Integrated Biorefinery for Biofuels Production

Final Report

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Executive Summary

This project has focused on very low grade fats, oil and greases found in municipal, commercial and industrial facilities around the country. These wastes are often disposed in landfills, wastewater treatment plants or farm fields or are blended illegally into animal feeds. Using any of these waste fatty materials that are unfit for human or animal nutrition as a clean alternative fuel makes good sense.

This project defines the aforementioned wastes in terms of quality and prevalence in the US, then builds on specific promising pathways for utilizing these carbon neutral wastes. These pathways are discussed and researched at bench-scale, and in one instance, at pilot-scale.

The three primary pathways are as follows:

1. The production of Renewable Diesel Oil (RDO) as a stand-alone fuel or blended with standard distillate or residual hydrocarbons,
2. The production of RDO as a platform for the further manufacture of Biodiesel utilizing acid esterification and
3. The production of RDO as a platform for the manufacture of an ASTM Diesel Fuel using one or more catalysts to effect a decarboxylation of the carboxylics present in RDO

This study shows that Biodiesel and ASTM Diesel produced at bench-scale (utilizing RDO made from grease trap waste as an input) could not meet industry specifications utilizing the technologies that were selected by the investigators. Details of these investigations are discussed in this report and will hopefully provide a starting point for other researchers interested in these pathways in future studies.

Although results were inconclusive in finding ways to utilize RDO technology, in effect, as a pretreatment for commonly discussed technologies such as Biodiesel and ASTM Diesel, this study does shed light on the properties, performance and cost of utilizing waste greases directly as a retail liquid fuel (RDO). The utilization as a retail RDO as a boiler fuel, or for other such applications, is the most important finding of the study.

The thirteen tasks which comprise the study are presented sequentially herein.

Task 1: Engineering, Design and Evaluation of a Thermal Depolymerization Plant (TDP)

CWT and its joint venture partner, Renewable Environmental Solutions, LLC, spent considerable time over the span of many months with its engineers and other business consultants to assess opportunities to commission the construction of a plant in Colorado in accordance with Task 1. Early site visits and meetings in the Greely, Colorado area along with information about the existing Carthage plant and general market conditions were used as the basis for evaluating the viability of a waste-to-oil plant for that region. A site reconnaissance report **(Appendix A)** is included in this summary as a non-confidential example of the level of review the company undertook in determining the suitability of the area given the following market conditions at that time:

1. cost of mixed agricultural feedstock - input
2. cost of petroleum – off take and input
3. government incentive to supplement market sales price of outputs
4. government incentive to supplement the cost of constructing and operating a facility in the geographic area
5. cost of fertilizer - off take
6. cost of land and other utilities
7. cost of plant construction based upon current market cost and company experience in Carthage, Missouri.
8. cost of operations based upon company experience in Carthage, Missouri
9. time required for obtaining permits and other operating permissions

Detailed pro formas and other correspondence (not attached due to confidentiality) were created and tested using many different "what ifs" relating to sensitivity and cost.

After many months of working toward the construction and operation of a bio-refinery, the company determined that is was not the right time to construct in Colorado. Work on this task ended and negotiation commenced to re-define the scope of this project to focus on waste greases to oil on the East Coast.

Detailed site visit report to Greely follows as an example of the effort that was undertaken during the execution of Task 1 (see **Appendix A**):

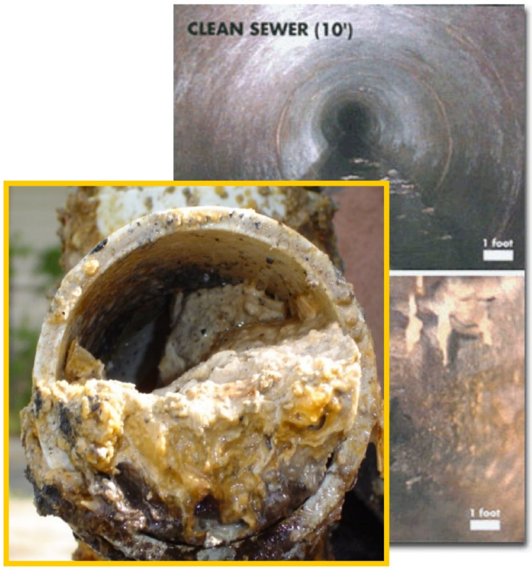
Task 2: Characterization of Waste Material Resource

Introduction

Industrial waste greases in manufacturing, wastewater treatment facilities (scum) and in restaurants (trap greases and used cooking oil) have been identified as a significant cost to municipalities when they are improperly handled. The discharge of these Fats, Oils, and Greases (FOG) from Food Service Establishments (FSEs) and other industrial processing plants creates significant environmental and public health problems in wastewater collection and treatment systems. The risk to the environment is exacerbated by the lack of capacity in many regions to handle these wastes.   This situation makes these sources of organic material an attractive feedstock option for densely populated areas. In the report, “Urban Waste Grease Resource Assessment” by NREL, approximately 9 pounds of yellow grease and 14 pounds of trap grease are produce per person per year.

There are numerous sources of greases that can be used in TCP, including yellow grease, brown grease, trap grease and wastewater treatment skimmings. As for brown and yellow, the main difference is moisture content and free fatty acid percentage. Greases are typically low value material with high moisture, making it very costly to transport, unless water is removed. Trap grease and skimmings are found in “traps” located in restaurants and sewer systems and at wastewater plants. If it is not collected at the source, this trapped waste material poses problems to both municipalities and the public. Often trap grease gets into the sewer system, hardens when temperatures drop, and cause sewer backups and overflows and subsequent health problems. There are numerous collectors of this material who usually use large vacuum trucks to pump this waste out of the trap. Once it is collected, it is transferred to a dewatering facility where some of the water is removed and in some cases chemicals are added. One of the main dewatering facilities located on Long Island is in Lindenhurst, NY. This company provided us with numerous waste grease samples for evaluation and testing.

The Lindenhurst operator has helped educate project collaborators on how the trap collection business works, due to their desire to find ways to improve their overall waste business. This company first dewaters trap grease, then adds chemicals (typically lime), dries the material into a cake like form, and ships it out of state to an approved landfill. For TCP, full dewatering is not required thus reducing chemical demand and operating costs. TCP utilizes the water as it is an essential element in the process. The TCP facility would be ideally located near the dewatering facility which would allow for a local, more environmentally friendly disposal option.



Utilization of waste material for making renewable fuel is becoming more important. Alternative energy production facilities are continually looking for new sources of feedstock to convert to fuel. EPA and state agencies understand that processes that use food crops for fuel can do more harm than good to the environment. States are beginning to mandate that renewable fuels must be produced from waste material. One of the first States to pave the way was Massachusetts, who in July 2008 signed the Clean Energy Biofuels Act, which limits the production of renewable fuels to waste and resources grown "in a sustainable manner" and does not at this time give credits or incentives for food-based fuels produced from soybean or other vegetable oils.

Once confirmed that these feedstocks are viable, wastewater treatment facilities would look to help reduce their processing costs. There in effect could be a symbiotic relationship, as TCP would provide a much needed service by removing trap greases from the sewer systems, resulting in fewer operating issues and providing a renewable fuel they could use at their treatment plant and meet fossil fuel reduction goals. In return, TCP would be able to discharge excess water from the process into the sewer system, instead of installing expensive pretreatment systems to meet tighter discharge standards. The wastewater characteristics (C.O.D/B.O.D) would still be well within the limits of what the wastewater facility would be able to process.

Several sampling and data events occurred during this project to help characterize and shape decisions about what wastes should be used in subsequent feedstock conversion / value added tasks later in the project. In many ways, Task 2 was critical to the rest of the project since characterizing waste has proven to be difficult. Compare skimmings from a wastewater treatment plant to corn for ethanol of soybean oil for biodiesel and the reader will understand that simplicity of homogeneous products vs. complexity in the ebb and flow of waste means that great care and broader research and testing are critical to defining value added process success and economics.

Sample/Data Event 1

Two separate samples were collected from a Long Island source. The initial sample was unrepresentative due to a misunderstanding of when in the process, sample collection should have occurred. The representative sample is characterized on an as-received basis below.

Another sample from a grease transport company in the Massachusetts area was also collected on a small-scale. Results are tabulated below:

As Rec'd Feedstock-Clear Flo Cake	
Test	**Value**
Moisture%	56.8
Fat%	33.4
Ash%	5.85
pH	N/A

As Rec'd Feedstock-McVac Trap Grease	
Test	**Value**
Moisture%	59.3
Fat%	35.8
Ash%	1.9
pH	5.09

Sample/Data Event 2

As a follow-up to the above, another approximately 20 gallons, was collected from Lindenhurst, and initial visual inspection was in line with expectations of raw material. This sample was homogenized and transported to Brookhaven National Laboratory. Their observations follow:

The work in this project is focused on the production of fuels primarily from regional trap grease. A large feedstock sample was obtained from a Long Island renderer – with the intention of using this at both Changing World Technologies (CWT) and Brookhaven National Laboratory (BNL) as our model feedstock. The sample was received at the CWT pilot plant facility in Philadelphia and there heated and blended to a uniform constancy. Analysis of this feedstock was started at CWT and a sample was also sent to BNL for analysis. The tables below provide the results of the basic analysis of this feedstock.

Table 1. Basic Characterization of the As-Received Trap Grease Feedstock

% Loss on drying (water) (1 hour @ 105 C)	28.43
% ash by weight	1.53
% FFA (free fatty acid)	52.12
% total fat	57.09

Table 2. Fatty Acid Profile (only components > 1% included)

C18:1 Octadecanoic (Oleic)	33.67 %
C18:2 Octadecadienoic (Linoleic)	24.62 %
C16:0 Hexadecenoic (Palmitic)	22.42 %
C18:0 Octadecanoic (Stearic)	7.72 %
C14:0 Tetradecanoic (Myristic)	2.34 %
C16:1 Hexadecanoic (Palmitoleic)	1.73 %
C 20:1 Eicosenoil (Gadoleic)	1.00 %

Table 3. Ultimate Analysis of Trap Grease

Carbon	53.41
Oxygen (by difference)	33.90
Hydrogen	11.10
Nitrogen	0.18
Ash	1.26
Sulfur	<0.1
Chlorine	<0.1

The analyses of the trap grease feedstock, including fatty acid profile are very similar to results presented by K. Shaine of Tyson (Brown Grease Feedstocks for Biodiesel, 2002, presentation).

The results in Table 1, indicate that some 5% of the as-received sample, or 7% on a dry basis is non-fatty acid fats and these are expected to be a distribution of mono-, di-, and triglycerides. There is also 13% of the as-received sample not accounted for as fats, ash, or water and these are expected to be other hydrocarbons.

A sample of the trap grease feedstock was ashed in a high temperature furnace and the product analyzed for key elements using a EDXS-SEM tool. Results, shown in Figure 1, below, indicate the primary trace elements. Generally these results do not indicate elements of strong concern.

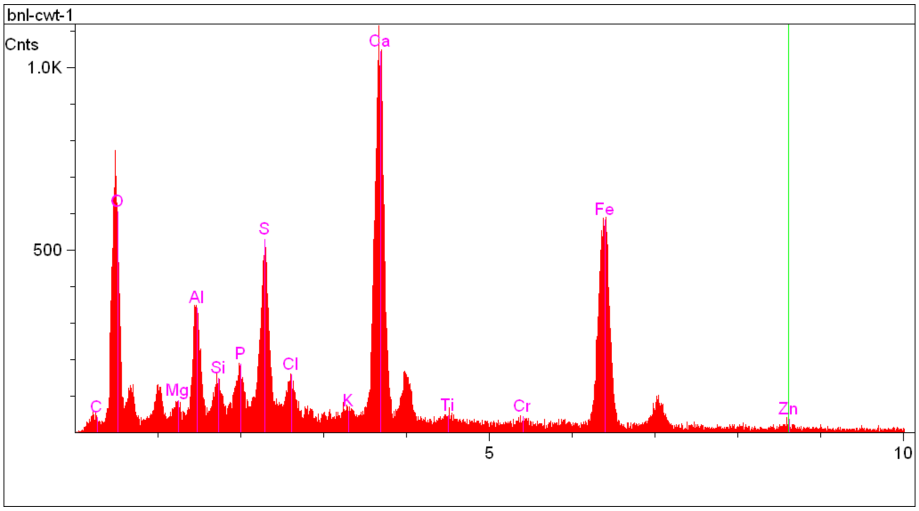


Figure 1. Results of EDXS analysis of feedstock trap grease ash.

