiments had good reproducibility and showed that feedstock isomerization is dependent on mass velocity, temperature, and pressure. The information gained from these experiments was used to design the isomerization reactor to be built at the pilot plant. The final deliverable for the isomerization reactor design effort was a dimensioned reactor schematic, including reactor internals selection and insulation strategy. A schematic of the isomerization reactor is shown in Figure 25.

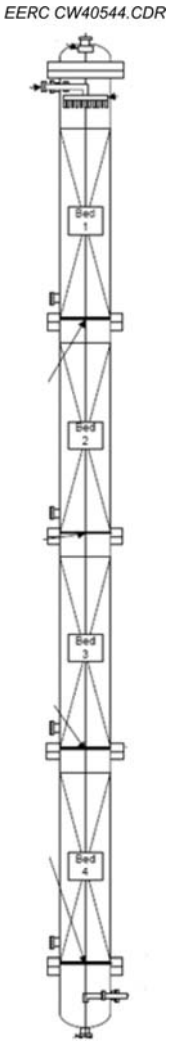

Figure 25. Isomerization reactor schematic.

Plant Design

WorleyParsons, an engineering firm with an extensive background in chemical process plant design, was contracted to develop the balance-of-plant design for the renewable oil pilot plant. The major process units of the CHI pilot plant include the HDO unit, the ISOM unit, the distillation unit, the hydrogen gas treatment unit, the tail gas recovery unit, and the tank farm and unloading/loading unit. Crop oil from the tank farm unit will be pumped to the HDO unit for conversion to hydrocarbon product. The hydrocarbon product will then be pumped to the ISOM unit where its cold-flow properties will be improved through isomerization and molecular weight reduction. The ISOM product will then be pumped to the distillation unit where it will be separated into naphtha, jet fuel, and diesel fuel products. Heat integration was not included in the pilot plant design in order to reduce pilot plant complexity and cost. Additionally, electric resistance heaters were included in the design where process heat is required.

The pilot plant site location has not been determined. Initially, the pilot plant was to be located at the Tesoro refinery in Mandan, North Dakota; however, during the first quarter of 2011, Tesoro Mandan announced a $35M plant expansion to boost its petroleum-refining capacity by 10,000 barrels a day.[10] This expansion is partly due to record oil production in western North Dakota. As a result of the newly announced refinery expansion, all of Tesoro Mandan's resources will be focused on completing the expansion effort. At this time, construction and operation of a renewable oil pilot plant at the Mandan, North Dakota, refinery are impossible; however, Tesoro remains interested in commercial-scale renewable fuel production, and a future project may be possible. Accordingly, the renewable oil refinery pilot plant design was generalized to enable implementation at any industrial location.

The pilot plant design basis anticipates that the process equipment, with the exception of storage tanks, will be assembled into skids that can be transported by flat-bed trucks. The skids are envisioned to bolt together and rest on a prepared earth/gravel bed in order to minimize concrete foundation requirements, cost, and schedule impact. Because of the height of reactors and distillation columns, however, foundations will be required for these pieces of equipment. The pilot plant design assumes that the HDO and ISOM reactor catalysts will require periodic replacement, that sorbent beds for gas cleanup will need to be periodically regenerated, and that all units in the pilot plant will be operated simultaneously. The design also calls for floating-roof storage tanks where vapor pressure dictates.

Process throughput is based on the ultimate goal of producing a 100,000-gallon sample of jet fuel in approximately 5 months. The design canola oil feed rate for the facility is 336 gph. The design criterion for producing quality jet fuel product was based on the military's specification for jet fuel (MIL-DTL-83133F Appendix A).

A total project cost was estimated based on the summation of capital equipment costs, total direct costs, total indirect costs, and engineering and management costs. The capital equipment cost was based on an equipment list that included equipment data sheets and specifications for major pieces of equipment along with price estimations. The total direct costs were calculated based on factors multiplied by capital equipment costs. Direct costs included process equipment, internals, site preparation, site improvement, concrete, structural steel for platforms, racks and supports, building costs, underground piping, above-ground piping, electrical costs, instrumentation, insulation, painting, and scaffolding. Indirect costs were estimated based on direct costs and included construction equipment costs, overhead costs, and other indirect costs. Engineering and management costs were calculated based on multiplying factors by the sum of direct and indirect costs. The total installed cost for a 336-gph (192-bbl/day) CHI facility was estimated to be $37 M.

Process flow diagrams (PFDs) were developed for the entire pilot plant, and piping and instrument diagrams (P&IDs) were developed for the HDO unit and the ISOM unit. Figure 26 shows the PFD for the tank farm unit. The tank farm was designed to hold 7 days' worth of canola oil. This equates to a tank volume of 60,000 gallons. The HDO and ISOM products from

[10] MacPherson, J. Tesoro Plans $35 million Expansion of Mandan Refinery. *The Bismarck Tribune*, March 21, 2011. www.bismarcktribune.com/news/local/article_52ec198a-53d8-11e0-ad90-001cc4c03286.html (accessed April 2011).

their respective units are stored in intermediate tanks for testing prior to further processing. There is also a test tank for process-generated water. This tank serves as a holding point before water is released to an outside boundary limit (OSBL) location. In case of high water acidity, the process has been designed with a caustic injection system to bring the water's pH back to neutral. A light naphtha storage tank is included in the design to hold light naphtha at pressure before releasing it to an OSBL location. Heavy naphtha will be stored in the 10,000-gallon heavy-naphtha product tank. Jet and diesel fuel products will be stored in their respective tanks for testing prior to being transferred over to the final product tanks for loadout. This design includes a quality control component to fuel production and will ensure that fuel products meet specifications in a test tank prior to being transferred to product loadout. Assuming 7000-gallon tanker truck capacity, three tanker trucks will be loaded with fuel product each day from the pilot plant facility under steady-state operation.

The pilot plant also includes a hydrogen treatment unit. This unit consists of a pressure swing adsorption unit (PSA) and compression system that separates hydrogen from nonhydrogen gases prior to sending hydrogen to the HDO and ISOM units. The hydrogen treatment unit allows the pilot plant to utilize impure hydrogen streams that may be available if the pilot plant is collocated at an existing refinery. The PFD for the hydrogen treatment unit is shown in Figure 27.

The HDO unit PFD is shown in Figure 28. This portion of the pilot plant contains the HDO reactor and includes cold hydrogen quench and recycled liquid product quench for heat management in the HDO reactor. A high-pressure separator and a low-pressure separator are included to separate hydrogen, water, and light gases from the hydrocarbon product.

The ISOM unit PFD is shown in Figure 29. Similar to the HDO reactor, the ISOM reactor was designed based on extensive laboratory testing and modeling efforts. The hydrogen feed to the ISOM reactor is dried via molecular sieve prior to entering the reactor. Isomerized product is cooled and passes through a high-pressure separator and low-pressure separator before going to the ISOM product tank.

The distillation unit PFD is shown in Figure 30. The distillation unit separates the isomerized product mixture by boiling point and results in a naphtha stream, a jet fuel stream, and a diesel fuel stream.

The tail gas recovery unit PFD is shown in Figure 31. The tail gas recovery unit captures offgas from the PSA regeneration cycle, HDO low-pressure separator, ISOM low-pressure separator, and the distillation unit. This gas is then compressed so that is can be sent OSBL.

A detailed stream catalog was also delivered by WorleyParsons and contains detailed information about each numbered process stream. Information in the stream catalog includes vapor fraction, temperature, pressure, molar flow, mass flow, mass density, mass heat capacity, thermal conductivity, viscosity, actual volume flow, standard gas flow, mass enthalpy, and the molecular composition of each stream.

