Contract No. R004-010
"Renewable Oil Refinery Development for Commercialization"
Submitted by Energy & Environmental Research Center
Principal Investigator: Chad A. Wocken

PARTICIPANTS

Sponsor	**Cost Share**
Energy & Environmental Research Center	$ 500,000
North Dakota Industrial Commission	$ 500,000
Total Project Cost	$1,000,000

Project Schedule – 12 months
Contract Date – June 24, 2009
Start Date – June 1, 2009
Completion Date – June 30, 2011*

Project Deliverables:
Interim Report: October 31, 2009 √
Interim Report: January 31, 2010 √
Interim Report: April 30, 2010 √
Interim Report: July 31, 2010* √
Interim Report: October 31, 2010*√
Special Report -- Renewable Oil Refinery Economic Assessment: October 31, 2010* √
Interim Report: December 31, 2010*√
Interim Report: March 31, 2011√
Pilot Plant Design Biddable Package: June 30, 2011* √
Final Report: June 30, 2011* √

*Notes the changes made per no-cost extension requests

OBJECTIVE/STATEMENT OF WORK:
The objective of the project is to optimize renewable oil-refining technologies developed by the EERC and advance the technologies toward commercialization with ND grown feedstock. The primary deliverable of the project is a complete, ready-for-bid design of a pilot-scale renewable oil refinery capable of producing diesel fuel, jet fuel, and naptha. Tesoro expressed great interest in using the completed design plans for construction of a pilot plant at the refinery in Mandan. 3M offered a letter of support stating their interest in using naptha to produce carbon-neutral, bio-based plastics and consumer goods. It is anticipated that crambe oil will be utilized as a feedstock. Other oil seed crops such as camelina, canola, and soybeans have potential to be investigated with this research. Previous research conducted at EERC has shown that crambe oil has an optimum carbon chain length for diesel production.

STATUS
This project was broken down into three tasks.
Task 1 – Technology Tailoring for North Dakota Feedstocks
During the July – September, 2009 quarter a series of experiments were conducted at the EERC to produce a variety of hydrocarbon chemical intermediates and fully fungible, drop-in-compatible liquid fuels from a renewable oil feedstock. Canola oil was processed using the catalytic hydrodeoxygenation-isomerization (CHI) technology and samples of hydrocarbon were collected

from each stage of the process. Canola oil is readily available and is characteristic of a large fraction of renewable oils. A comparison of the fatty acid characteristics including carbon chain composition, distribution and saturation levels for several oils was summarized in the report. NDSU CREC has completed the 2009 harvest of crambe grown at test plots in North Dakota. This seed will be processed in the next quarter to provide oil for future EERC tests. Yield and oil content data is being collected and will be reported next quarter.

<u>Task 2 – Renewable Oil Refinery Economic Assessment</u>
This task has not begun.

<u>Task 3 – Renewable Oil Refinery Pilot Plant Design</u>
Data collected from experiments conducted during the period of July – September 2009 were summarized and provided to Tesoro and WorleyParsons Unifield. Following data review, meetings were held to establish a pilot plant design basis including available utility requirements, location, plant size, and plant configuration. Based on this information, WorleyParsons Unifield completed a scope of work and formal cost proposal for review by the EERC. A signed subcontract is anticipated during the next quarter.

The **status report** for the quarter ending **December 31, 2009** has been received. The Contractor has stated the following in the status report:

<u>Task 1 – Technology Tailoring for North Dakota Feedstocks</u>
Experiments were conducted to support the pilot plant design effort. Researchers analyzed the gaseous portions of the reactor effluent in order to generate compositional input for WorleyParsons Unifield's process model. Additionally, algal-derived fatty acid methyl esters were processed in the EERC's CHI process. The algae-derived feedstock was successfully converted in to hydrocarbons.

<u>Task 2 – Renewable Oil Refinery Economic Assessment</u>
This task has not begun.

<u>Task 3 – Renewable Oil Refinery Pilot Plant Design</u>
A project kick-off meeting was held with WorleyParsons Unifield. At this meeting EERC provided WorleyParsons Unifield the necessary information to begin developing process flow diagrams. The process flow diagrams will lay out the pilot plant's major pieces of equipment and piping and will include a catalog showing individual stream temperatures, pressures, compositions and flow rates.