The trap grease as received is an emulsion with some components of the grease as a wax at room temperature. Figure 2 shows a photomicrograph and the appearance is one of water as the continuous phase.

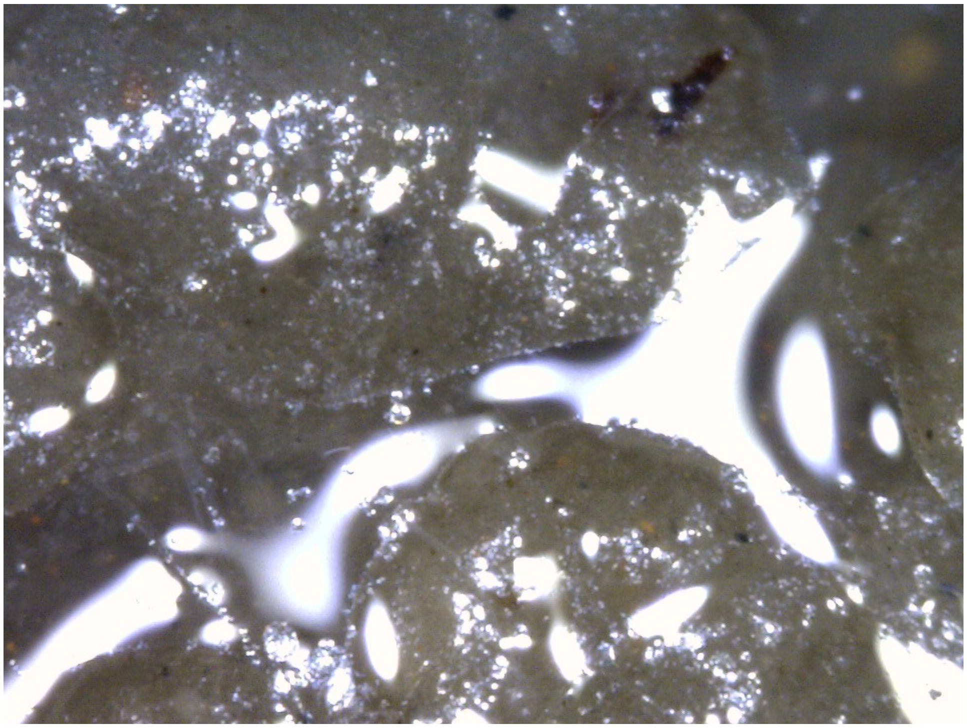


Figure 2. Trap grease photomicrograph

During the first stage of the CWT process the wax melts allowing separation of the oils from the water. It should be noted that in prior work CWT has heated emulsified trap greases at atmospheric pressure without observing a considerable separation. This could indicate that there is a degree of feedstock variability and/or there are more complicated interactions characterizing a separation in some cases. It may be advantageous to at some point obtain a second sample from a different source in order to further explore this separation. Table 4, below, provides literature values for the melting points of the major components in the feedstock fatty acid profile. Stage 1 of the CWT process is run at temperatures in the range of 250 C, clearly well above the melting points of these feedstocks.

Table 4. Literature Values for the Melting Points of the Major Fatty Acid Constituents in the Feedstock

fatty acid	melting point (C)
oleic	13-14
linolic	-5
palmitic	63-64
stearic	69.6
myristic	58.8
gadoleic	20

Sample/Data Event –Subsequent Events

There have been many subsequent events where samples were obtained to look at different technologies (subsequent tasks) and to run pilot work where more raw data was collected and recorded in the due course of this project. Subsequent testing showed that although feedstock has considerable variability (waste is variable from day to day, that is a given) that from a general characterization, the data outlined above held up and was consistent with subsequent feedstocks obtained and utilized.

Task 3: Lab-Scale Thermal Depolymerization Runs to Evaluate Properties

The work done under this task was conducted over the course of the project and addressed the initial characterization phase required by the task to provide a baseline and then in subsequent phases providing support to value added technology experiments to see if a change in basic operation of the TCP would have a more desired outcome to improve upon an aspect of the product made by a value added process. For example, TCP temperatures were adjusted in bench tests later in the project to see if higher hydrolysis temperatures might have an impact on Total Glycerin numbers obtained when making biodiesel.

The lab-scale conversion studies done under Task 3 were all done at the CWT pilot facility in Philadelphia, Pa. TCP is a three step process. The first step or stage is a modest temperature and pressure stage utilized for energy recovery and inorganic solids removal. Stage two is a high pressure medium temperature regime (hydrolysis stage) utilized to convert organics into easily separable, molecularly altered organics, inorganic and aqueous phases. Stage three (thermal cracking temperature and pressure regime) is a high temperature, relatively low pressure environment utilized to further process organics produced from the first two stages. In this study, the project team has focused primarily on the first two stages of the process. This is because the intent of the project was to produce separable bio-oil from stage two and to then look at multiple physical / chemical routes for value adding the bio-oil produced at that point in the process. CWT has experience with taking the bio-oil produced after the second stage of its process and selling it as a neat fuel for stationary boilers already. This project looks at alternatives to this approach and to the continued validity of CWT's existing approach using high percentages of wastes such as grease trap waste as its feedstock.

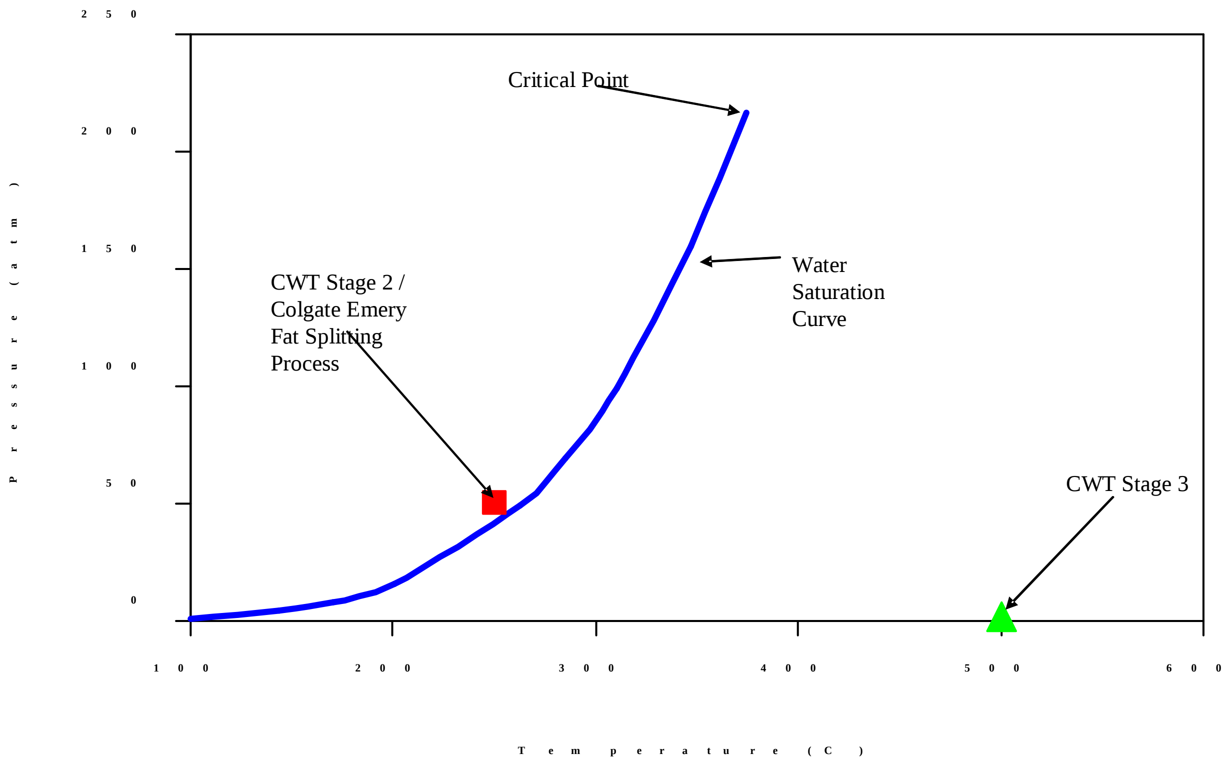
Some specific highlights in terms of process conditions and technologic approach are detailed as follows:

In the first stage the trap grease feedstock which includes water is heated to 150 C to begin the depolymerization of the organic and to then separate some of the high specific gravity solids. In the second stage, the feed material is processed at ~250 to 280 C, with a resulting pressure of between 50 and 65 bar. During this second stage reactions occur including two of the more important ones noted for trap grease; mono- di- and triglycerides are converted to free fatty acids (FFA) while proteinatious material is converted to amino acids and amines which are a mixture of polar and non-polar compounds. Following the second stage the liquid fractions are removed and separated into their aqueous and organic phases. Separation methods are a combination of gravity and/or centrifugal techniques. Gravity techniques employ standard glassware for bulk water-oil separations. The application of any centrifugation further enhances water removal from the oil, as well as reduces ash content in the final oil phase. Both of these improve the overall quality of the final bio-oil product. The organic phase separated from the inorganic and aqueous phases can (as mentioned previously then be placed in a pressurized high temperature heater to decompose the organic into a fuel gas, a mixture of decarboxylated hydrocarbon bio-oil and a carbon char (this latter stage, stage three was performed on some second stage bio-oil and is discussed further below).

Discussion of Literature as it Relates to Process Conditions

The first 2 stages of the CWT process are run at conditions near 200 to 250C and 50 atm. This point is essentially at or below the condition for the Colgate-Emery Fat Splitting process (King, J.W. et. al., Hydrolysis of Soybean Oil, Green Chemistry, 1999. Peterson, A., et. al., Themochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies, Energy and Environmental Science, 2008.). The third stage of the CWT process is nominally at much higher temperature (500 C). Because most of the water is separated between the first and second stage this stage can be run at much lower pressure (~ 2 atm) (Adams, T. et. al., Converting turkey offal into bio-derived hydrocarbon oil with the CWT Thermal Process, Power-Gen Renewable Energy Conference, 2004).

The figure below provides a pressure-temperature chart illustrating the equilibrium vapor/liquid curve for water and the locations of the CWT Stage 2 and Stage 3 processes.



Pressure / temperature chart illustrating basic process conditions

While CWT has a basic set of conditions for their Stage 2 operations there was a need to evaluate the impacts of changing temperature (and corresponding pressure) as well as residence time on the Stage 2 products. For this BNL and CWT worked together to develop a basic test and products analysis matrix. The matrix included tests at 230, 250, and 270 C and residence times of 20, 40, and 60 minutes.

Most tests were been done at 250 C with the three planned residence times. For all three cases the process was very effective in separating the water and oil/fat phases and this would be expected based on the component melting temperatures. For all cases, analyses of the total fats and free fatty acids as well as of the fatty acid profiles indicated no significant difference from that of the moisture-free feed. These results are based on one source of feed, and further work with samples from additional sources would be required to make more broad conclusions.

Nevertheless, based on these results it was agreed to suspend further exploration of the Stage 2 conditions unless a downstream technology that we were to explore would dictate further look at bench conditions (i.e. at one juncture we looked specifically at higher bench temperatures for Stage 2 to look at Total Glycerin) .

Initial Bench Work Summary

A test matrix was planned for the second stage conversion with temperatures ranging from 230 to 280 C and residence times ranging from 20 to 60 minutes. All of these tests were to be done at the natural acidity of the feed material, no pH adjustment. The first set of tests were done at 250 C and essentially yielded the same product FFA content, about 92% at all residence times tested. (Special note: the test method used for FFA determination was AOCS Method Ca 5a-40. There is no evidence at this point to suggest that we can account for 8% tri, di fatty acid. In fact 92 % may only be a test method interference). An additional test was done at 280 C with the same result (this would seem to indicate that since the spitting efficiency should rise to 100% asymptotically with increasing temperature that the 92% may actually be much closer to 100% than the test method indicates). This essentially indicates that the process is effective, even at the shortest residence time of producing a nearly 100% FFA product. GC analysis conducted by BNL indicated that < 0.5% is un-oxygenated hydrocarbons. We discussed the possibility of using shorter residence times but the team feels that times of 20 to 60 minutes are reasonable commercial flow through reactor design times that can be optimized further at a later date but should not have a negative impact on our work with value added strategies.