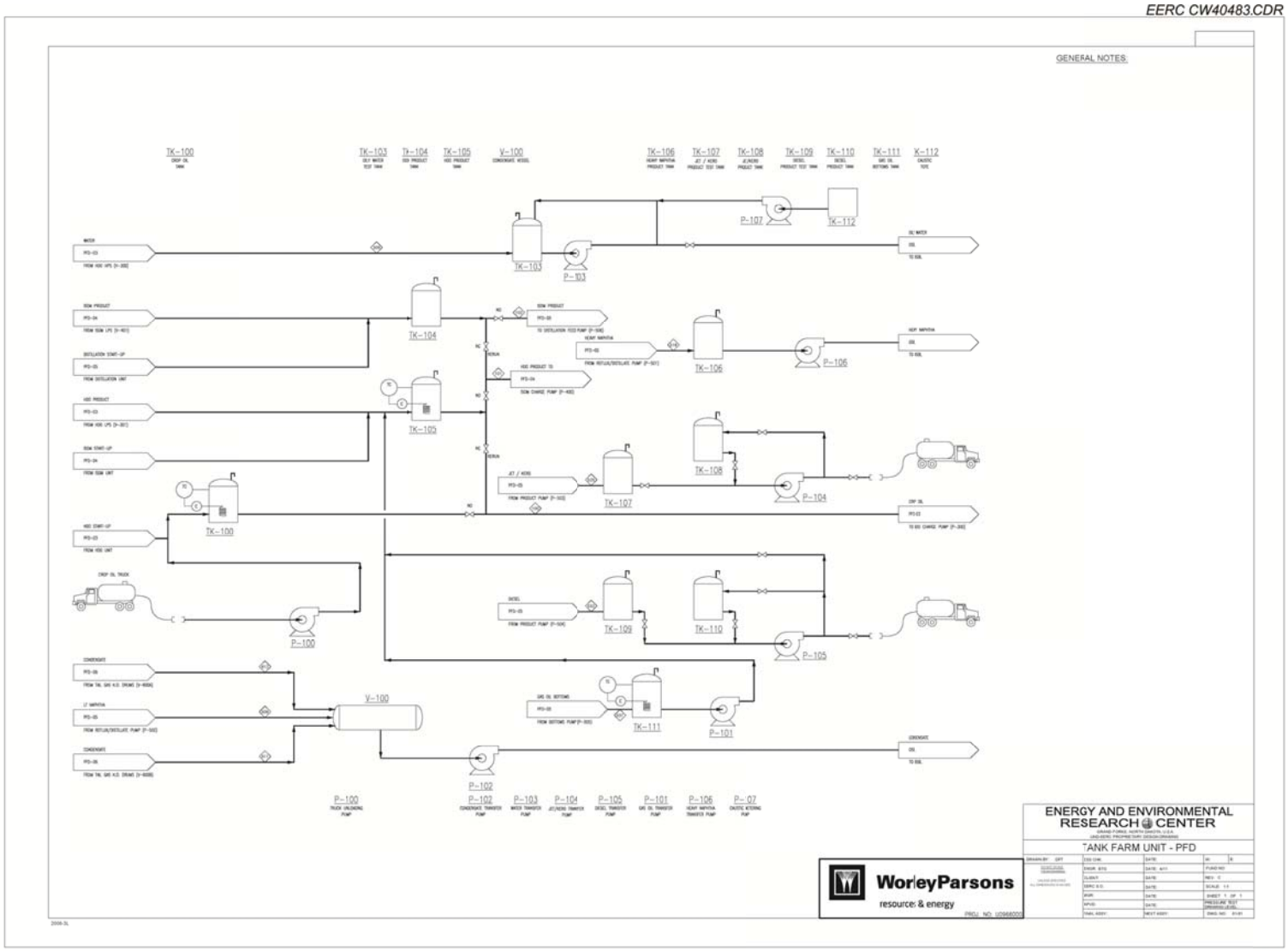

Figure 26. Tank farm unit PFD.

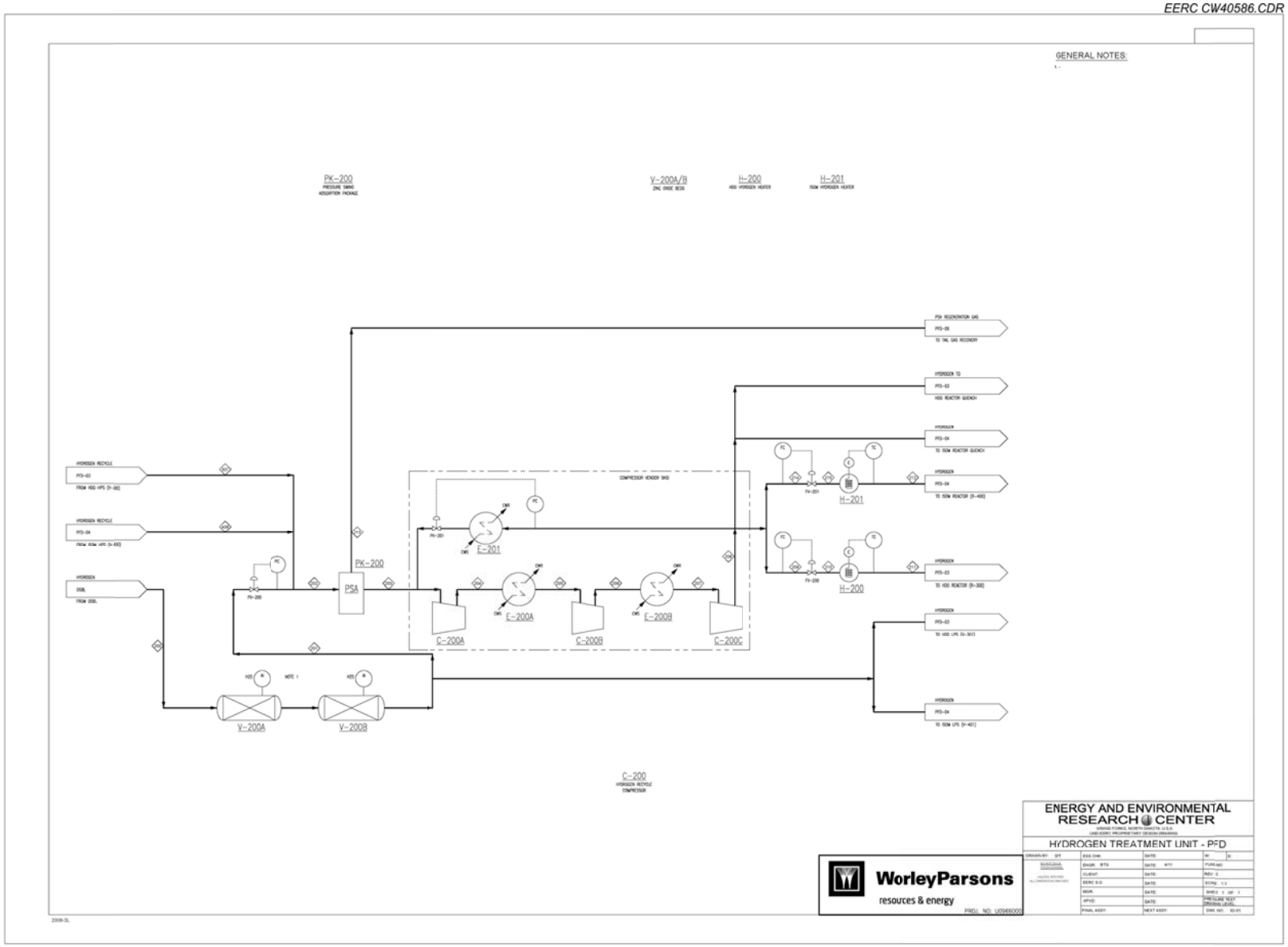

Figure 27. Hydrogen treatment unit PFD.

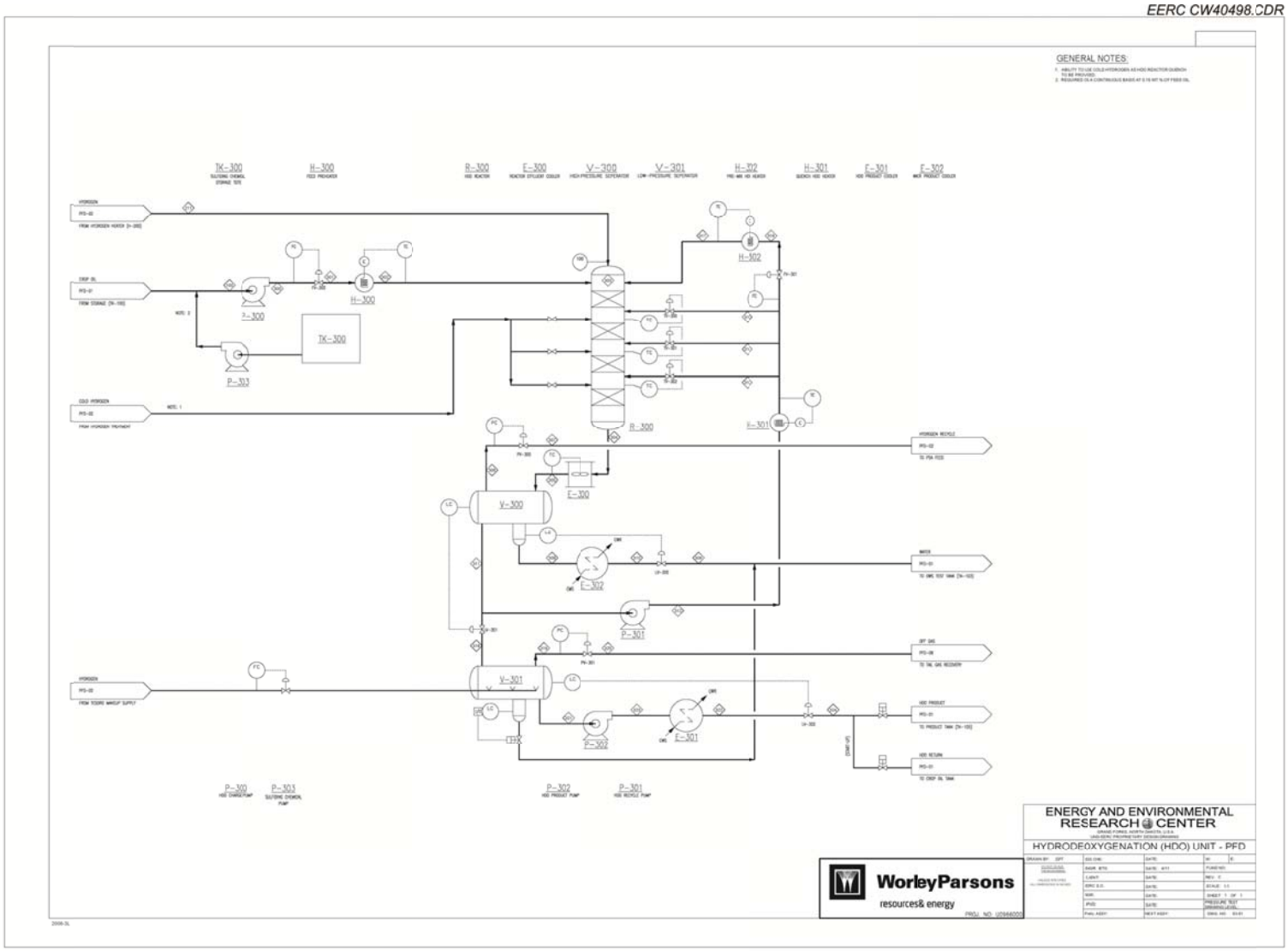

Figure 28. HDO unit PFD.