The **status report** for the quarter ending **March 31, 2010** has been received. The Contractor has stated the following in the status report:

<u>Task 1 – Technology Tailoring for North Dakota Feedstocks</u>
The NDSU CREC-grown crambe seed, harvested in fall of 2009 has been crushed and oil-refined to provide feedstock for testing at EERC. Approximately 50 gallons of fully refined crambe oil will be available to the EERC during the next quarter. During the refining process 2-gallon oil samples were retained after each refining step which will allow EERC researchers to evaluate the oil quality of crude crambe, degummed oil and lastly degummed and bleached oil.

At the EERC, process variable (PV) experiments were conducted to define operational conditions which will form the basis of design. A series of tests were conducted using two different catalysts to evaluate the effect of temperature and flow rate on conversion. Temperatures ranged from 310° to 360°C, and flow rate ranged from 0.5 to 2.0 liters/hour. Data generated from these experiments were summarized and submitted to project partners for review.

The next critical design parameter focuses on catalyst life under the conditions described in the PV tests completed in March. To evaluate catalyst life, experiments will be run for 1000 hours of continuous operation while product quality and reactor temperature and pressure are monitored. To acquire these data, a small reactor system is being fabricated that can be operated with minimal oversight for extended periods of time. Four reactors are being built; each with a catalyst volume of 1-5 milliliters to enable continuous testing of up to four conditions consecutively. Testing of these 1000-hr catalyst life reactors will be conducted in the next quarter.

<u>Task 2 – Renewable Oil Refinery Economic Assessment</u>
This task has not begun.

<u>Task 3 – Renewable Oil Refinery Pilot Plant Design</u>
Process design activities are ongoing in collaboration with WorleyParsons. A preliminary balance of plant process flow diagram and general arrangement diagrams (plot plan) were completed and work began on defining the reactor design of the hydrodeoxygenation and isomerization reactors. Additionally, engineering calculations are being performed to evaluate system capacity relative to available utilities and hydrogen supply at the Tesoro Mandan refinery. Data provided to the EERC by Tesoro Mandan personnel suggest that hydrogen availability will dictate process throughput capacity. Initial modeling suggests that a plant of approximately 100 ghp can be achieved. Detailed reactor design and modeling will begin next quarter and will provide the necessary detail to refine system capacity.

A no-cost extension has been granted for this project. The completion date has been extended from June 30, 2010 to December 31, 2010.

The **status report** for the quarter ending **June 30, 2010** has been received. The Contractor has stated the following in the status report:

<u>Task 1 – Technology Tailoring for North Dakota Feedstocks</u>
Fabrication of four 1000-hour catalyst life reactors was completed during this quarter and testing commenced. The 1000-hour reactor system consists of four identical reactor trains in parallel. Each reactor has its own feed system, reactor system, and product collection system. Each reactor is being 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 is canola oil.

Process data, including temperatures, pressures, and flow rates, is being logged by a computer. When productin is collected, it is analyzed for composition using gas chromatography-mass spectroscopy, acid concentration using potassium hydroxide titration, water content using phase separation, and overall mass conversion using product weight. After operating for at least 1000 hours, the catalyst will be removed and sent in for detailed analysis by the catalyst supplier.

Approximately 50-gallons of refined, NDSU CREC-grown crambe was shipped to the EERC this quarter. The refined crambe oil will be converted into jet and diesel fuel samples over the upcoming months using continuous reactor systems and distillation.

Task 2 – Renewable Oil Refinery Economic Assessment
This task has not begun.

Task 3 – Renewable Oil Refinery Pilot Plant Design
Process design activities are ongoing in collaboration with WorleyParsons. A reactor design firm, Impact Technology Consultants, was selected and will work with the EERC to develop the conceptual design for pilot plant hydrodeoxygenation and isomerization reactors. The reactor design effort will use laboratory data and computer models to ensure that the scaled-up reactor systems perform similar to or better than laboratory reactors. Chemical kinetics, mass diffusion, and heat management strategies are being investigated. Once the reactor design is sufficiently defined, WorleyParsons will proceed with designing the remaining process systems, which include feed systems, gas supply liquid recycle, thermal management, product and intermediate tankage, distillation, process control, utilities, and structural equipment.

The EERC is evaluating the feasibility of increasing the pilot plant's capacity to enable the production of 100,000 gallons of jet-grade synthetic paraffinic kerosene during the warmer months of the year (approximately 7 months processing time). Initial engineering calculations indicate that 1) a hydrodeoxygenation flow rate of 340 gph and an isomerization flow rate of 430 gph will achieve this production rate and 2) a hydrogen recycle stream will be necessary. Reactor design, plant design and supporting experiments will continue next quarter.