Essentially the product produced by any of the conditions selected is considered to be representative of what the Stage 2 process product will be and a decision was made to consider this the feedstock for upgrading to biodiesel or synthetic diesel without further optimization of the Stage 2 process conditions at this time. The fatty acid distribution for the Stage 2 product was found to be essentially the same as for the feed trap grease – a mixture of saturated and unsaturated fatty acids from C16 to C 20. The stage 2 product is a semi solid at room temperature but becomes a liquid at temperatures of less than 120 F. The aforementioned test matrix with resultant data were presented in previous quarterly reports .

After Stage 2, some exploratory Stage III "thermal cracking" runs were done with just the oil phase separated from the Stage 2 product. With minimal water present, this reaction could be run at 500 C with pressures of 15-30 bar with minimal gas extraction during the run. Process times were on the order of 60-120 minutes at target temperatures. Example of 3rd stage yields with FFA and API values were presented in earlier quarterly reports.

A GC analysis of the products indicated clear production of hydrocarbons over a wide range from C 16 to C40.

Some Specific Example Results

Initial bench scale tests were performed in Philadelphia on both the Lindenhurst and Massachusetts samples to begin identifying process conditions and % yields of output streams for future characterizations by BNL. A flow diagram of test conditions, process steps and output streams was produced. Percent outputs obtained from each test are also summarized in Table 1 below.

The Lindenhurst results can be viewed as a preliminary exercise to establish some refinement of technique and required steps in the bench process, perhaps as ‘a worst-case scenario’. However, the absolute data is not that meaningful.

Massachusetts test results indicate a consistent oil yield in the middle 30% range. Runs 1 & 2 were subjected to pH adjustment, while Run 3 had no acid addition.

It is important to note that these tests are from small sample sizes and therefore with so few runs, solid conclusions or trends are difficult to assess with a high degree of confidence. The results are based upon the mix of feedstocks fed into the process.

TABLE 1: Summarized Lab Scale Results

General Test Parameters: first stage 150C for 30 min, ramp to second stage 260C for 60 min

Lindenhurst RUN 1 RUN 2

Component	Percent	Percent
Overheads	5	8.9
NCG & Transfer Loss	2.5	2.7
Cake	15.3	15.0
Produced H20	51.4	57.3
Oil	25.8	16.1
Total	100	100

General Test Parameters: first stage 150C for 30 min, ramp to second stage 250C for 60 min

Massachusetts RUN 1 RUN 2 RUN 3

Component	**Percent**	**Percent**	**Percent**
Overheads	6.3	6.8	1.9
NCG & Transfer Loss	11.1	3.9	3.8
Cake	4.3	5.9	3.6
Produced H20	39.5	46.6	55.6
Oil	36.8	36.8	35.1
Rag Layer	2.0	6.8	1.9
Total	100	100	100

Discussion of Lab Methods

The following text provides an introduction to the major bench-scale testing components and their overall purpose and control. This section, along with more detailed operating instructions that are at end of the operating procedures, are provided as part of the project to give project team members and reviewers a clear understanding of the methods and apparatuses used to generate a non-standard fuel product. Renewable diesel fuel oil was produced in this manner for baseline evaluation and for value-added evaluations at Brookhaven National Lab. The bench-scale testing discussed herein was conducted exclusively at CWT's research center located in Philadelphia, Pennsylvania.

The following provides instruction on various aspects of operation. Two overviews are provided: one for 1st and 2nd stage reactions and a second for 3rd stage reactions.

First Stage (depolymerization) or Second Stage (hydrolysis) Processing:

- The Parr Reactor is loaded with a feedstock containing some predetermined amount of organic and water (and in some instances another reactant as well).
- The reactor is then bolted closed.
- All piping connections are tightened and safety devices are inspected externally.

- A temperature set point, residence time, mixing rate and frequency, a pressure maximum, a degassing strategy, etc. are selected for the experiment.
- The operator begins applying heat to the reactor at a controlled rate while observing all selected control conditions. Pressures, temperatures, times, etc. are all recorded on run sheets routinely by the operator throughout each experiment.
- The operator continues to apply heat to the reactor until set-points are reached.
- Temperature and pressure at set point are then maintained for the prescribed residence time.
- The operator then terminates the addition of heat to the reactor.
- Over several minutes the operator then depressurizes the reactor using the manual valve that directs hot vapor to the system's condenser. Some flashed water and organic are thus removed in order to drop the pressure and temperature of the reactor to ambient conditions.
- The operator removes the pressure slowly, so as not to overrun the condensing capacity of the system. The bulk of the reacted product in first stage and second stage experiments will be located in the reactor since only a percentage (usually about 30%) of the water vapor will be removed from the reactor during a typical run. The reactor is opened and material removed to be separated in the laboratory to obtain mass balance and other quantitative and qualitative data. In addition to the products in the reactor, non-condensable gases are removed and so are the condensed liquids at the flash vessel.

Third Stage (hydro-pyrolysis or direct liquifaction):

Portions of the organic product from a first or second stage reaction can be reloaded into the same reactor system to perform a third stage reaction. This is usually a product stream separated after the first two stages to remove a significant proportion of the free water and inorganic fraction. This is done to simulate the concept of a commercial TCP plant upgrading its stage two product. Procedures listed below are quite similar to stages one and two, with some exceptions as follows:

- The Reactor is loaded with a feedstock (and in some instances another reactant as well). A crude water/organic separation step is required.

- The reactor is then bolted closed.
- All piping connections are tightened and safety devices are inspected externally.
- A temperature set point, mixing rate and frequency, a pressure maximum and minimum (nitrogen gas blanket to maintain minimum pressure), a degassing strategy, etc. are selected for the experiment.
- The operator begins applying heat to the reactor at a controlled rate while observing all selected control conditions. Pressures, temperatures, times and other data are all recorded on run sheets routinely by the operator throughout each experiment.
- The operator valves in a supply of high pressure bottled nitrogen to the vapor space in the reactor when he first begins heating the feedstock. This nitrogen pressure provides a partial pressure in excess of the vapor pressure of the organics as they are heated. This holds a high percentage of the organic material in the reactor that would otherwise boil and be carried out of the reactor prior to the prescribed temperature set-points being reached.
- The operator continues to apply heat to the reactor until the temperature set-point is reached.
- Temperature and pressure at set point are then maintained for the remainder of the reaction
- Over a substantial period of time the operator sends “cracked” organic vapor using the manual valve MV-1 to the system’s condenser. Heat continues to be applied to the reactor and nitrogen gas continues to be added to maintain the prescribed pressure and temperature needed to crack the entire portion of the organic stream that can vaporize at third stage temperatures.
- This organic vapor removal and partial condensation continues until all organics that will evolve from the reactor have evolved.
- At this point, the operator terminates the heating and discontinues the application of the nitrogen blanket and removes all products from the apparatus for subsequent evaluation.

Procedures and Protocol for TCP Bench-Scale Testing

TEST CONDITIONS:

Mixing	**200 RPM**

1st Stage Temperature	100°C - 175°C
1st Stage Duration	~10 - 30min
2nd Stage Temperature	200°C - 300°C
2nd Stage Pressure	~500 - 600 psig
2nd Stage Duration	~60 min

- The reactor contents are heated to 150°C with rigorous mixing to ensure intimate contact of the water/ trap grease mixture. The condition is maintained for approximately 10 minutes and followed with a slight degassing before proceeding to the Depolymerization step.
- The reaction is maintained between 500 – 560psi as the material is heated to Stage 2 temperature of 250°C.
- Excess water vapor, produced gases and only a small quantity of FFA is removed through a secondary condenser – accumulator set up.
- The heating cycle is immediately terminated and the reactor vessel is cooled below the water boiling point through the application of cold water to the outside of the vessel.
- Any residual pressure is vented to atmosphere. The contents are photographed, weighed and recorded for yield calculations and quality of separation observation.

Bench Work with Municipal Sewage Sludge Mixed with Waste Greases

As reported in previous quarterly reports, favorable results were obtained when converting wastes and trap grease into fuel oil at bench-scale. Yields and effects of various process conditions on reaction were measured and used to optimize a new pilot reactor at the TDP Philadelphia facility.

The final stage of bench-scale work in this project involved adding sewage sludge to the aforementioned waste greases. This was to see if the combination of the sludge and waste grease, as feedstock to the TCP, will result in an effective means of utilizing sewage sludge to produce RDO with only 2 stages of TCP technology. This aspect of the study looked strictly at whether we could combine municipal sewage sludge (carbonaceous) with waste greases and get an effective separation of an oil derived from the combined streams utilizing only the first two stages of the TCP (its known the process can produce oil from sewage sludge using the third stage of TCP). (Note: Research following this project, if funding is secured, will focus not only on separation and yield, but on the production of co-products such as nitrogen concentrate and class-A biosolids at various process conditions so that a complete techno-economic model can be constructed).

Building on commercial experience and intensive earlier bench-scale research, it was observed that when turkey offal and carcasses are converted, about 35% of the protein component ends up as a carbon and hydrogen component of RDO. The non-polar fraction of amino acids in animal tissue and the non-polar fraction of amino acids in sewage sludge appear quite similar on a percent mass basis, this gave us confidence and good reason to have optimism about sludge and its conversion potential.

In previous quarterly reports literature was presented that showed there was strong similarities between the amino acids in sewage sludge and poultry byproduct waste. The sewage sludge data which was obtained from *"Assessments of Nutritional Value of Singe Cell Protein from Waste Activated Sludge"* (Moses Lebitso, 2010). The poultry theoretical analysis was proven at bench-scale through yield testing and the math tied to physical observation. Based upon this analysis, yield calculations can be made with sewage sludge in line with previous conversions from animal tissue.

In conformance with the aforementioned findings and hypothesis, many bench-scale attempts were made with sewage sludge obtained from Suffolk County, New York, and mixed with waste grease. The team was unable to get definable separation of water from oil from solids that would demonstrate that the amino acid in the sewage sludge could be harvested in a similar fashion as was turkey waste amino acids via the first two stages of TCP processing. Although great water separation was apparent from the first 2 stages as was predicted, the solid and oil phases were not distinct and in the limited scope of this task, work was terminated as a result of the lack of measurable yield enhancement.

Task 4.0 Development of Upgrade Processes to Convert to D6751 Biodiesel

Introduction - Literature

Each year, large amounts of waste fats and oils, along with a small fraction of other food constituents, are collected as trap grease from restaurants and foodservices kitchens. Recently, there has been a major thrust to produce biodiesel from this waste product because of its economic- and environmental merits.

Oils and fats from plants and animals essentially are esters of fatty acids (mainly C12 - C18) with glycerol, known as triglycerides. Because triglycerides have many limitations for use as diesel type fuel (e.g., high viscosity), they are converted to methyl esters, referred to as biodiesel. Fatty acid Methyl esters (FAMEs) have a viscosity close to that of No.2 diesel fuel. Alternatively, a potential approach to converting fatty acids and triglycerides to diesel like fuel would be to produce hydrocarbons through catalytic transformations, including decarboxylation reactions.

While raw oils and fats mainly are composed of the triglycerides of fatty acids, waste cooking oils and trap grease contain a significant fraction of free fatty acids (FFA's) generated through hydrolysis during cooking. Commonly, glycerides are converted to FAMEs by an alkaline-catalyzed trans-esterification reaction with methanol. Practically, acid catalysis is not possible in transesterification because kinetically it is very slow. However, FFA's are converted to FAMEs mainly via acid catalysis using mineral acids, such as sulfuric acid. Thus, a two step process is employed, involving a sequential application of acid-catalyzed esterification, and an alkaline-catalyzed transesterification to convert feedstocks that contain considerable amounts of both FFAs and triglycerides to FAMEs. Because FFAs form soap with alkalis, such as NaOH, which interferes in subsequent steps, direct esterification should be carried out before transesterification.