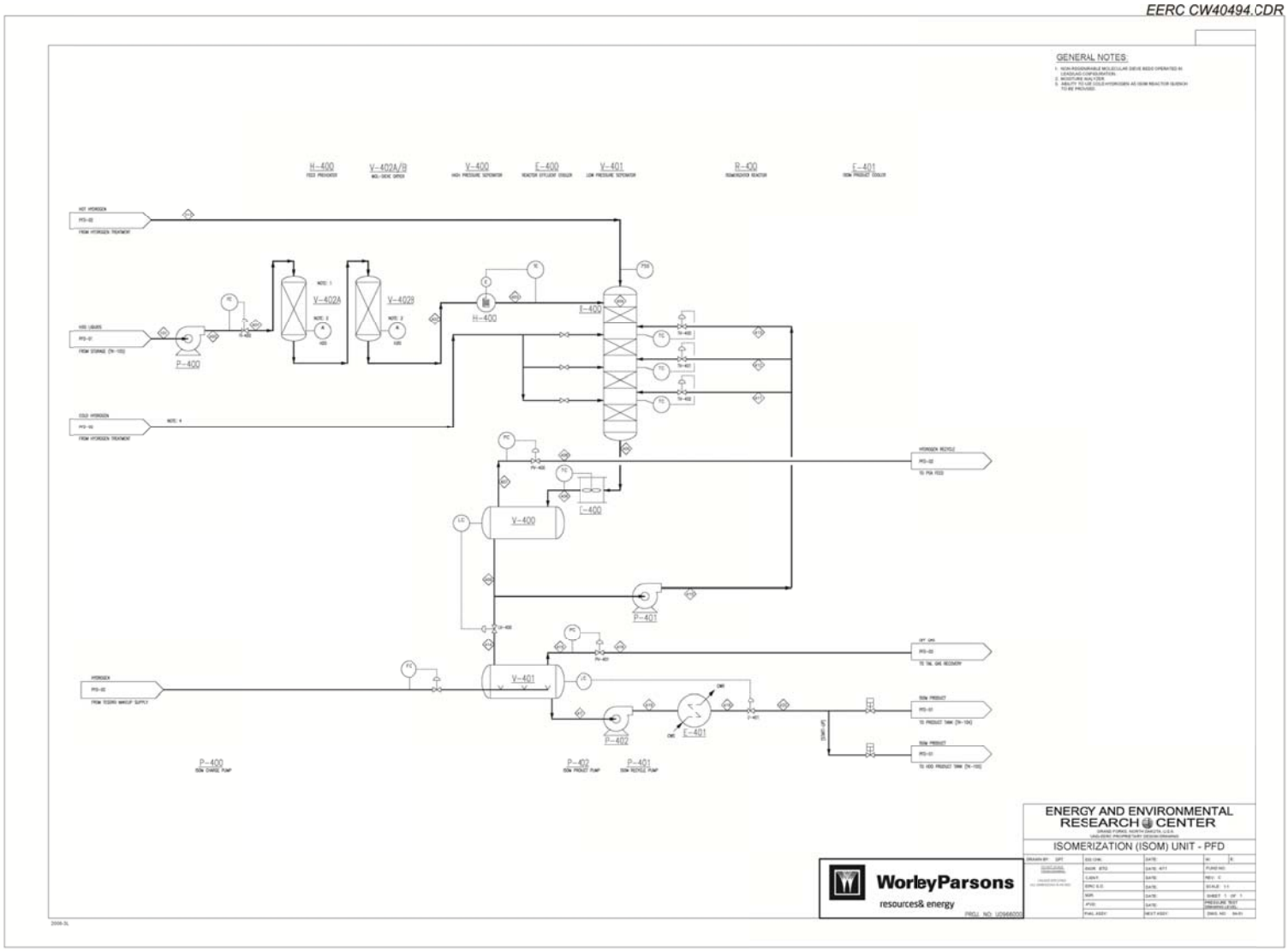

Figure 29. ISOM unit PFD.

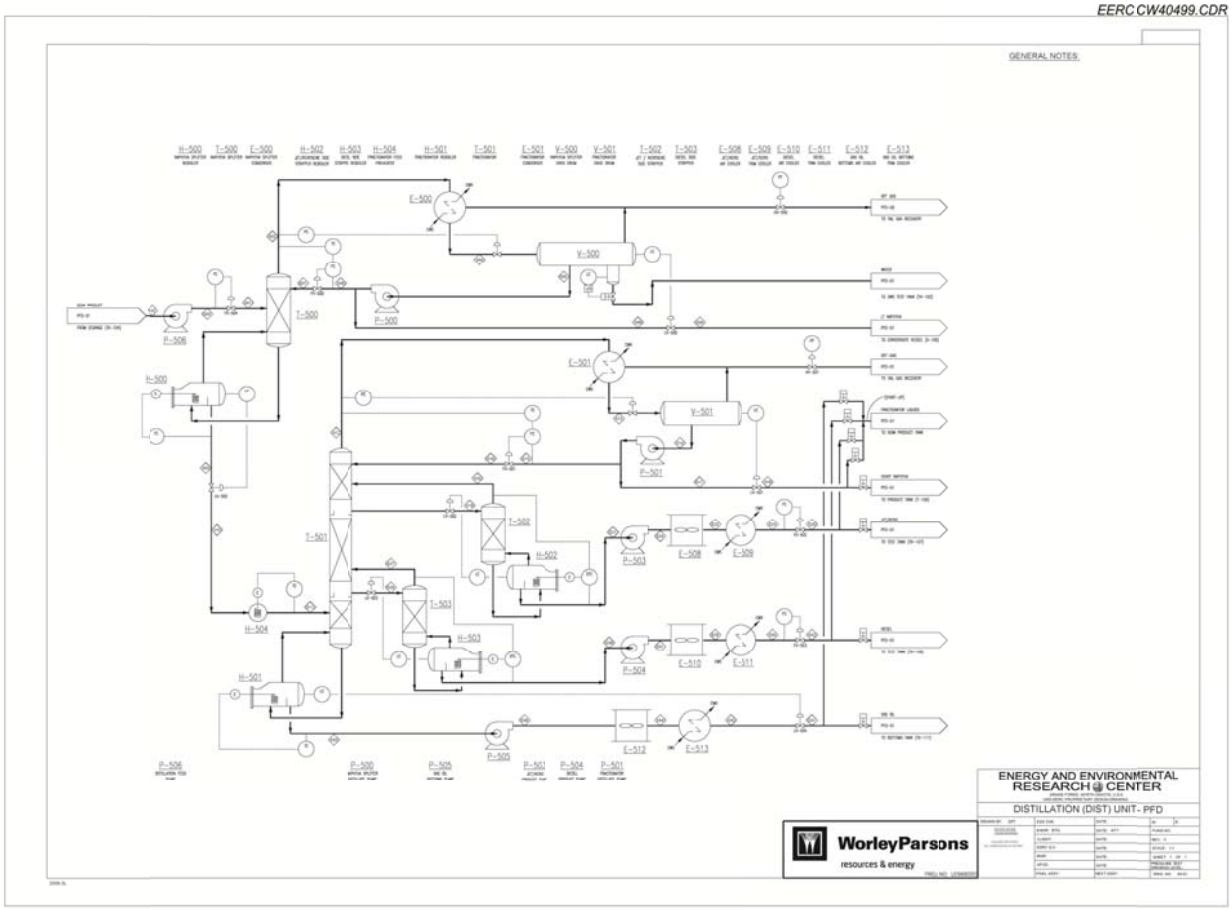

Figure 30. Distillation unit PFD.