The **status report** for the quarter ending **September 30, 2010** has been received. The Contractor has stated the following in the status report:

Task 1 – Technology Tailoring for North Dakota Feedstocks
Catalyst life experiments were completed this quarter and demonstrated long-term catalyst activity. Three continuous flow reactors were operated for 2300+ hours while analyzing the hydrocarbon product 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. The hydrocarbon product from each of the three 1000-hour reactors was analyzed over time via gas chromatograph-mass spectrometer. The hydrocarbon product composition did not change over the test period. To compare remaining catalyst activity after 2300+ hours of time onstream, the three reactors were operated over a similar temperature range while analyzing product composition.

Research efforts continued to focus on North Dakota crop oils as fuel production feedstocks. An extensive analysis of crambe oil was conducted this quarter. Basic parameters including oil content, free fatty acid content, moisture and color were analyzed at a USDA facility. Additional analyses were obtained from an independent analytical laboratory. Additional analysis measured metals content, C-H-N, sulfur, and oil density. The data suggests that the degumming process almost completely removed 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, stayed fairly constant between 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. 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.

Approximately 55 gallons of fully refined crambe seed oil was passed through a reactor to convert the triglyceride-rich oil to hydrodeoxygenated hydrocarbon components, and the product was analyzed using a GC/MS. 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.

Task 2- Renewable Oil Refinery Economic Assessment

Commercial plant economic data will be based on projections made using the finalized CHI pilot plant design. The pilot-plant process design and capital equipment cost estimate is not yet complete and therefore cannot be used to estimate commercial plant economics. However, a preliminary economic model has been developed which can be updated as more capital and operating cost data become available. The EERC deliverable entitled "Special Report: Renewable Oil Refinery Economic Assessment" has been completed. This special report is confidential.

Task 3 – Renewable Oil Refinery Pilot Plant Design

Extensive laboratory testing was conducted to support the kinetic model being developed by Impact Technology Development. Chemical kinetics, mass diffusion and heat management strategies were investigated. A kinetic expression was developed that fit all temperature studies and an activation energy was determined. The final kinetic model will calculate reaction rates and feedstock conversion as a function of catalyst bed volume and will be utilized to design a scaled-up reactor that functions similarly to the laboratory-scale reactor. Heat and mass balances were also calculated for the HDO reactor, allowing heat management strategies to be evaluated.

A similar modeling effort has begun for the scale-up of the isomerization reactor. A statistical design of experiments was formulated and laboratory experiments are planned that will gather reaction rate data for the isomerization reaction. These experiments will support the modeling effort by first conducting experiments in a differential reactor and then conducting experiments at higher conversion in a longer catalyst bed.

The balance of plant is being designed by WorleyParsons. This effort was on hold while the HDO reactor was being modeled and defined. There is now sufficient detail around the HDO reactor so that the balance-of-plant design effort can commence in parallel with the modeling of the isomerization reactor. The balance-of-plant design includes feed systems, gas supply, liquid recycle, thermal management, product and intermediate tankage, distillation, process control, utilities, and structural equipment.

The EERC has made significant progress toward completion of the pilot plant design. The project is behind schedule and, therefore, EERC has requested a no-cost contract extension.

A no-cost extension has been granted for this project. The completion date has been extended from December 31, 2010 to May 1, 2011.

The **status report** for the quarter ending **December 31, 2010** has been received. The Contractor has stated the following in the status report:

Task 1 – Technology Tailoring for North Dakota Feedstocks
Analysis continued on the catalyst life experiments that had been conducted. To date the tests have shown that the acid number and hydrocarbon composition of the hydrodeoxygenation production did not change. The acid concentration remained below 0.5 mg KOH/g fuel in both reactors, and the temperature was not increased. This result indicates that catalyst activation does not occur rapidly during the first 1000 hours of operation and suggests that more time on-stream is required to gather the data needed to estimate catalyst life. The analysis of the testing also showed that the product from both reactors consistently contained normal hydrocarbons ranging from pentadecane (C15) to eicosane (C20).

Research efforts continued to focus on North Dakota crop oils as fuel production feedstocks. Last quarter 55 gallons of crambe seed was converted to hydrocarbons via hydrodeoxygenation. Crambe oil is a North Dakota-grown feedstock with chemical properties that make it an advantageous diesel fuel feedstock. To improve the fuel's cold-flow properties, the crambe-derived hydrodeoxygenation product will be isomerized in a second reaction step. The EERC's continuous tubular reactor (CTR) was configured and loaded with isomerization catalyst this quarter and isomerization activities were begun.