Esterification of Fatty Acids to Biodiesel

The direct esterification of FFA with methanol to form FAME is a reversible equilibrium reaction catalyzed by a mineral acid, usually sulfuric acid.

$$\mathrm{FFA} + \mathrm{Methanol} \xrightleftharpoons{H^+} \mathrm{FAME} + \mathrm{Water}$$

The reversibility of this reaction is a disadvantage, as the forward reaction cannot go to completion. However, we can shift the equilibrium toward ester formation by using excess methanol, and/or removing the product water. Furthermore, we can move the kinetics towards the forward reaction by changing the type and concentration of the acid catalyst and the reaction temperature.

Catalysis by Sulfuric acid

In studies of biodiesel production with feedstocks containing high levels of free fatty acids, including waste grease, Canakci and Van Gerpan (**1-3**) used a combination of acid-catalyzed esterification and alkaline-catalyzed transesterification to convert FFAs and triglycerides, respectively, to FAMEs. Because esterification is an equilibrium reaction, it does not give high yields in one single step when the product water remains in the reaction mixture. To maximize yield, Canakci and Van Gerpen undertook a two step conversion. After the first step, the ester layer containing residual FFA was separated from the methanol-water layer, and, in the second step, reacted again with acidified methanol. The first step employed 5% sulfuric acid and a 20:1 molar ratio of methanol, both based on the FFA content of the feedstock. In the second step, the sulfuric acid was 5%, and the molar ratio was 40:1, again based on the level of FFAs. The reaction temperature was 55 - 60 0C. This two step treatment resulted in final product with less than 1 % FFAs.

Several other investigators combined acid-catalyzed esterification and alkaline-catalyzed transesterification to produce FAMEs from raw oils containing high levels of FFAs. Ramadhas et al. (**4**) investigated the optimal conditions for producing biodiesel from rubber-seed oil that has a high FFA level (acid value 34 mg KOH/g). They reported that acid-catalyzed esterification reached a maximum at a molar ratio of 6:1, and 0.5 % sulfuric acid, based on the FFA content. The reaction was carried out at about 50 0C for 20-30 min. In a study of biodiesel production from mahua oil having high FFA content (19%), a 2-step esterification reduced the FFA level to less than 1% under optimal conditions of about 10: 1 molar ratio of methanol and 5% sulfuric acid, based on the FFA level (**5**). The reaction time was 1 hr at 60 0C for each step. In another study, Veljkovic et al. (**6**) used a similar 2-step approach to esterify FFAs in tobacco-seed oil. However, the molar ratio of methanol to oil differed for the two steps, viz., 4.5:1 and 18:1. Zhang and Jiang (**7**)reported that a one-step esterification was adequate to produce biodiesel from Zanthoxylum bungeaum seed oil, but used a high methanol-to-oil molar ratio of 24:1, 2% sulfuric acid, 60 0C and 80 min reaction time.

Removing water from the reaction mix will increase the yield of methyl ester by shifting the equilibrium of the esterification reaction toward products. Recently, Lucena et al. (**8**) relied on this principle in the esterification reaction of oleic acid and methanol, catalyzed by sulfuric acid. The system consisted of a reactor coupled to a column containing zeolyte 3A, a selective absorbent for water. The esterification reaction was carried out above the boiling points of methanol and water to evaporate the water produced during the reaction. A condenser placed above the adsorption column condensed the water and methanol vapor, returning water-free methanol to the reactor after passing through the adsorption column. The authors reported yields up to 99.7 % biodiesel under optimal conditions at 100 0C, 1.0% w/w catalyst, and a methanol-to-oleic-acid molar ratio of 3:1. According to them, removing water via the absorption column not only increased the yield in a single reaction step, but also allowed them to use lower alcohol to FFA molar ratios in producing biodiesel.

Other Catalysts

While sulfuric acid has been widely used to esterify FFAs to biodiesel, it has some disadvantages; for example, it cannot be reused or recycled, and also presents problems with separation. Thus, there is growing interest in developing and applying other catalysts that are more effective or can be reused.

Ngo et al. (**9**) demonstrated recently that certain diarylammonium compounds are highly effective and give higher yields than sulfuric acid in biodiesel production from FFAs. Importantly, these compounds can be incorporated into insoluble porous polymers, enabling their use as heterogeneous solid catalysts that are easily separated from the system, and can be recycled and reused.

Several studies reported the use sulfonic-functionalized ion-exchange organic resins as heterogeneous catalysts to convert FFA to FAME (**10,11**). Recently, Rohm and Haas Company introduced a solid-phase catalyst, AMBERLYST™ BD20, which the company reported as being the fastest solid esterification catalyst that converted feedstock with any FFA content to achieve <0.1% FFA.

Wang et al. (**12**) Reported that ferric sulfate, which is a Lewis acid, can be used as an effective catalyst in the esterification of FFA’ s from waste cooking with methanol. When 1 wt% of ferric sulfate was added, 94.4 % of FFA was converted into FAME in 3 hr. Compared with sulfuric acid, this catalyst is easy to separate from the system, and environmental friendly.

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Bench Work Results from Brookhaven National Labs

The bench work to develop process conditions is attached as Appendix B in its entirety due to its length. The bench work established acid esterfication as the best route for attempting to produce a Biodiesel specified fuel from Renewable Diesel. The work identified some hurdles to reaching specification both technically and economically. Additional work was conducted at TDP Philadelphia to help answer the questions about this chemical pathway and are discussed further below.

Further Testing at TDP Philadelphia Subsequent to Brookhaven Study

The Brookhaven and CWT teams continued to investigate producing a D6751 biodiesel from CWT 2nd Stage fuel. The Philadelphia team took over the task from the Brookhaven and ran several replicates from the "recipe" established at Brookhaven. 10 runs were conducted in hopes of validating the upgrading process while gathering data in order to optimize the method for production of larger scale quantities.

As discussed previously, the process involves the reaction of the FFA with methanol over a homogeneous acid catalyst (H_2SO_4) followed by a number of separations and a polishing step using Calcium Oxide (CaO) and Calcium Hydroxide ($Ca(OH)_2$). Previous work by Canakci et. al. was helpful in establishing this methodology and a stepwise procedure in chart form was presented in the preceding report.

During further optimization of this process through experimentation, the group focused on both acid number and glycerol content. While both are crucial to meeting the D6751 specification, acid number is also key in determining the extent of esterfication.

The acid numbers reported through BNL's testing on biodiesel samples from three of the ten runs performed at TDP were 0.76, 0.78, and 0.81 mg KOH/g using ASTM method D-664. It was theorized that the slightly high values possibly resulted from less efficient clean up in the $CaO/Ca(OH)_2$ polishing step.

Table 1: Acid Number Analysis – ASTM Method D664

Analysis	**3:1 ratio (CaO/Ca(OH)2**	**1:1 ratio (CaO/Ca(OH)2**	**ASTM D6751**
Acid Number	4.90	1.13	0.50 max

As can be seen in Table 1, the 1:1 ratio used in the polishing step improved the acid number when compared to the 3:1 ratio of CaO/Ca$(OH)_2$. The 3:1 ratio and 1:1 ratio were performed on the same sample to ensure continuity. The acid number values were obtained through an analysis by Midwest Laboratory and although still above the D6751 limit of 0.50, it was agreed and apparent in subsequent experiments and analysis that a value within the limit can be achieved with the current methodology.

With regard to glycerin, as seen in prior results the water washes seem to successfully reduce the free glycerin in the final biodiesel while the total glycerin has not been able to be controlled below the D6751 limit of 0.240. This may be due to an incomplete hydrolysis during the CWT 2nd stage process with the parameters being used. It was suggested that running the CWT 2nd Stage at higher temperatures will reduce the total glycerin carried through the upgrade to biodiesel. Following this train of thought, it is hypothesized that bumping up the operating parameters on the front end of a commercial size plant will allow glycerin levels to be controlled with a very modest energy and capital cost. In order to help confirm this, three runs were performed where CWT hydrolysis was held at 260°C, 270°C, and 280°C before upgrade to biodiesel.

Table 2: Biodiesel Glycerin Analysis – ASTM Method D6584

Analysis	**260 °C Sample**	**270 °C Sample**	**280 °C Sample**	**ASTM 6751 (EN14214)**
Monoglycerides	0.083	0.101	0.139	NA (0.80 max)
Diglycerides	0.110	0.135	0.207	NA (0.20 max)
Triglycerides	0.014	0.016	0.032	NA (0.20 max)
Free Glycerin	None detected	None detected	None detected	0.020 max (0.20 max)
Total Glycerin	**0.206**	**0.252**	**0.379**	**0.240 max (0.25 max)**

The values obtained in Table 2 were obtained on samples produced at TDP and analyzed by Midwest Laboratory. This data is contrary to the hypothesis formulated by the project group, and the higher temperatures during CWT 2nd stage fuel did not lower the total glycerin in the resultant biodiesel. This observation continues to be an area of concern as to date all biodiesel produced through upgrade of the CWT 2nd stage fuel has not met the glycerin specification for D6751.

Large Scale Bench Work

Based on the 10 TDP biodiesel runs, BNL biodiesel upgrades and recommendations, observations, and analytical results, it was decided that at this plateau it would be advantageous to proceed with running a larger scale process formulated on the lessons and background of the earlier work. This would be a prelude to both a full D6751 profile as well as adding to the base of knowledge and results that the project group would use design a biodiesel facility.

Figure 2 below shows the final configuration of the larger scale apparatus used at TDP to perform 3 biodiesel runs. The configuration uses a 12 L heated (temp. variable) reactor with a glycol filled condensing column along with a chiller and attached vent line.

Figure 2: Larger Scale Biodiesel Production Apparatus

Approximately 12 kg of biodiesel was produced of which a gallon was sent to both Southwest Research Institute (SWRI) and Brookhaven National Laboratory. SWRI performed a complete D6751 profile on the sample as seen in **Table 3** below.

Table 3: D6751 Analysis by SWRI on TDP biodiesel sample

Test Method	***Description/Property***	***Test Units***	***Test Results***	***6751 Limit***
D1160	Vacuum Distillation (AET)			
	IBP	*Deg C*	341	
	5%	*Deg C*	343	
	10%	*Deg C*	346	
	20%	*Deg C*	347	
	30%	*Deg C*	346	
	40%	*Deg C*	348	
	50%	*Deg C*	349	
	60%	*Deg C*	350	
	70%	*Deg C*	351	
	805	*Deg C*	354	
	90%	*Deg C*	364	360
	95%	*Deg C*	440	
	FBP	*Deg C*	472	
	Pressure	*mm Hg*	10	
D130	Copper Corrosion Strip	*rating*	1A	
D2500	Cloud Point	*Deg C*	could not determine Cloud Point - sample too dark.	Report Only
D2709	Water & Sediment	*Vol%*	0.01	

D445	Viscosity at 40°C	*cSt*	5.566	
D4530	Carbon Residue	*m/m*	0.3519	.050 max
D4951	Phosphorus	*ppm*	< 5	
D5453	Sulfur by UV [1]	*ppm*	105.8	
D613	Cetane Number	--	50	
D6584	Free & Total Glycerin			
	Free Glycerin	*wt%*	0.009	
	Total Glycerin	*wt%*	0.415	.24 max
	Monoglycerides	*wt%*	0.497	
	Diglycerides	*wt%*	1.395	
	Triglycerides	*wt%*	0.807	
D664	Acid Number			
	Inflection Point	*mg KOH/g*	0.16	
	Buffer End Point	*mg KOH/g*	0.2	
D6751_A1	Cold Soak Filterability			
	Seconds	*s*	>720	360 max
	Volume	*ml*	45	
	Pass or Fail	--	fail	
D7111 Mod.	Metal Analysis			
	Calcium	*ppm*	105.8	5 max
	Potassium	*ppm*	<1	
	Magnesium	*ppm*	1.6	
	Sodium	*ppm*	1.7	

D874	Sulfated Ash	*wt. %*	0.15	.020 max
D93	Flash Point	*degF*	315	
	Flash Point	*degC*	157.2	
EN14112	Oxidation Stability (Rancimat)	*hours*	5.8	
1 D 6751-03a allows two sulfur limits: Grade S15 allows for a maximum value of 0.0015% (15ppm) sulfur. Grade S500 allows for a maximum value of 0.0500% (500ppm) sulfur				

As can be seen, there are a number of values that fall outside the D6751 limits and are therefore highlighted with the D6751 limit provided. It was agreed that many of the out of spec results are related and if one did not fall within the limits it would be likely that others also not as well. For instance, calcium, sulfated ash, and carbon residue resulted in higher values than acceptable and would therefore make sense that the cold soak filterability would also fail. This combined with elevated total glycerin levels leading to the existence of a higher percentage of relatively heavy material, would raise the boiling points in the vacuum distillation. Although the existence of these extra constituents may not be the only factor, they may likely also contribute to the dark nature precluding the completion of a cloud point test.