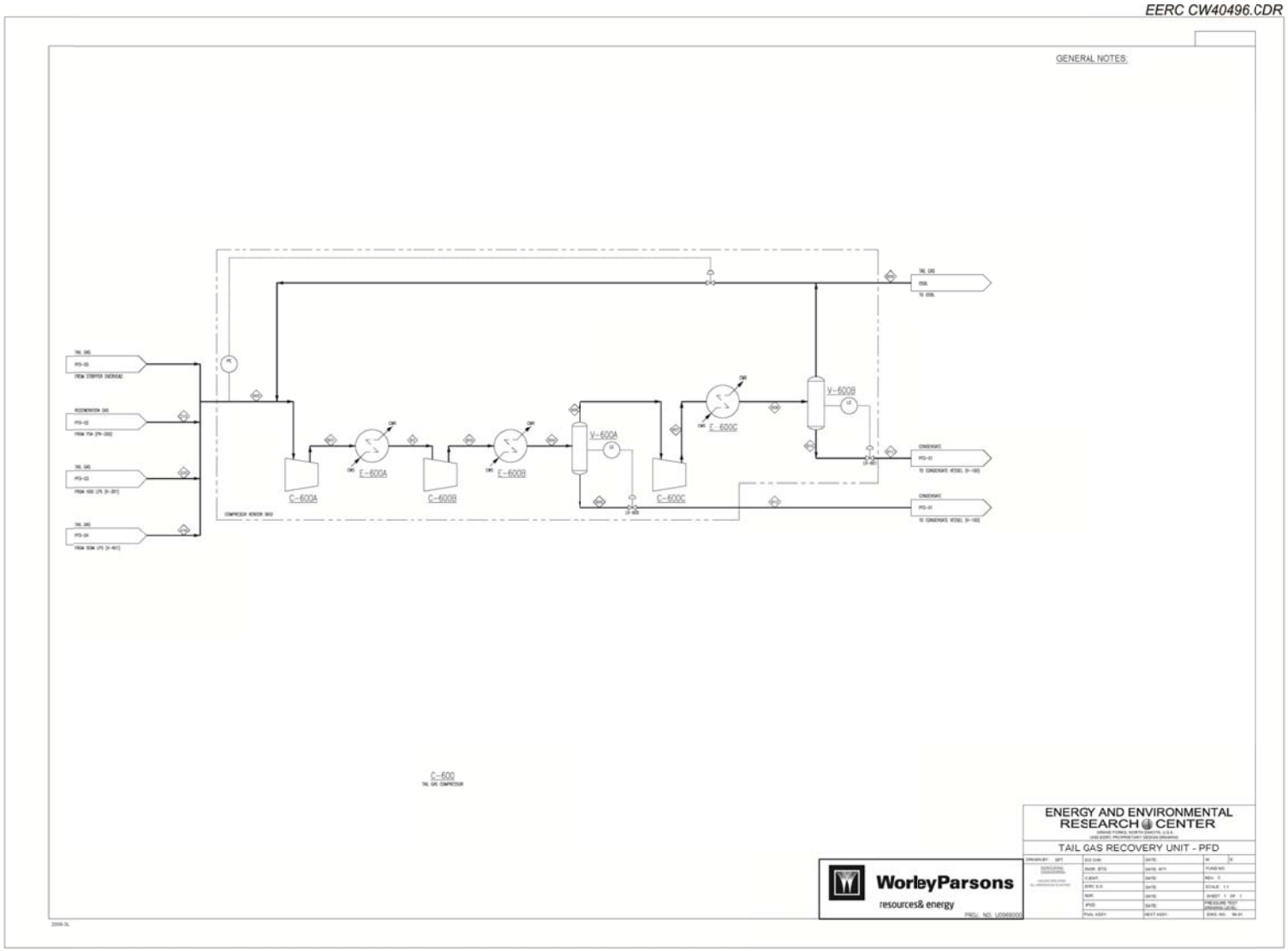

Figure 31. Tail gas recovery unit PFD.

SUMMARY

Several tasks were completed to support the ultimate project goal of producing a pilot plant design biddable package. Two North Dakota-grown crops, crambe and canola, were investigated for their suitability as feedstock to a CHI processing facility. The fatty acid profile of crambe makes it an ideal crop for maximizing diesel production; however, both diesel and jet fuel can be produced from either crambe or canola oil.

An economic model was developed and showed that the major factors influencing CHI plant economics are feedstock cost, blend strategy, and RIN credit value. Capital cost and hydrogen cost were also studied but showed less of an effect on overall plant economics.

Laboratory experiments were conducted to support the reactor design and plant design efforts. The data gathered from these experiments was used to design scaled-up versions of the HDO reactor and ISOM reactor. These reactors include a heat management scheme based on laboratory data and are dimensioned to ensure performance similar to what was observed in the laboratory reactors. A balance-of-plant design effort was completed and includes PFDs, select P&IDs, a stream catalog, a plot plan, and an estimated total installed cost for the pilot plant facility.

APPENDIX A

USDA SUMMARY REPORT

Crambe Seed Oil Extraction and Refining
(Cooperative Agreement No. 58-3620-0-408)

Oil extraction

Whole crambe seed (190 lbs/batch) was cooked at 180-210 ^{o}F and dried to around 4.5% MC using a seed cooker/ conditioner (French Model 324 Lab Conditioner, French Oil Mill Machinery Company, Piqua, OH). Total cooker residence time was 65 min. The oil was extracted from the cooked/dried seed using a screw press (French Model L250 Laboratory Screw Press). The seed meal (foots) in the oil was allowed to settle before decanting the oil into a 55-gallon drum. The pooled oil was filtered before degumming to remove the remaining finer solids in the oil.

Oil refining

Degumming. The oil was heated to 120 ^{o}F and 0.3% (w/w) 50% citric acid (ADM Citrosol 502) was slowly added with continuous mixing. After 15 min, 2% (w/w) warm (150 ^{o}F) deionized water was sprayed on top of the oil and mixing continued for another 30 min. The water and gum fraction was allowed to settle overnight and then drained.

Bleaching. The degummed oil was heated to 195 ^{o}F under 28 inches Hg vacuum and held for 20 min. After breaking the vacuum, 5% (w/w) bleaching clay (Pure Flo Perform 4000, Oil-Dri Corporation, Chicago, IL) was added under constant mixing. The vacuum was restored and the oil was heated to 230 ^{o}F and held at this temperature for another 30 min. The oil was then cooled to 150 ^{o}F and the bleaching clay was filtered out.

Deodorization. The bleached oil was heated to 200 ^{o}F (under 28 inches Hg vacuum) using steam-heated coils inside the deodorizer. The oil was agitated by turning the sparging steam on and off when the oil temperature was around 180 ^{o}F. The band heater was then turned on to continue heating the oil to the target temperature of 480 ^{o}F. The vacuum was increased to 5 mm Hg and the steam sparger was left on when the oil temperature was around 350 ^{o}F. (Note: Only 60 gallons of oil was left after bleaching. A full deodorizer charge is 100 gallons. As a result, only the lower portion of the heating zone was covered by the oil. The oil heated up very slowly and the temperature only went up to around 430 ^{o}F after 4 hours. The deodorization was aborted at this point and the oil was cold down to 150 ^{o}F and then filtered. Three gallons of oil were re-deodorized using the 1.5-gallon deodorizer.)

Seed and oil analyses

Moisture and oil contents of the seed and press cake samples were obtained by following AOCS official methods Ba 2a-38 and Ba 3-38, respectively. The free fatty acid (expressed as oleic acid) in the crude oil was determined using a Methrohm 702 SM Titrino (Methrohm, Ltd., Herisau, Switzerland) following AOCS official method Ca 5a-40. The peroxide value was determined using Metrohm Titrino 712 titrator fitted with Pt 6.043.100 electrode. The oil (2 g) was dissolved in 10 ml solvent mixture (glacial cetic acid/1-decanol (3:2) and 25 mg iodine) and kept in the dark for 1 min. Distilled water (50 ml) was added and immediatelt titrated. The titrant was 0.01 M $Na_2S_2O_3$ prepared fresh from 0.1 M $Na_2S_2O_3$. A blank sample was also titrated to determine the baseline. Oil color was measured using the Gardner and CIE L*a*b* color scales in the Lovibond PFX 995 Tintometer (The Tintometer Ltd., Amesbury, Wiltshire, UK) employing a 10 mm cell pathlength.

Seeds received from and samples sent back to EERC

1. Crambe seeds received: 3,580 lbs
   a. Oil content = 31% (by pNMR)
   b. Moisture content = 7.8%
   c. Crude oil extracted = 601 lbs (after filtration)
2. Shipped back to EERC
   a. 2,151 lbs press cake (about 15% oil content)
   b. 16 lbs each of filtered crude oil, degummed oil, and bleached oil
   c. 404 lbs deodorized oil
   d. 22 lbs re-deodorized oil
   e. Some degummed and bleached oils recovered from holdup in piping, pump or filter bags.

Analyses of crude, degummed, bleached, and deodorized crambe oils

	Crude oil	Degummed oil	Bleached oil	Deodorized oil 1[a]	Deodorized oil 2[b]
FFA, % (as oleic)	0.39	0.49	0.38	0.2	0.19
Peroxide, meq/kg	0.03	0.02	0	0	0
Color:					
Gardner (10 mm)	11.0	10.9	3.1	3.6	4.1
L*a*b* (10 mm)					
L* (0=black, 100=white)	75.99	74.63	92.95	90.68	89.41
a* [(-) green, (+) red]	13.42	11.14	-2.83	-1.85	-1.47
b* [(-) blue, (+) yellow]	124.87	122.7	15.72	19.48	23.72

a - 100 gallon deodorizer
b - 1.5 gallon deodorizer

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APPENDIX B

CATALYST LIFE

CATALYST LIFE

Catalyst longevity is a critical component to an economical chemical process and maximizes run time between reactor shutdowns. To evaluate catalyst life, long-duration experiments were run for over 1000 continuous hours while product quality and reactor temperature and pressure were monitored. To acquire these data, a small reactor system was fabricated that could be operated with minimal oversight for extended periods of time. Four reactors were designed and fabricated to allow simultaneous long-term operation.

The catalyst maintenance reactor system consisted of four identical reactor trains in parallel. Each reactor had a dedicated feed system, reactor, and product collection system. Figure 1 shows the four feed pots and corresponding feedstock pumps. Figure 2 shows the four reactors and the four product collection systems. Each reactor was operated at slightly different operating conditions to study the effect of temperature, hydrogen availability, and catalyst type on product quality and catalyst life. The feedstock for these experiments was canola oil.