Task 2- Renewable Oil Refinery Economic Assessment
No new information was provided regarding the Economic Assessment.

Task 3 – Renewable Oil Refinery Pilot Plant Design
WorleyParsons has continued to develop process flow diagrams (PFDs), mass and energy balance data, and pilot plant layout based on the information previously provided by the EERC and IMPACT Technology Development. A draft general arrangement of the pilot plant facility has been developed. PFDs, which include diagrams and mass and energy data, are expected to be complete in January 2011. The PFDs will be reviewed by the EERC, Tesoro, and Accelergy to ensure that the design basis meets the requirements and expectations of the partners. Review comments will be documented and a meeting will be held to discuss necessary PFD modifications. Once all of the comments have been addressed, WorleyParsons will begin to produce detailed piping and instrumentation diagrams (P&IDs) and equipment lists, followed by safety review and pilot plant costs estimates.

Isomerization testing was conducted at the EERC to support the kinetic model being developed by IMPACT Technology Development. Experiments were conducted in which a crop-oil-derived hydrocarbon was fed 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 from these experiments will be used by IMPACT Technology Development to design the pilot plant isomerization reactor. IMPACT Technology Development now has all of the data necessary to finalize both the hydrodeoxygenation and isomerization reactor designs. These detailed reactor designs will be submitted to WorleyParsons in January for inclusion into the P&ID.

The **status report** for the quarter ending **March 31, 2011** has been received. The Contractor has stated the following in the status report:

Task 1 – Technology Tailoring for North Dakota Feedstocks

Two jet-range and two diesel-range fuel samples were produced from canola- and crambe-derived seed oil utilizing optimized conditions developed during the design effort. Both jet-range fuel samples, one canola-based and one crambe-based, were submitted to the Air Force Research Laboratory for evaluation of military JP-8 fuel specification compliance. The two diesel samples, one each from canola and crambe oil, were submitted to a contract laboratory in Texas for Diesel fuel specification compliance. To date, only the data from the diesel fuel specification testing has been received. 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 are excellent properties for diesel transportation fuel.

A bulk (8-gallon) sample of the crambe diesel has been shipped to the University of Mankato for static engine performance and emission evaluation. These results are expected by the end of May.

Task 2- Renewable Oil Refinery Economic Assessment

Commercial plant economic data will be based on projections made using the finalized CHI pilot plant design. A preliminary economic model has been developed and will be updated with the plant cost estimate when it is complete in May or June 2011.

Task 3 – Renewable Oil Refinery Pilot Plant Design

Reactor design efforts for both the hydrodeoxygenation and isomerization reactors are complete. Kinetic models were developed, based on experimental data. Results from the kinetic models were used to determine the amount of catalyst required to achieve complete conversion, the location of quench nozzles required for heat management, the overall dimensions of the reactor shell, and the amount of insulation required. Useful plots were generated that predict conversion as a function of distance traveled down the reactor length. These plots will be helpful during pilot plant operation.

WorleyParsons continued the balance-of-plant design effort under a modified design basis. Initially, the design basis assumed that the pilot plant would be located at the Tesoro refinery in Mandan, North Dakota. Limitations unique to that facility, such as plot space and availability of utilities, were accommodated for in the pilot plant design. During the first quarter of 2011, Tesoro Mandan announced a $35M plant expansion that will boost their petroleum-refining capacity by 10,000 barrels a day. 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 is not possible; however, Tesoro remains interested in commercial-scale renewable fuel production, and a future project may be possible. The renewable oil refinery pilot plant design is being modified for implementation at another site yet to be determined.

The pilot plant design effort is near completion. The pilot plant design basis has been updated and compiled. Process flow diagrams are complete with only a few minor drafting updates remaining. Stream catalogs are complete and up to date. The plot plan is being revised to reflect the size of major pieces of equipment. Equipment data sheets and an equipment list are being finalized. A utility list, tie-in list, and piping and instrument diagrams are also being completed.

Due to the recent change in pilot plant location, the EERC has requested a no-cost project extension from the North Dakota Industrial Commission (NDIC) that would extend the project end date to June 30, 2011. This extension will allow the time required to produce a useful, non-site-specific pilot plant design and cost estimate.

A no-cost extension has been granted for this project. The completion date has been extended from May 1, 2011 to June 30, 2011.

The **final report** dated **June 30, 2011** has been received and is linked to this website. In addition an addendum dated **July 25, 2011** is also linked to this website. The Summary in the Final Report states the following:

"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."

This project is now complete.

04/04/12