As predicted, it was possible to meet the acid number specification using the group’s current biodiesel upgrade methodology, but once again it was shown that total glycerin continues to be a problem area. It may be worth mentioning one observation that coincides with many of the experiences CWT has had throughout the lifetime of the company when it comes to analysis of fuels derived from CWT product. It has been the norm that in many cases standard industry analyses are not optimal for fatty acid based fuels or derived fuels as well as the specifications that they must meet. In this case, Southwest Research Institute indicated the following regarding the glycerin analysis, “The sample is unusual. There was some material that dominated the internal std 2 and the di-, tri- glycerine regions. On top of this material were peaks that lined up with our di-, tri-, glycerides peak retention times…. In other words, this sample could be considered “not-applicable” for this procedure due to the interference.”

After all of the preceding work was complete and some preliminary cost data on adding an acid esterification section to a renewable diesel plant (see section 9), the group concurred that the Biodiesel route, as optimized, does not appear acceptable to meet the D6751 specification cost effectively. This coincides with the obstacles historically faced by industry when dealing with waste greases. The project group agreed that more work and investigations would be required to sufficiently “clean up” the resultant biodiesel, if possible at all. TCP derived RDO does not appear to provide a better cost structure for the feedstock in the production of biodiesel. This would make further study inconsequential as it would not have commercial feasibility.

Task 5.0 Development of Upgrade Processes to Convert to ASTM Diesel

Introduction

This project was focused on the production of fuels which can displace petroleum distillates and which are derived from trap grease, processed by the CWT hydrothermal system. The product of the CWT conversion of trap grease can be simply modeled as 100% free fatty acids (FFA). The route considered in this report is removal of oxygen from the FFA feed and production of synthetic hydrocarbons.

A considerable amount of work has been done on the direct conversion of oils to hydrocarbon fuels but much less has been done on the conversion of FFA feedstocks. However, much of the work done on oils is seen as relevant for FFA conversion. For this reason, this report presents a review of what is seen as the most relevant prior work with a wide range of oil and oil derivative feedstocks. Based on this review, a test plan is then developed for work to be done at Brookhaven National Labs in evaluating fuel production from the CWT Stage 2 product.

Goal

Oils, fats and greases primarily contain carbon chains between C16 – C18. An ideal process would be to decarboxylate these molecules to produce a hydrocarbon product that fall within the diesel range. The goal of this effort is to develop an economical technology to process trapped grease, a nuisance waste, into hydrocarbon fuels that can replace fossil fuels for transportation and/or home heating.

Known catalytic systems

Hydroprocessing is a well-established process in petroleum refineries. It involves contacting crude oil with a catalyst (typically, cobalt-molybdenum supported on alumina) under hydrogen atmosphere at T: 200- 450°C and P: 0.5 – 30 MPa. The principle reactions that may be involved are:

- hydrogenation of unsaturated hydrocarbons (HDOlef and HDA),
- Hydrocracking of large molecules (MHC)
- Hydrodeoxygenation of oxygen containing molecules (HDO)
- Hydrodesulfurization of sulfur containing molecules (HDS)
- Hydrodenitrogenation of nitrogen containing molecules (HDN)
- Hydrodemetallation of metals such as Ni and V (HDMe).

HDO and HDA reactions reduce the portion of olefins and aromatic hydrocarbons, respectively, in the oil, while the hydrocracking reactions decrease the molecular weight. During HDO, HDS and HDN, the heteroatoms are eliminated by reactions with H_2 to form H_2O, H_2S and NH_3, respectively, which are easily removed from the reactor as off-gases in a flow-through mode.

Processing of oils and fats and their derivatives (such as FFA) to hydrocarbon fuels is simpler than upgrading crude oil so hydroprocessing-type catalysts have been investigated (1-15). The catalysts used can be divided here into three broad categories. These are:

Hydroprocessing-type Catalysts

Some of the earlier work involved shape-selective Zeolite type catalysts in a micro-reactor at 340-400°C and ambient pressure to process feedstocks such as canola oil (1). The effects of reaction temperature and oil space velocity on the conversion and selectivity were reported. Poor yields of gasoline fraction (up to 12wt%) and high undesirable C3-C4 gases and aromatics (to 41 wt%) were obtained though the oil conversion was in the 60 - 95 wt% range. As expected, high reaction temperatures were found to favor higher gas yields. The spent catalyst could be completely regenerated at 600°C and 1 hour in a stream of dry air. Recently, the work has been extended to the fluid catalytic cracking (FCC) catalyst, a mixture of zeolite-type (11). The catalyst evaluation was carried out in a two-stage riser FCC unit. The temperature was typically maintained at 500°C (Stage I) and 520°C (Stage II), with short contact times, 1.4s and 1.7s, respectively. The feedstock was 50% palm oil co-fed with vacuum gas oil. With pure palm oil, the conversion reached over 97% to yield 45% LPG and 23% propylene, and 77.6% total liquid. The O content of liquid products was very low (about 0.5%), so the oxygen atoms are expelled mostly as H_2O, CO, and CO. After blending VGO in palm oil, the LPG yield can reach 39.1%, propylene yield is 18.1%, and total liquid yield is 79.2%.

Further work in hydrodeoxygenation (HDO) used variations of commercial hydroprocessing-type catalysts, molybdenum on an alumina-type support, Mo/Al_2O_3 (2,5,6,8,10,14). The catalysts typically included either Ni or Co to enhance the activity. The feedstock was fatty esters, fatty acids, and co-fed with petroleum-derived oils. The catalyst evaluation was carried out in fixed-bed tubular units. The temperature was typically maintained in the 300-450°C range. The goal was to increase the yield of either diesel and/or gasoline fractions in the product. With sulfided Ni or Co activated Mo/Al_2O_3. After studying the effect of temperature and pressure, the best results were reported with $Ni\text{-}Mo/Al_2O_3$ at 350-450°C and 5 MPa pressure (8). The feed, vegetable oils co-fed with heavy vacuum oil (50%/50%), the product yielded a fraction between 250-358°C that contained 75% n-C15 - n-C18 fraction (diesel). In another study, a series of runs with both Ni and Co activated Mo/Al_2O_3 at 250°C and 1.5 MPa pressure under continuous H_2 flow mode were conducted to establish the effect of water on hydrocarbon production (5). With model systems, ethyl and methyl heptanoate as 3% solution in m-xylene, three observations were made during HDO in the presence of water: 1) It decreased the conversion of feedstock esters and suppressed O removal, 2) of the two, $Co\text{-}Mo/\gamma\text{-}Al_2O_3 > Ni\text{-}Mo/\gamma\text{-}Al_2O_3$, 3) hydrogenation reactions were inhibited in the NiMo catalyst but the CoMo catalyst was not affected, 4) a comparison of the two deoxygenation reactions, i.e. dehydration and decarboxylation, decarboxylation was affected because suppression of C6 hydrocarbons was noted, 5) the addition of H_2S (normally added to keep sulfided catalysts active) compensated the inhibition by water but changed the product distribution by increasing the main products toward C6 hydrocarbons. This also increased undesirable CO_2. The life cycle analysis of $Co\text{-}Mo/\gamma\text{-}Al_2O_3$ is also reported (10). At < 320 C, the catalyst was not effective as it yielded solid or semi-solid products instead of liquid hydrocarbons. The cetane number of the product was ≥ 100 (2).

Supported Pd and Nb Catalysts

The use of Pd/C as a deoxygenation/decarboxylation catalyst has been investigated (4,9,12,15). A catalyst loading of 1-5 wt% has been evaluated. Both esters and free fatty acids that are found in oils and fats were used as feedstocks and the catalyst was found to be effective for hydrocarbon production mainly via decarboxylation. For example, stearic acid produced n-heptadecane with 70% selectivity, the rest consisted of CO, CO_2, C_2H_4 and C_2H_6. The temperature was lower (270-360°C) than that used for hydroprocessing (4). At T = 300◦C, P = 1.7 MPa and 5 vol% H_2 in Argon, 15 mol% ethyl stearate converted in 1 hr. Product selectivity: n-C17 ~50%; Other C17: ~23% (9).

With 1wt% Pd/mesoporous C of surface area 220-330- m^2/g, the decarboxylation was carried out at 300°C/1.7 MPa under an argon atmosphere (15). The catalyst activity was very much dependent on the feedstock FFA/catalyst ratio with a lower ratio increasing the reaction rate. For the 5 FFA tested, though conversion up to 93% was obtained after 2.5 hours, it was very much dependent on the purity of the feed. Impure feed samples lowered the rates as well as conversion by as much as a factor of four. The poisoning effect of P was especially noted. The data show that the rates were independent of the chain length of the feed. With C19 FFA feed, extensive coking on the catalyst was noted.

Though it is possible to achieve good selectivity in the diesel range, the reaction time of 5-6 hours is an issue. The reaction was mostly conducted in a semi-batch unit-here the reactor was loaded with a feedstock but the gas flowed through the reactor during decarboxylation.

In the absence of a catalyst, no cracking was observed at 350°C /1 atm with Oleic as a feedstock Among H_3PO_4/Nb_2O_5 and $NbOPO_4$ catalysts, the conversion of up to 82% was noted for the latter. The hydrocarbon product distribution included ~33% diesel product and 65% lubricant oil (C19 – C22) with the $NbOPO_4$ catalyst. However, no data on the catalyst life are available to make a judgment on the commercial potential of this catalyst.

Non-metal type Catalysts

The use of supercritical water (ScH_2O) in the absence of any metal catalyst has been investigated in a batch mode (17). With stearic acid (a C17 acid) as a feedstock, C17 hydrocarbons were the major product but only 2% feedstock conversion was obtained. On adding KOH and NaOH, the decomposition was 32 and 13% respectively. Metal oxides such as ZrO_2, CeO_2 and Y_2O_3 enhanced decomposition- it was 68% with ZrO_2. The main products were CO_2 and C17 alkane, formed by decarboxylation, when KOH was used. With metal oxides, bimolecular decarboxylation occurred because the products were long-chain (C35) ketones not hydrocarbons.

Preliminary work on biodiesel production from yellow and brown greases has been reported (13). It is known that FFA in brown grease can be as high as 40 wt%. The first step was to convert all FFA to FAME by heating the grease with methanol at 95°C for 2 hours. However, it is acid catalyzed and sulfuric acid was used as a catalyst. The pretreated greases were then subjected to base-catalyzed transesterification reactions to afford FAME and glycerol. A large amount of base was required, however, to neutralize the acid catalyst remaining in the pretreated greases using this two-step process. The diarylammonium sulfonate salt catalyst was used to avoid sulfuric acid addition. It can be recycled but the FFA to FAME conversion drops off severely after four cycles as follows: Fresh: 99%, Recycle 1: 92%; Recycle 2: 87%; Recycle 3: 47%. Therefore, the system still needs improvement for potential commercial applications.