Process data, including temperatures, pressures, and flow rates, were logged by a computer. When product was collected, it was analyzed for composition using gas chromatography–mass spectroscopy (GC–MS), acid concentration using potassium hydroxide titration, water content using phase separation, and overall mass conversion using product weight.

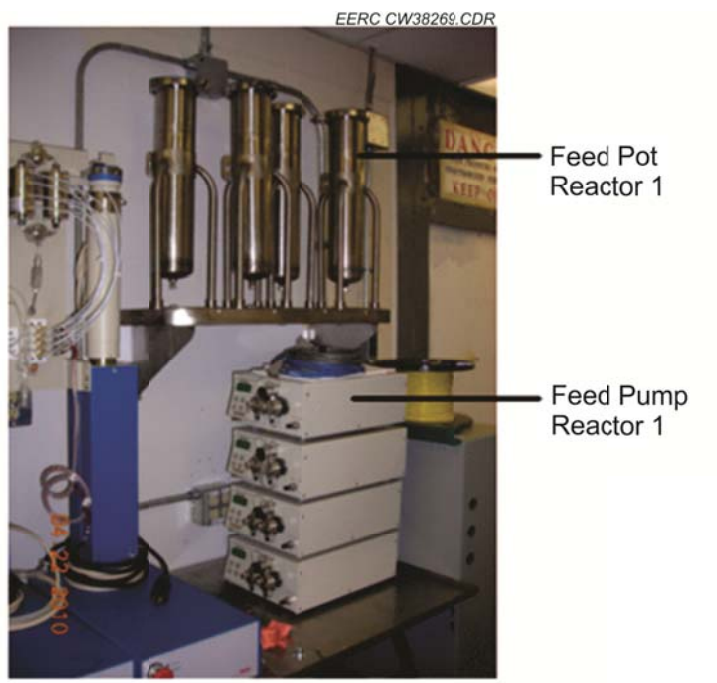

Figure 1. 1000-hr feed system.

Figure 2. Catalyst maintenance reactors and product collection systems.

Figure 3 shows a schematic of one of the catalyst maintenance reactor systems. The canola oil feed was pumped from a feed storage pot by a dual-piston high-pressure liquid chromatography (HPLC) pump capable of pumping 0.00–24.00 mL/min at pressures up to 6000 psig. Hydrogen was fed from bottled gas cylinders and metered by a Porter mass flow controller. Liquid feedstock and hydrogen were fed to the bottom of each reactor. The reactor vessels were ½ inch in diameter and 18 inches tall. 120-V, 500-W cable heaters from Entherm were wrapped around the catalyst-filled, bottom portion of the reactors to provide heat. Catalyst and glass beads were inserted into the reactor along with a top and bottom thermocouple. Pressure transducers measured system pressure upstream and downstream of each reactor. Exit tubing was heated by heat tape from the reactor outlet to the product collection vessel inlet. Liquid hydrocarbons and water were condensed in the collection vessel. Noncondensable gases exited the product collection vessel and were passed through an activated carbon trap before exiting through a back-end mass flow controller. The back-end mass flow controller controlled the system pressure by restricting the flow rate of noncondensable gases exiting the system. When sampling was done from an on-stream product collection vessel, a pressurized, bypass product collection vessel was brought online. After liquid product was collected from the on-stream product collection vessel, the vessel was repressurized with hydrogen to system pressure and brought back online. This sampling technique prevented loss of system pressure during product collection.

The result of catalyst life experiments demonstrated long-term catalyst activity. Three continuous flow reactors were operated for 2300+ hours while the hydrocarbon product was analyzed for signs of catalyst deactivation. The reactors operated at slightly different conditions, allowing researchers to investigate the relative effects of hydrogen and temperature on catalyst activity. Specifically, the reactors operated at a baseline condition, a reduced hydrogen condition, and a high-temperature condition. Table 1 shows the test matrix for these experiments.

Table 1. Catalyst Maintenance Reactor System Test Matrix

Reactor No.	Condition	Hours Logged	T, °C	P, psig	Feed Type	Feed, mL/min	H_2, mL/min	Catalyst Weight
1	High Temp.	2764	$T_2 \pm 5$ºC	P_1	Canola Oil	0.06	99	8.3g
2	Baseline	3026	$T_1 \pm 5$ºC	P_1	Canola Oil	0.06	99	8.3g
3	Reduced Hydrogen	2398	$T_1 \pm 5$ºC	P_1	Canola Oil	0.06	80	8.3g

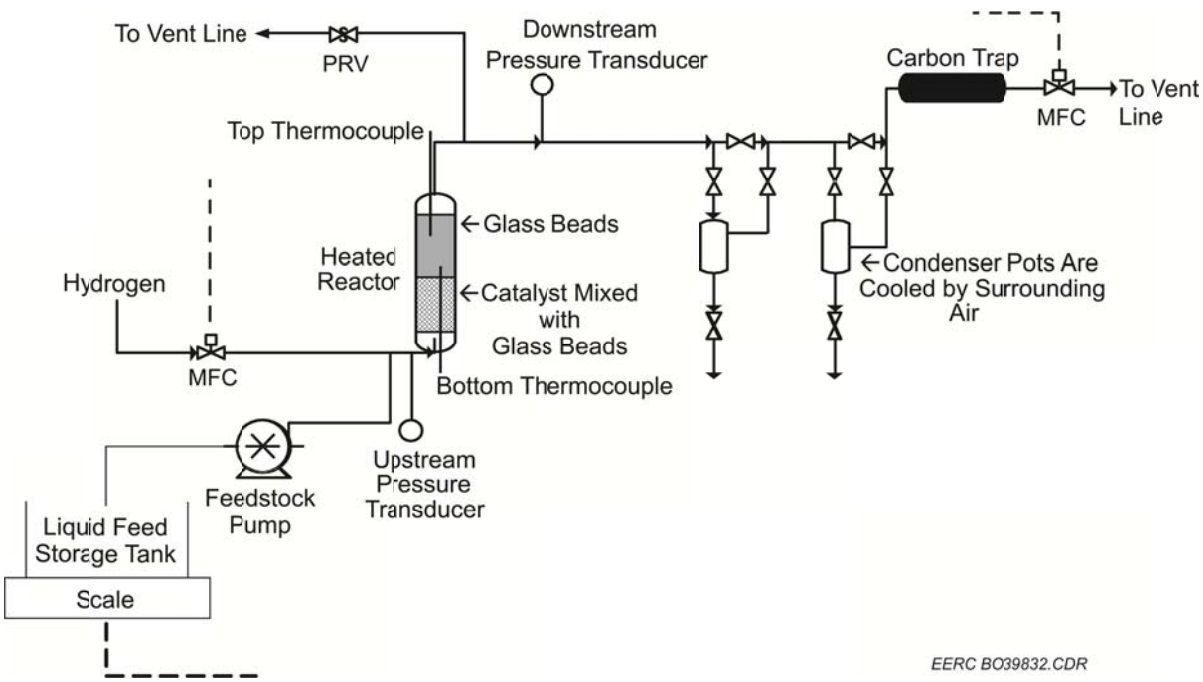

Figure 3. Schematic of catalyst maintenance reactor system.

The hydrocarbon product from each of the three reactors was analyzed over time via GC–MS. The hydrocarbon product composition did not change over the test period as shown in Figures 4–6.

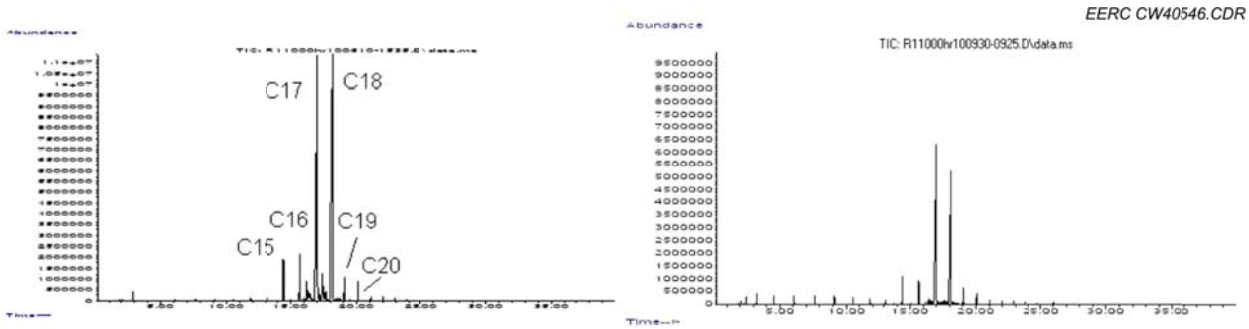

Figure 4. Reactor 1 – first steady-state sample (left) and end-of-run sample (right).

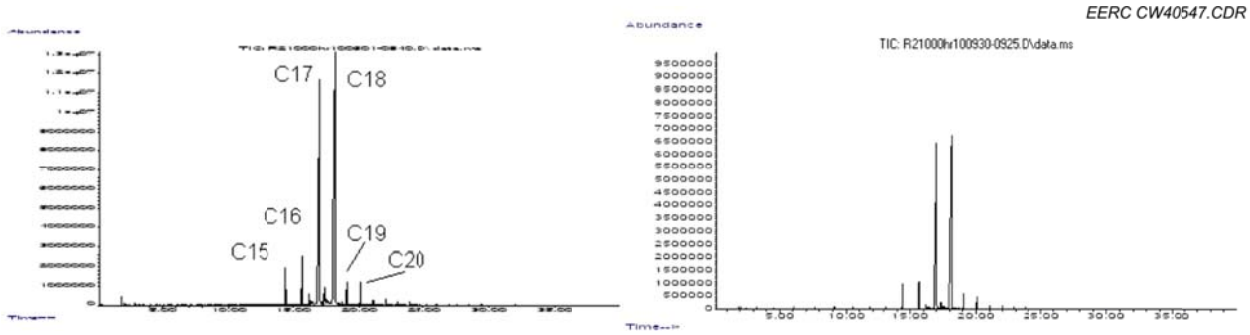

Figure 5. Reactor 2 – first steady-state sample (left) and end-of-run sample (right).

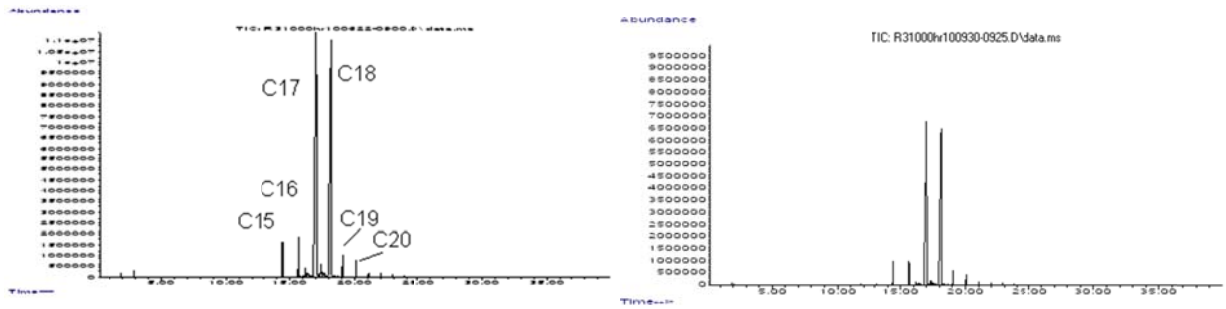

Figure 6. Reactor 3 – first steady-state sample (left) and end-of-run sample (right).

To compare remaining catalyst activity after 2300+ hours of time on stream, the three reactors were operated over a similar temperature range while product composition was analyzed via GC–MS and product acid number was measured via potassium hydroxide titration. Within a 60°C temperature range, Reactors 2 and 3 produced a product with similar hydrocarbon composition and acid content. This indicated that the reduced hydrogen flow rate to Reactor 3 did not have a significant effect on catalyst activity, compared to the baseline condition. Reactor 1, however, consistently produced a higher-acid product than Reactors 1 and 2 at similar temperatures, indicating that long-term operation at high temperature caused the catalyst to deactivate faster than the baseline condition. These results are shown in Figure 7.

CATALYST TOLERABILITY TO METHANE AND CARBON MONOXIDE

At the completion of the initial catalyst life evaluations utilizing pure hydrogen feed gas, a second set of tests were conducted to evaluate potential catalyst life implications utilizing a impure feed gas consisting of hydrogen, methane, and carbon monoxide. The mixture of these gases, specifically 95% hydrogen, 4.5% methane, and 0.5% carbon monoxide, was selected to replicate a typical nonpurified gas stream found available at petroleum refineries.

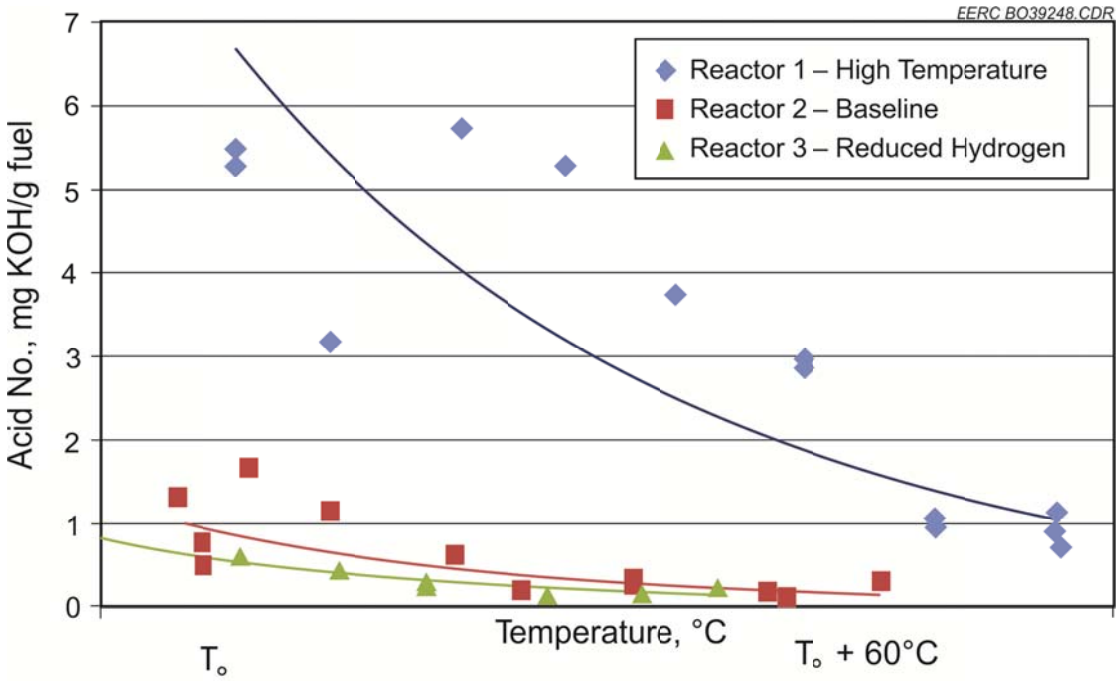

Figure 7. Product acid concentration after 2300 + hours of continuous operation at three conditions.

Two reactors were utilized: one containing a hydrodeoxygenation catalyst and the other reactor containing an isomerization catalyst. Samples of each product were collected every 2 days and analyzed by GC–MS, and the acid content was measured on the hydrodeoxygenation (HDO) product only. After over 1400 hours of operation, the acid number of the HDO product was still below 0.5 mg KOH/g fuel, as shown in Figure 8, and the hydrocarbon composition remained constant. The acid number of the product increased to above the 0.5 mg KOH/g fuel level for a short period of time around 800 hours. At this time, there was a significant loss of gas feed because of mechanical failure, which caused an increase in unreacted fatty acids in the product, leading to an increased acid number. Once the gas feed was restored to the appropriate concentrations, the product quality returned. The acid number also tends to cycle from extremely low concentrations of approximately 0.1 up to 0.4 because of fluctuations of reactor temperature.

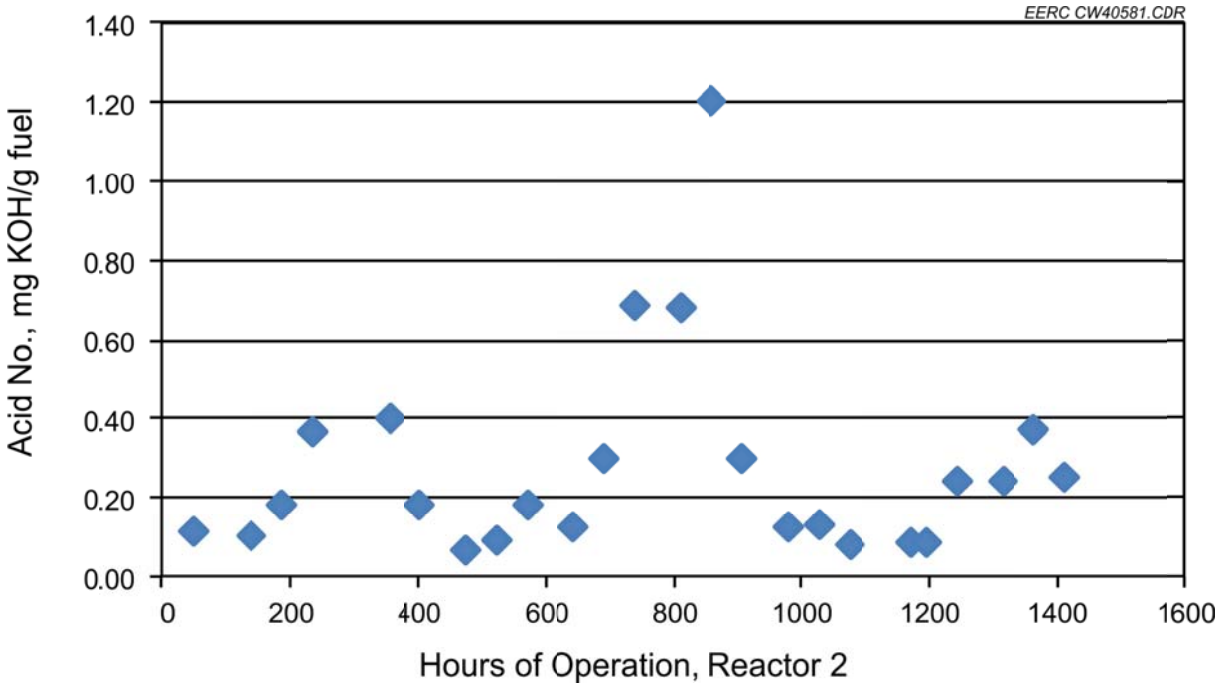

Figure 8. Hydrocarbon product quality over approximately 1400 hours of operation.