Mechanism

The processing of oils, fats and their derivatives may involve several reactions. A proposed reaction pathway for conversion of triglycerides into alkanes is as follows (8). In the first step, the double bonds in triglycerides are hydrogenated and broken down into various intermediates that are presumed to be monoglycerides, diglycerides and carboxylic acids. These intermediates are then converted into alkanes by three different pathways (equations 1 - 3):

Decarboxylation $R\text{-}CH_2\text{-}COOH \rightarrow R\text{-}CH_3 + CO_2$ (1)

Decarbonylation $R\text{-}CH_2\text{-}COOH + H_2 \rightarrow R\text{-}CH_3 + CO + H_2O$ (2)

Hydrodexogenation

(or dehydration/hydrogenation) $R\text{-}CH_2\text{-}COOH + 3H_2 \rightarrow RCH_2CH_3 + 2H_2O$ (3)

The deoxygenation of ethyl stearate, an ester, has been investigated (9) and a mechanism to yield C-17 hydrocarbons, free fatty acid and aromatic fraction that involves ring closure has been proposed (Figure 1). The mechanism of fatty acid decarboxylation involves simple elimination of CO_2 molecule. However, direct production of hydrocarbons from triglycerides or fatty acid esters are more complex. It must go though not only CO_2 elimination but also involved hydrogenation, C-C bond cleavage.

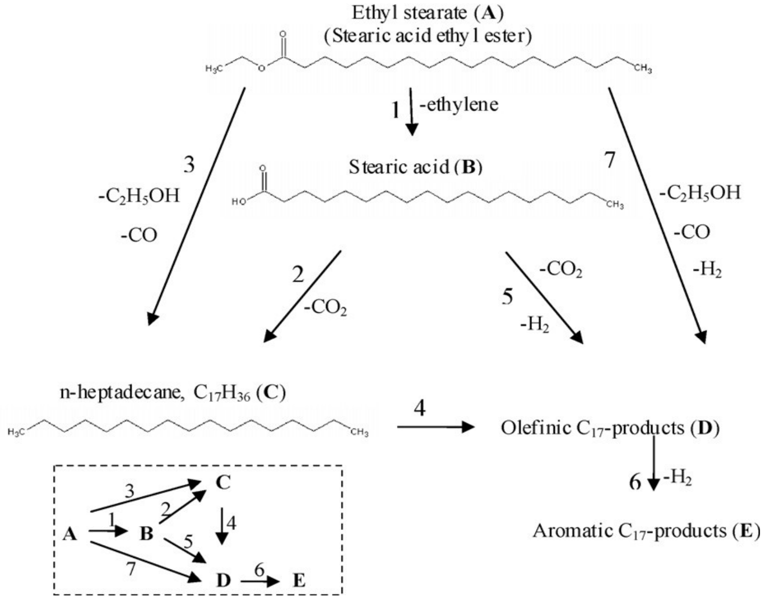

Figure 1. Proposed deoxygenation mechanism of ethyl stearate, as ester, to yield a variety of observed products (reference 9).

During another reported study of HDO of methyl heptanoate (5), the production of heptane and hexane has been explained via steps that involve all three equations 1-3 (Figure 2).

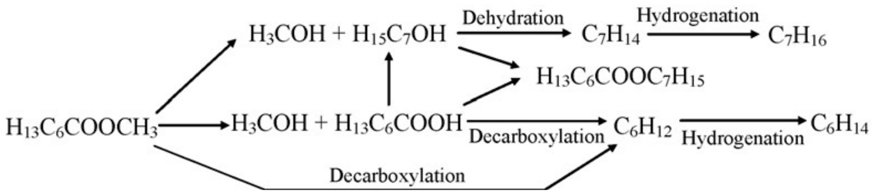

Figure 2. Hydrodeoxygenation (HDO) reaction scheme for methyl heptanoate conversion to hydrocarbons.

The processing of FAME and FFA using an FCC catalyst has been probed with FT-IR. These spectra established that there were no aryl groups in the feed, so high aromatics in the product are formed by hydrogen-transfer, cyclization and aromatization reactions.

Work Plan

The option for biofuels production in existing petroleum refineries via hydrotreating of vegetable oils is well documented and remains attractive especially when co-processed with petroleum based heavy oils such as heavy vacuum oil. Typical hydrotreating catalysts operate under relatively high temperatures (300 – 520°C) to achieve multi-functions, i.e., they remove S, N, O heteroatoms, perform hydrogenation of double bonds and catalyze carbon-carbon bond cleavage in a single vessel. However, this comes at a penalty in selectivity because commercially known sulfided Co-Mo and Ni-Mo catalysts yield a variety of products that range from light gases, gasoline fraction, diesel fraction and aromatics, the last fraction promoted through cyclization. The aforementioned systems lay the foundation but fall short of a working system that can be considered ideal for commercial application. Process if FFA in existing refineries also raises concerns about corrosion in the reactors. It is expected that new vessels would be required and it is likely best done in new, reactors, dedicated to FFA processing.

Our focus here is to use trap grease as a feedstock for conversion into fuels. As indicated earlier, typical greases primarily contain triglycerides (TG), diglycerides (DG), monoglycerides (MG), and free fatty acids (FFA) (8–40 wt %). The FFA content varies from 8–12 wt % for yellow grease and up to 40 wt % for brown grease. A trapped grease sample selected for this study has the following elemental analysis:

C: 53.41%

H: 11.105%

N: 0.18%

Ash: 1.26%

S: < 0.1%

Cl: < 0.1%

Total ~ 66%

O: balance

The major problematic impurities such as S, N, and halogens adds up to < 0.4%. A small ash content also establishes that the metal content is very low. CWT has a patented process in which the sample was treated that converts constituents of the raw trapped grease to a material that is ~91% FFA. The remaining non-FFA constituents could be glycerides or other organics. The FFA profile of the grease is as follows:

<u>FFA Profile</u>

Tetradecanoic acid (C14:0): 2.34%

Hexadecanoic acid (C16:0): 22.42%

Hexadecenoic acid (C16:1): 1.73%

Octadecanoic acid (C18:0): 7.72%

Octadecenoic acid (C18:1): 33.67

Octadecadienoic acid (C18:2): 24.62%

Octadecatrienoic acid (C18:3): 2.79%

Eicosenoic acid (C22:1): 1.0%

Total: 96.3%

The C16-C18 fraction dominates the FFA content and the balance is made up of other FFA from C8 - C24. This composition shows that trapp grease is an ideal precursor to diesel cut if the decarboxylation reaction proceeds smoothly with minimum side reactions. It is, therefore, our focus to design a catalyst that can achieve just that. It also follows that a simpler process would operate at a lower temperature to maximize decarboxylaiton while minimizing carbon-carbon bond cleavage.

A low level of impurities in the grease feedstock after CWT Stage II treatment (250°C and 5 MPa for 20 minutes) allows us to evaluate catalysts other than those used for hydrotreating. The goal is to enhance decarboxylation to produce hydrocarbons at the lowest possible temperatures and avoid C-C cleavage or other side reactions. Since supported Fe and Cu are two metals that are good hydrogenation catalysts, the former is an Fischer-Tropsch (F-T) catalyst and the latter is a methanol and higher alcohols synthesis catalysts. Runs in the following tasks are now underway.

Baseline runs

We investigated the use of γ-Al_2O_3 as a catalyst at 350°C and 6.5 MPa using oleic acid as a feedstock. The overall conversion of oleic acid was 96% and the selectivity to hydrocarbons was ~92%. However, the reaction time was 6-8 hours- too slow to be of commercial interest. The results are comparable to those reported in Reference 3 with a Nb catalyst with oleic acid feedstock. The Nb catalyst achieved 82% conversion. Further runs will include:

Task 1-1. Run with oleic acid /γ-Al_2O_3 at 280°C; 2MPa

Task 1-2. Evaluate CWT Stage-II sample, a mixture of FFA, with γ-Al_2O_3 as a catalyst.

Supported Fe Catalyst

The choice of support is γ-Al_2O_3. Fe catalyst will be evaluated for activity. T: 280°C; P: 2 MPa.

Task 2-1. Synthesis of Fe/γ-Al_2O_3 using in situ thermal decomposition of pentacarbonyl iron. Characterize using TEM, SEM and XRD.

Task 2-2. Evaluate Fe/γ-Al_2O_3 catalyzed decarboxylation: 1) Oleic acid and 2) CWT Stage-II sample.

Supported Cu Catalyst

The choice of support is γ-Al_2O_3. Cu catalyst will be evaluated for activity. T: 280°C; P: 2 MPa.

Task 3-1. Synthesis of Cu/γ-Al_2O_3 using in situ reduction of copper chloride. Characterize using TEM, SEM and XRD.

Task 3-2. Evaluate Cu/γ-Al_2O_3 catalyzed decarboxylation: 1) Oleic acid and 2) CWT Stage-II sample.

Analytical.

The evolution of CO_2 will be quantified using GC in all the runs. The moles CO_2 released will be used as a measure of the extent of FFA decomposition. The hydrocarbon products will be identified and quantified using GC.

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Work Conducted Subsequent to Work Plan

As is described in detail above, Brookhaven explored the production of synthetic diesel via decarboxylation. Much of the early work done at Brookhaven and Stony Brook University was done with oleic acid as a surrogate for the product of CWT Stage 2 conversion. A range of catalysts and conditions were explored which included solvent-free feed, dodecane solvent mixed with feed, and EthylFlo 164 solvent mixed with feed; These runs were done in the presence of Al_2O_3, $NiCl_2$, $NiCl_2/Al_2O_3$, $Fe(CO)_5/Al_2O_3$, $Co_2(CO)_8/Al_2O_3$, Pd/Al_2O_3, and Pd/C catalysts. All studies were done in a 300 ml Parr reactor. Temperatures ranged from 280 to 300 °C. Overpressure was maintained consistently with a 90% nitrogen / 10% hydrogen at 400 to 500 psi. The reaction time for all runs was 400 minutes.

The first set of testing was done without solvent and these generally yielded low conversion efficiency. These did show, however, that the $NiCl_2/Al_2O_3$ had the highest selectivity to the production of C_{17} hydrocarbons. With the use of a solvent, and in particular the EthylFlo 164 conversion efficiency to 96% was achieved using either Al_2O_3 or NiCl2/Al_2O_3 catalysts. Conversion efficiency with dodecane solvent was much lower ~ 10%. At the high conversion efficiency, liquid products included C_{12} and C_{17} hydrocarbons. Some initial runs were also done with the CWT Stage 2 product instead of the oleic acid and conversion efficiencies in the 94% range were also measured. The conversion efficiencies are based on a material balance from GC analysis of products. Acid number tests of the products to confirm the achieved conversion were also undertaken as a check for the GC measurement of conversion. There was a distinct difference between acid number results and GC method and due to this difference, testing done subsequent to the first tests was done suing acid number as a means of assessing conversion efficiency.

Much of the early test results and methods are attached as **Appendix C.**

Integration and Practicality of Catalysts in combination with CWT TCP Technology

The work then focused on methods of integrating a conversion to ASTM Diesel with the CWT second stage process and the practical implications of catalyst selection. The pressure and temperature conditions that have been explored to date are not far from the CWT 2nd stage conditions leading to some optimism for a low cost integrated process. The high selectivity of the Ni catalyst is attractive although there is some concern about the cleanup implications. Fe catalysts will be the lowest cost but not apparently as selective.

Use of an organic solvent in an integrated process is undesirable and would require a downstream separation. Also the CWT process has considerable water. For these reasons more runs were done with water mixed in, CWT feedstock, and no organic solvent. 9 runs in total were subsequently conducted at TDP Philadelphia using $NiCl_2/Al_2O_3$ in the presence of water at TCP normal operating conditions for stage 2 of their process. Very low conversion efficiencies were obtained during these runs as measure using acid number as an indicator for conversion.

The nine runs at TDP are discussed below:

In this task, work continued in exploring the production of synthetic diesel via decarboxylation through use of a catalyst. As it was previously shown that the $NiCl_2/Al_2O_3$ had the highest selectivity to the production of C_{17} hydrocarbons, this catalyst was chosen for use in combination with the CWT second stage process. The pressure and temperature conditions that had been explored during the catalyst investigations were not far from the CWT Stage II conditions which gave hope for a low cost integrated process. Feasibility and success of such a process was examined through a series of experimental runs at BNL and TDP.

For these experiments, the use of an organic solvent was not used as in an integrated process the downstream separation would be undesirable. A considerable amount of water is characteristic of the CWT process and therefore it was added during these catalytic runs.