GC–MS chromatograms for the HDO and isomerization products are shown in Figures 9 and 10, respectively. The hydrocarbon distribution of the HDO product remains consistent, containing hydrocarbons ranging from pentadecane (C15) to eicosane (C20). The hydrocarbon composition of the isomerization product also remains consistent and contains hydrocarbons ranging from pentane (C5) to eicosane (C20).

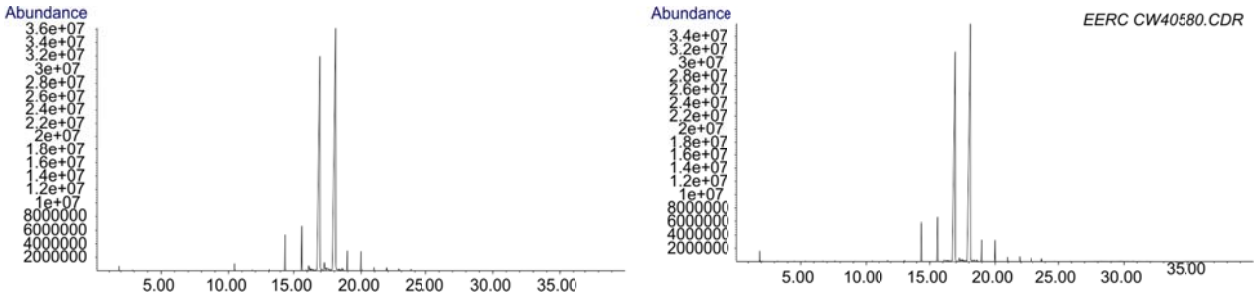

Figure 9. HDO product – first steady-state sample (left) and end-of-run sample (right).

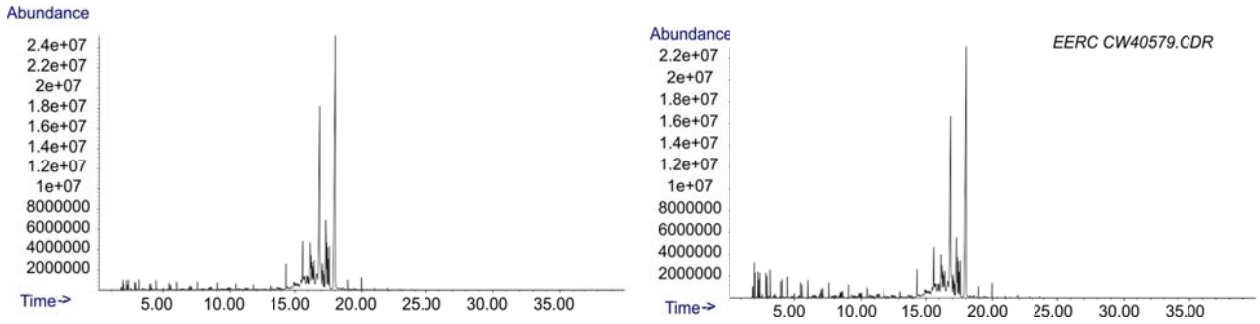

Figure 10. Isomerization product – first steady-state sample (left) and end-of-run sample (right).

The overall results of the catalyst life tests, utilizing mixed gas, indicate that the presence of methane and carbon monoxide in the hydrogen feed do not impact the quality of product and catalyst activation does not occur.

APPENDIX C

MANKATO STATE UNIVERSITY'S REPORT

MnCAR

Minnesota Center for Automotive Research

6/21/2011

TO Marc Kurz
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RE Fuel Consumption and Gaseous Emissions Testing Results of a Renewable Diesel Fuel

INTRODUCTION

Below you will find specific testing details for the program to measure the fuel consumption and gaseous emission characteristics of a compression ignition engine operating on both petroleum Diesel fuel and renewable Diesel fuel provided to MSU by the EERC. All testing was conducted using the ISO 8178 testing procedure for engine emissions following SAE J-1088 Recommended Practice. The constituent fuels used in the study were 2007 ULSD Emissions Certification Diesel fuel and the fuel provided by the EERC.

TEST ENGINE and DYNAMOMETER

The engine used in the study was a Briggs & Stratton Vanguard, 4-cycle, 3 cylinder, in-line, liquid cooled Diesel engine (Photo 1). The model number of the engine is 582447 and the engine displacement is 952 cc.

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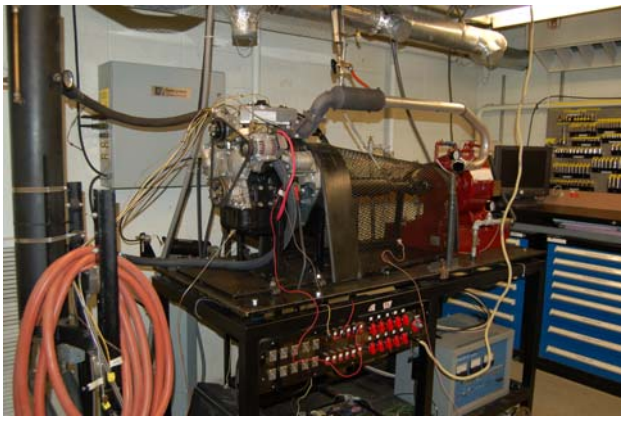
Photo 1

Photo 2

The engine was mounted to a MW Model 66HS eddy current engine dynamometer with automated controls shown in Photo 2. The dynamometer control package and data acquisition system enabled the engine to be operated at specific load and rpm set points that corresponded to EPA testing protocol. At each specific set point gaseous emissions along with particulate emissions were measured following the ISO 8178 type C1 standard, which is designed for off road stationary engine applications. The emissions measured were hydrocarbons, oxides of nitrogen, carbon dioxide, carbon monoxide, and oxygen.

All gaseous emissions measurements were made using California Analytical Instruments Emission Equipment. The emissions bench is shown in Photo 3. The emission analyzers consisted of the following:

* CAI 300-HFID Heated Flame Ionization THC Analyzer
* CAI 300-CLD Chemiluminescence NO_x Analyzer
* CAI 300 NDIR Non-Dispersive Infra-Red CO and CO_2 Analyzer
* CAI Paramagnetic O_2 Analyzer

Particulate measurements were measured using a particulate trap shown in figure Photo 4 and the sample probe shown in Photo 5.

Photo 3

Photo 4

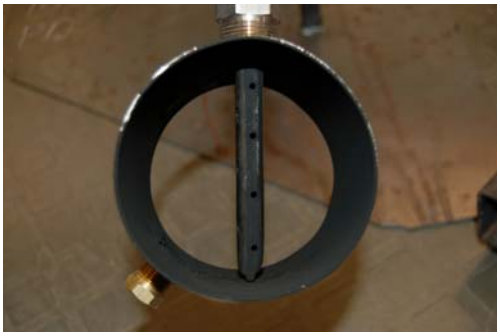
Photo 5

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TEST PROCEDURE

The engine was placed on the dynamometer and the power curve was measured to determine the maximum output of the engine. This was necessary because the test procedure used is referred to as the ISO 8178 11 Mode test procedure. A mode is when the engine is operating at a specific rpm and load point. Figure 1 shows the 8 mode points that were used for this study.

Mode Points	Max.	1	2	3	4	5	6	7	8
Torque (lbf)	26	26.0	19.5	13.0	2.6	25.0	19.5	13.0	0
Rated Speed (RPM)	3600	3600	3600	3600	3600				
Peak Torque Speed	3400					3400	3400	3400	Idle

Figure 1

The test procedure was conducted starting with Mode 1 and continuing to Mode 8. Once the engine was stabilized at each mode point measurements were recorded for 300 seconds. Specific data recorded included:

* HC concentration
* CO concentration
* NOx concentration
* CO2 concentration
* O2 concentration
* Engine RPM
* Engine torque
* Fuel consumption

The test sequence was conducted three times on each fuel. The raw data from each test mode was used to determine the brake specific emissions and fuel economy data that is reported in the results section of this report.

TESTING RESULTS and DISCUSSION

The data presented will include a comparison and summary of three specific operating characteristics of the engine operating on both Certification Diesel fuel and the EERC Renewable Diesel.

The emission certification requirements for the engine used in the testing are shown in Figure 2 below. The federal requirements set maximum levels of NMHC (Non-Methane Hydrocarbons) + NOx; CO and PM (Particulate Materials). Individual test results are mathematically calculated by weighting each individual mode and summing the total.

Tier 1 Engine Emissions Requirements

	NMHC+NOx	CO	PM
Maximum Concentrations (g/kWh)	9.5	6.6	0.80

Figure 2

PM data is determined by determining the amount of PM that is deposited on a filter paper during the 300 second test. Photo 6 shows the scale and filters used while Photo 7 shows a group of filters after they have been used.

DRAFT

Photo 6

Photo 7

Fuel Consumption

The measure of fuel efficiency for the classification of engine used in the study is the Brake Specific Fuel Consumption (BSFC). The BSFC is the amount of fuel consumed by the engine to generate 1 horsepower for 1 hour. The specific unit of measure for BSFC is the pounds of fuel used per horsepower per hour (LBS/HP-HR). Lower BSFC values indicate that less fuel was used to create a horsepower indicating that the engine was operating more efficiently.