A series of 9 runs were performed at TDP. A representative run was 600g of a 50/50 trap to used restaurant grease mix, 400g water, 20g Al_2O_3, and 5g of $NiCl_2$. A 2 liter Parr vessel was used as the reactor and aggressive mixing was maintained. The contents were held at operating temperature (both temp. and pressure variable for the series of runs) for one hour. Figure 5 shows the contents after removal from the reactor for one of the runs.

Figure 5: Sleeve contents after removal from reactor during a catalytic run at TDP

Upon completion the RDO was separated and acid value, ash, yield, and moisture were recorded. Any observations relative to the amount of gas evolution were also noted as this would be an indicator of decarboxylation. Table 4 shows the operating conditions and resultant acid number for the nine catalytic runs at TDP. Upon completion results will be discussed and depending upon the outcome other methods in converting to an ASTM diesel may be revisited.

Table 4: Operating Conditions and Acid Number for 9 Catalytic Runs at TDP				
Run #	**Max. Pressure (psig)**	**Max. Temperature (°C)**	**Time (hrs)**	**Acid #**
1	**680**	**263**	**1**	**179.0**
2	**690**	**265**	**1**	**183.0**
3	**660**	**261**	**1**	**179.9**
4	**850**	**277**	**1**	**190.9**
5	**825**	**276**	**1**	**185.2**
6	**1220**	**301**	**1**	**182.3**
7	**1180**	**299**	**1**	**190.1**
8	**1225**	**300**	**1**	**178.3**
9	**1220**	**300**	**1**	**Pending**

As the acid numbers are relatively high and no pressure above the saturation pressure of water was achieved, the feasibility of a CWT Stage II catalytic process must be reevaluated. CWT will perform a few runs using a 50/50 (water/grease) mixture at lower pressure in an attempt to emulate a semi-continuous batch environment where gases can evolve as they are produced. BNL will perform a run using the catalyst in a dry environment to affirm a successful reaction before the addition of water.

It was agreed that TDP would discontinue further catalyst runs characterized by the methods used in the previous 9 runs, but the project group chose to investigate further before ending this ASTM Diesel route for value adding Renewable Diesel.

While a considerable amount of water is characteristic of the CWT process and was therefore added during the previous 9 runs performed at TDP, it was agreed to try a run in the absence of water using dehydrated RDO with the $NiCl_2/Al_2O_3$ catalyst. Additionally, TDP performed a few runs using a 50/50 (water/grease) mixture at lower pressure in an attempt to emulate a semi-continuous batch environment where gases can evolve as they are produced. Like was the case in the previous 9 runs, a 2 liter Parr vessel was used as the reactor and aggressive mixing was maintained. The contents were held at operating temperature (both temp. and pressure variable for the series of runs) for one hour, but gases were allowed to evolve by continually opening the reactor overhead valve throughout the run.

Table 5: Acid Number Analysis for 2 Catalyst Experiments at TDP

Analysis	Degassing Run	Dehydrated Run on RDO
Acid Number (mg KOH/g)	129	153

As can be seen in Table 5 above, the acid numbers once again proved to be higher than anticipated for both experiments. The run attempting to simulate a semi-continuous batch environment did seem to improve the outcome, but not to the point that can be considered a successful conversion.

There were discussions about other experimental work at UOP and Wayne State that may have provided an alternative protocol, but at this point the group felt that the experimental work has been exhausted without any sufficient success justifying continuation on this path.

Task 6.0 Properties of Non-Standard Fuel Product

Introduction

Task 6 involved looking at the CWT baseline product, RDO, as a blend stock with traditional hydrocarbons such as No 6 or No 2 fuel. This was the premise at the start of the project and was explored until the investigators had the opportunity to burn RDO neat. A B-100 blend of RDO was combusted at Brookhaven early on in the project as a baseline for future blended product combustion tests.

The successful trial using B-100, from a combustion characteristics standpoint and handling standpoint (albeit, the fuel must be warmed), caused investigators to pursue neat fuel performance in lieu of blending in a majority of the work conducted under this task .

Early Work on Blending

The project team explored blending RDO with No 2 oil in many different percentages ranging from 1% to 5% and eventually to as high as 50%. Much data and physical observations were reported in earlier quarterlies about these blends and what was learned from blending.

The 1 to 5% tests showed that RDO and No 2 fuel oil generally are not compatible enough to obtain long term stable blends. There was not a blend on the low end that could be considered totally transparent to the fuel oil distribution network for reasons that varied from potential for product separation to the amount of sulfur (RDO is not hydrotreated and contains more sulfur than would be allowable in an ultra low sulfur product).

A 50% blend of RDO and No 2 Fuel oil was also investigated understanding full well that there would be some characteristics of the blend that could be non-conforming to No 2 fuel. The 50/50 ratio as a feedstock could directly displace distillate fuel and might have some advantages over 100% neat RDO. Initial testing with this blend showed that it must be stored above 80 F. At lower temperatures the fuel does not gel but does accumulate a small wax layer on the surface. The team also found a significant separation layer on the bottom after ~ 1 week of storage at 40 C. This was found to be simply water with some wax. For all further tests of this blend only desicated CWT Stage 2 product was used.

One 50/50 blend was stored at 40 C for two months. The fuel blend was basically stable against separation although some bottom deposition was been noted. This is shown in Figure 4, below. The team expects that this could be eliminated with better fuel clean-up.

Figure 4. Small sludge deposits at the bottom of a beaker of 50% CWT Stage II product and 50% # 2 fuel oil after 2 months of storage at 40 C.

There was also some initial exploration of the corrosion of copper in this fuel blend. A cleaned copper coil was placed in a fuel blend for 2 months and no surface corrosion was observed, consistent with the copper strip corrosion test. This coil, after the test period is shown in Figure 5.

Compatibility of this fuel blend with seal materials was also initiated. The most common pump used in stationary boilers in the US is made by Suntek, Inc. This manufacturer sent samples to the team of the shaft seal which is used in roughly 75% of the pumps currently in the field. This is a nitrile seal cast around a metal “cup”. It is a custom material which has been developed over many years and has a durometer in the 70-80 range. Although the manufacturer of the seal material in the same pump has indicated they are not willing to send the team “slab” samples of the material the team took stock seals that have been provided and soaked them as well in the fuel blend and made measurements of swell using microscopic measurements. Over test periods consistent with the UL 157 standard, the swell was found to be essentially zero. This is not a standard measurement but is clearly encouraging.

Figure 5 copper coil after 2 months exposure in 50/50 fuel blend

The results of the 50/50 blend showed the team the strong potential for displacement of distillate oil using this approach, although improved polishing of the fuel product would be required and the fuel would have to be heated. These requirements, (heating and polishing) taken in conjunction with subsequent combustion tests using 100% RDO at Brookhaven gave invetigators a perspective that there was little to gain commercially in blending. Since blending can not be done in a manner that would make RDO transparent, it would seem advantageous to the waste producer and to the entity converting the waste into RDO to limit fuel blending.

100% RDO as a Stand Alone Fuel

Introduction

As was alluded to in the introduction to Task 6, following our prior exploratory tests on mixing, separation potential, and wax points the team decided to proceed with combustion tests using a small scale burner. To support these tests CWT sent to BNL 10 gallons of Stage 2 product made with a blend of trap grease and waste vegetable oil. This particular sample was made from a feedstock which appeared to have a higher content of waste vegetable oil than trap grease as it was fully liquid at temperatures just above room ambient ~ 22°C. For this reason, a decision was made to attempt direct combustion without blending with No. 2 oil as a limiting case. (Note: future testing has been done with higher percentages of waste grease and although the pour point may have increased due to the type of carboxylic oil in the mix, the combustion characteristics and the flame stability has not been measurably affected).

Short Duration Combustion Testing

The burner used in these tests was of typical size for a small residential burner, was pressure atomized with a nominal thermal input of 20 kW. The specific burner however has a prototype heater assembly located just before the nozzle. This heater, integrated with the burner by the manufacturer (Carlin Combustion Technologies) provides the ability to heat the fuel to levels as high at 400°F. The CWT fuel is heated to 230°F. The heater uses a very high surface area carbon element which avoids very high heater surface temperatures and coke formation. Testing was done with the burner started on No.2 oil and then switched to the CWT 2nd Stage fuel and also started from cold (cold boiler, heated nozzle). In both cases the burner ran essentially without incident. A sintered metal filter was used with a filtration rating of 42 microns. No observation of increasing pump pressure over time, a sign of wax blockage, was realized.

Table 6 below provides a summary of the most significant combustion parameters during this test.

Figure 3 and Figure 4 provide a photo of the flames for each of these two fuels. For this test the fuels were fired into a quartz research combustion chamber, 12” diameter x 18” long, fired on axis. Without adjustment of the air-fuel ratio, the flame of the CWT Stage 2 product is clearly a different color than for No.2 oil.

Table 6. **Summary of Preliminary Combustion Test Results**

Fuel		No. 2 oil	CWT 2nd stage fuel
Nozzle temperature	°F	105°	233°
Bacharach Smoke No.	-	0.5	1
Flue gas oxygen	% dry basis	4.6	6.2
CO	ppm	4	3
NOx	ppm	111	102
Flue gas temperature	°F	462°	516°
Pump suction	in Hg	0	0
Pump discharge	psi	255	260

Plan for Future Testing in Project (See Task 13)

Based upon the encouraging results from the combustion tests with the 100% CWT 2nd stage fuel several important decisions were made. The small burner system at BNL operates very well and provides an opportunity to gain experience with a large number of running hours without a large amount of fuel. For this reason it was planned to fire this burner with the CWT 2nd stage fuel for at least 100 running hours, in a boiler, with a combination of steady state and cyclic (on/off) operation. BNL is part way through this activity as this report is being submitted in it final form.. The key purpose of the test that is now underway is to evaluate durability and formation of head coke or ash deposits over time. Other parameters to be monitored include gaseous emissions, PM 2.5 (dilution tunnel method), filter blockage, control sensor output, nozzle fouling, and ignition reliability. CWT prepared large scale samples for BNL for conducting these tests using both its pilot (constructed under Task 12) and it just recently restarted production facility located in Carthage, Missouri.