During each mode of operation the amount of fuel consumed was measured and the BSFC was calculated. Figure 3 shows the BSFC values measured when the engine was operated on each fuel. As can be seen in the graph and accompanying data table when the engine was fueled with the EERC Renewable Diesel fuel slightly more fuel to produce the same amount of power.

Figure 3 shows the results of the before and after testing on the Certification Diesel. The results of this testing were different then the results when operating on Bio-Diesel. The engine used slightly more fuel to produce the same amount of power at each mode of the test. The one piece of data that was not supplied was the caloric value of the EERC Diesel Fuel.

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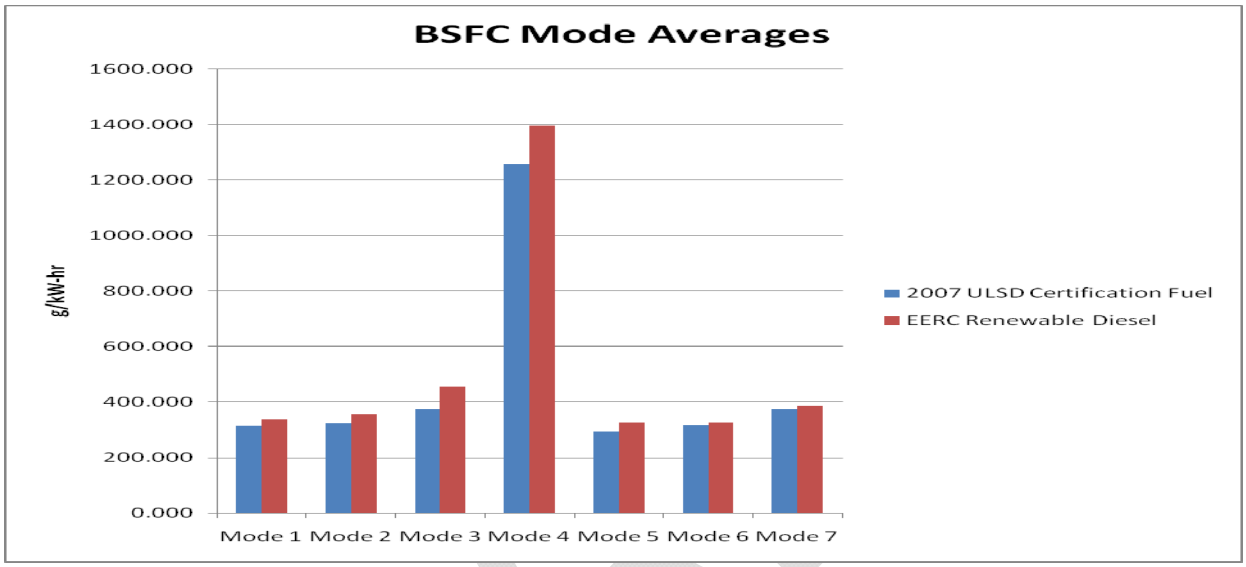
Brake Specific Fuel Consumption Mode Averages								
	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Mode 6	Mode 7	Mode 8
2007 ULSD Certification Fuel	313.398	324.129	373.874	1255.882	293.470	315.603	374.079	
EERC Renewable Diesel	336.824	354.978	454.705	1395.327	327.425	327.710	387.231	
% Change	6.95%	8.69%	17.78%	9.99%	10.37%	3.69%	3.40%	



Brake Specific Fuel Consumption Mode Averages								
	Mode 1	Mode 2	Mode 3	Mode 5	Mode 5	Mode 6	Mode 7	Mode 8
2007 ULSD Certification Fuel	313.398	324.129	373.874	293.470	293.470	315.603	374.079	
EERC Renewable Diesel	336.824	354.978	454.705	327.425	327.425	327.710	387.231	

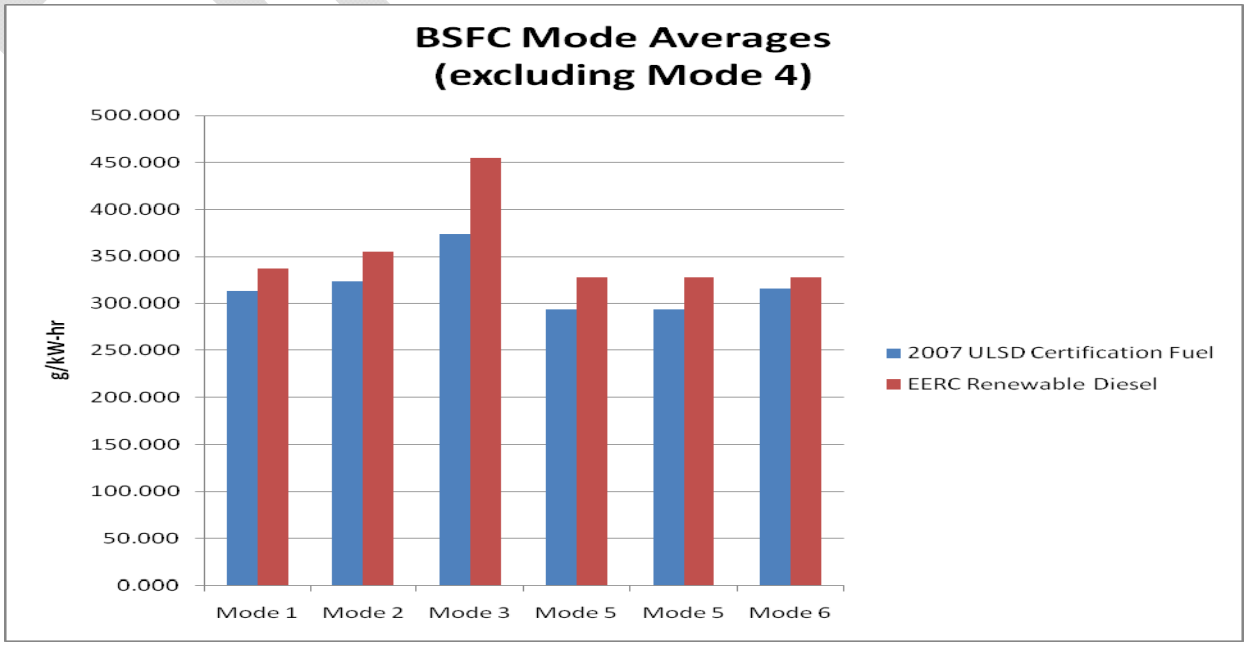


Figure 3

EPA Regulated Emissions

Displayed in Figure 4 are the values for each fuel when compared to the Tier 1 Emission Requirements set by the US EPA. It is important to note that all emission levels were well below the maximum allowable levels. The EERC Renewable Diesel fuel yielded lower weighted emissions for NMHC and NO x levels and higher CO levels.

Weighted Emissions Averages			
	NMHC+NOx	CO	PM
Tier 1 Emission Requirements	9.5	6.6	0.80
2007 ULSD Certification Fuel	5.5	2.2	0.27
EERC Renewable Diesel	3.9	4	0.30

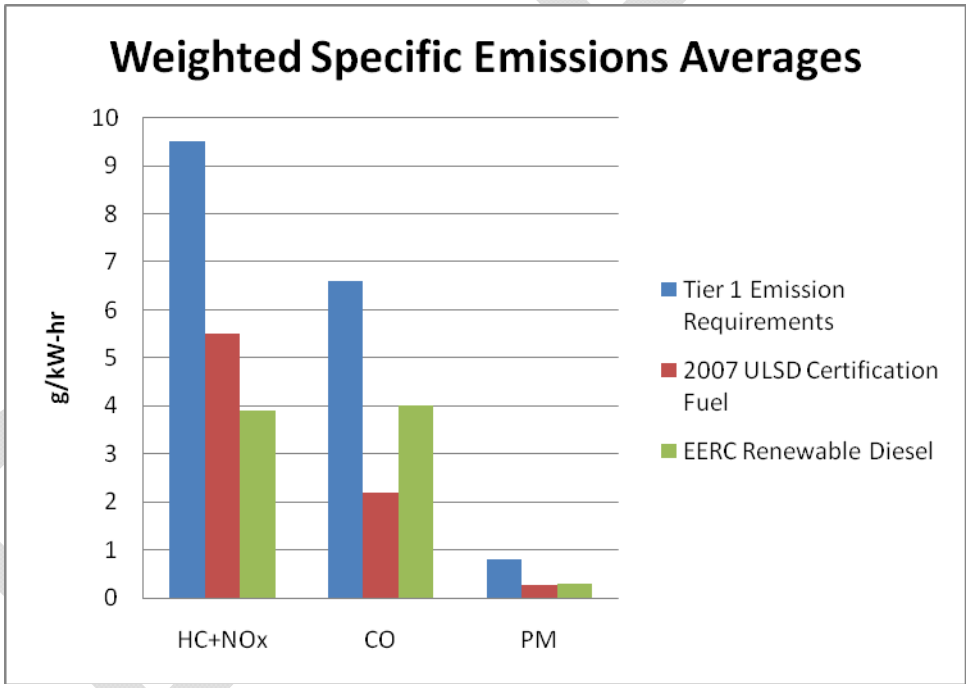


Figure 4