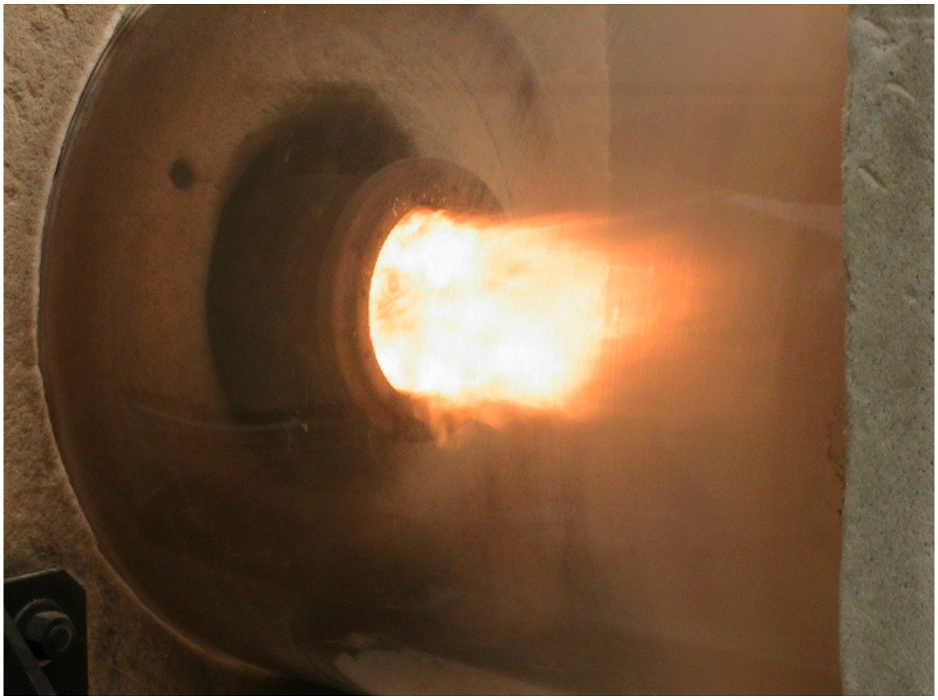


Figure 3: Flame produced by No.2 oil – quartz combustion chamber

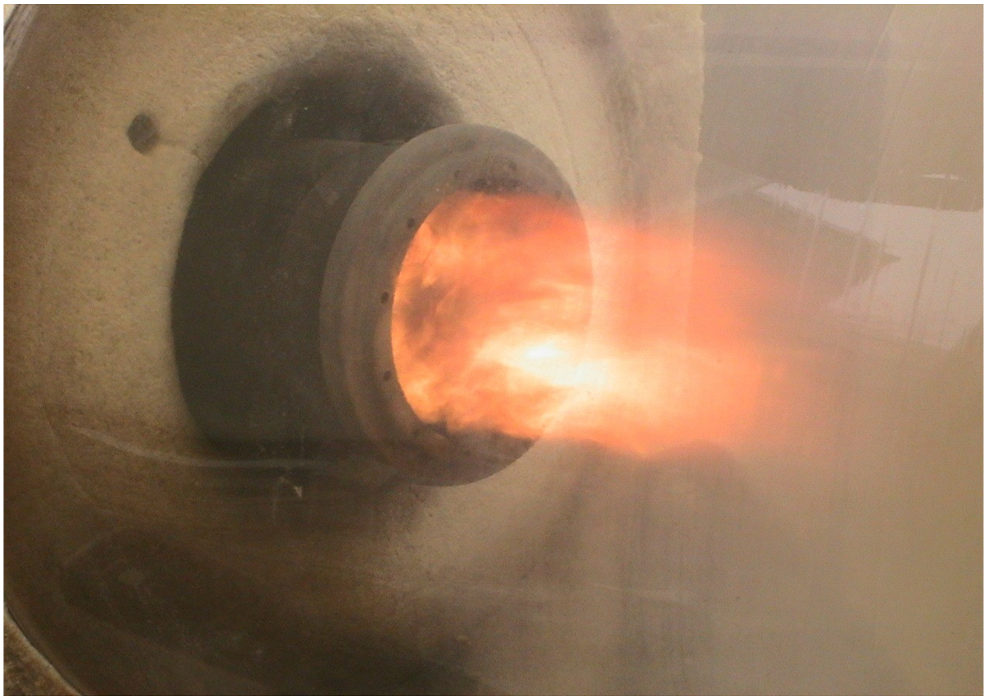


Figure 4: Flame produced by CWT Stage II product – quartz combustion chamber

Neat Fuel - Elastomers

Beyond combustion, there are always industry concerns about the impact that the CWT fuel will have on both seal material swelling and corrosion in both steel storage tanks and copper lines. For the swelling, samples of the nitrile seal material used in Suntek pumps were obtained and standard UL 72 hour swell tests were completed. A maximum swell of 25% is allowable and the observed swell was on the order of 4%. Longer tests should be performed at some point although these initial results are quite promising to the investigators.

Neat Fuel - Metallurgy

CWT RDO is composed of a broad profile of carboxylics, with an acid number greater than 180. Because of the high acidity of the fuel, existing materials commonly found in fuel distribution systems have been evaluated over the last 14 plus months of the project. Copper and steel samples have been subjected to long term storage submerged in CWT RDO at elevated temperatures. The two metal samples' characteristics were documented before the long term accelerated aging test. Mass and dimensions were recorded for both samples on 7/30/10, the start date of the test. Table 7 shows the original characteristics of each metal sample.

Table 7: 7/30/10 – Original Mass & Dimensions

	Copper	Steel
Length (mm)	55.76	55.45
Width (mm)	25.48	25.83
Height (mm)	2.33	0.74
Volume (mm^3)	3310.382	1059.882
Mass (g)	23.0331	8.156

After recording the metal test coupons' specifications, the samples were submerged in 250ml of RDO. The samples were then placed in a convection oven maintained at 40°C where they remain at this isothermal condition since that time.

After an exposure time of nearly 3 months, the samples were removed from the RDO and inspected for surface corrosion and deposits & gum formation. Additionally, dimensions and mass were measured to quantify any change in the material mass. Photos of the copper and steel strips were taken to document the condition of the surface. As seen in Figure 5, there were no deposits or gum formation on the surfaces. The surfaces appear to be very bright, shiny, and clean; there were no discoloration, obvious etching or surface roughness developing. Additionally, dimensions and mass were measured to determine if any material degradation had occurred over 3 months. This data can be seen in Table 8. Additionally, the difference between the data can be seen in Table 9.

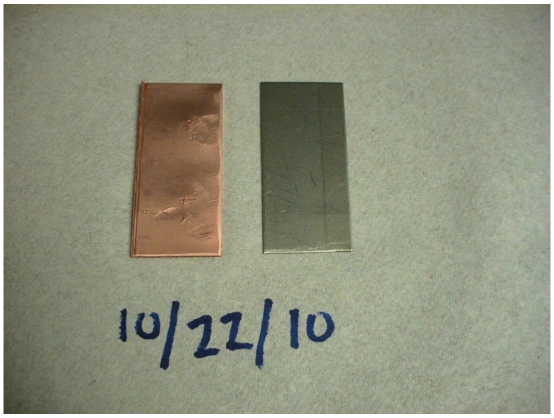


Figure 5: 10/22/2010

Table 8: 10/22/10 – Mass & Dimensions

	Copper	Steel
Length (mm)	55.75	55.41
Width (mm)	25.48	25.86
Height (mm)	2.29	0.75
Volume (mm^3)	3252.968	1074.677
Mass (g)	23.031	8.1559

Table 9: Differences from 7/30/2010 to 10/22/2010

Difference	Copper	Steel
Length (mm)	0.01	0.04
Width (mm)	0	-0.03

Height (mm)	0.04	-0.01
Volume (mm^3)	57.41408	-14.7946
Mass (g)	0.0021	0.001

Samples were then evaluated again after 8 months and again after 14 months. Dimensions and weights are reported below in table. Photos from 3/3/2011 and from 9/27/11 are included as figure 6 and figure 7:

Table 10: Differences from 7/30/2010 to 9/27/2010

	7/30/2010	10/22/2010	3/3/2011	9/27/2011
Copper				
L (mm)	55.6	55.75	55.61	55.74
W (mm)	25.48	25.48	25.47	25.47
H (mm)	2.33	2.29	2.33	2.3
Mass (g)	23.0331	23.031	23.0089	23.0027
Steel				
L (mm)	55.45	55.41	55.44	55.43
W (mm)	25.83	25.86	25.82	25.83
H (mm)	0.74	0.75	0.75	0.74
Mass (g)	8.1565	8.1519	8.1565	8.1564

Figure 6: 3/3/2011

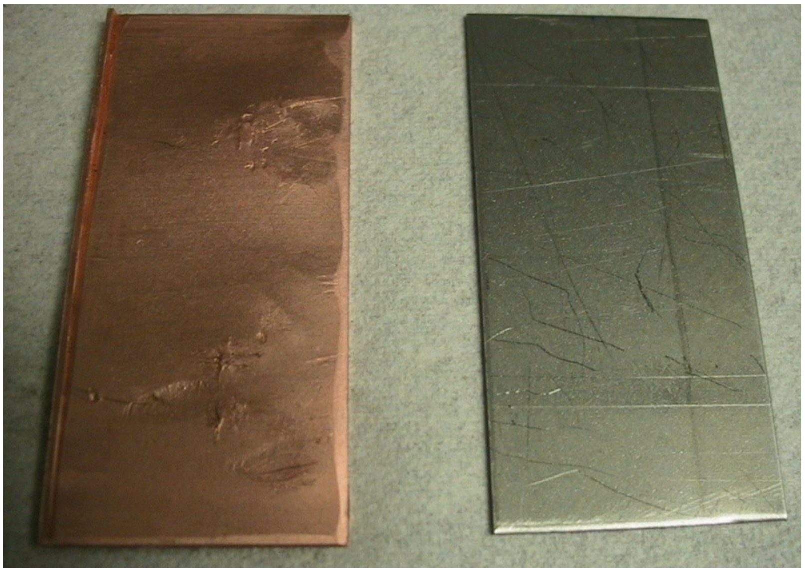


Figure 7: 9/27/2011

In general, the results from the material compatibility tests with steel and copper show that RDO does not have a dramatic impact. From a visual inspection, there is no obvious erosion of the material surface, there is no discoloration, and there are no gums or degradation products forming on the surface of the materials. Additionally, the dimensional changes of the materials are suspected to be within measuring technique error of digital calipers, and are insignificant. This supports the findings in the visual inspection of the material surfaces. Overall, it appears that copper and steel do not seem to be negatively effected by RDO at elevated temperatures of 40C after 14 months. This is a good sign for the use of RDO in existing fuel storage facilities since at normal handling conditions (before heating fuel for combustion), no corrosion has been detected in over a year of simulated storage.

Task 7.0 Facility Design for a Non-Standard Fuel Product

Introduction

It has been reiterated throughout this report that the investigators found 100% neat CWT RDO to perform well as a stand-alone renewable fuel without blending or converting into ASTM Diesel or Biodiesel (see Brookhaven National Lab's boiler test performance in Tasks 6 and Task 12). Additionally, both the attempts to make biodiesel from RDO (produced from low quality greases) and the attempt to find a catalyst or catalysts to split the carboxylic components of RDO to produce ASTM Diesel were unsuccessful (See tasks 4 and 5).

These insights provided the investigators strong incentive to confirm the commercial viability of using RDO as a direct stationary fuel on a large-scale. Under this task a production facility was preliminarily designed to determine capital expenditures required for a plant if built in 2011 for the sole purpose of handling low value and waste greases.

Historical data relating to the construction of Carthage, Missouri along with other engineering relating to Carthage over the last several years (agricultural feedstocks such as poultry carcasses and offal), were used as a basis for expediting/value engineering the costing necessary for a waste grease plant and comfort in addressing key areas for facility design.

Internal engineering documents were assembled and draft material and energy balances were prepared along with design suggestions for building a next generation RDO plant. Thermal Kinetics then assisted the investigators in conducting the bulk of the design and estimating.

Design Basis

It was determined that the plant would be designed for both 10% and 40% moisture feed (range of commercially attractive feedstocks with varying degrees of moisture), both at a production basis of 15,000,000 gallons/year of finished renewable diesel oil (RDO) production. 15,000,000 gallons was chosen as the output based upon the extensive data that was reviewed and written about earlier in the project on market size and what would make economic sense in large metropolitan areas.

The 10% moisture feed composition included:

- 10.0 wt% water
- 81.4 wt% grease of which 93% is converted to RDO
- 6.9 wt% protein of which 35% is converted to RDO
- 0.3 wt% fiber
- 1.5 wt% mineral

The balance for 40% moisture was based on the same “non-water” flows but with added water to make up the 40% moisture. Density of RDO to be used is 7.67 lb/gallon and plant availability is to be established at 92% or 336 days per year (based upon previous experience with the Carthage, Missouri installation).

Scope of Estimate

The scope of the engineering completed included the following :

1. Preparation of material and energy balances for full process.
2. Completion of process flow drawings (PFDs) with stream tables.
3. Development of preliminary P&IDs sufficient to establish line sizes and a rough loop count – I/O count.
4. Instrument list.
5. Equipment sizing, specification, and preparation of outline drawings as needed for RFQ effort.
6. Schedule A equipment list and cost estimate.
7. Facility cost estimate for the basic process areas and major utilities and services (steam boiler, hot oil system, cooling tower, and air quality systems). Cost estimates will be a combination of historical cost data based on the CWT’s Carthage facility, proposals secured by TKE purchasing group, and factoring methods.
8. Equipment general arrangement drawings to establish space requirements and preliminary facilities planning.
9. Utility and services summary including E&I requirements.

The investigators with Thermal Kinetics, completed detailed material and energy balances, process flow diagrams, draft process and instrumentation diagrams, a major equipment list, vessel and reactor outline drawings and major equipment sizing and specifications. All vessels and major equipment went out to bid and ultimately became the basis of the Capital estimate.

Summary of Estimate

A summary of the estimate prepared by from Thermal Kinetics is included as **Appendix D** to this report. Design documents and detailed information about equipment selection and design constraints are not presented due to their confidential nature.

The price established for constructing a TCP operation to process the wastes contemplated by this study (+- 25% estimate) is in the $ 20 to $25 million range.

As for other operating metrics other than capital cost, CWT in it restart of commercial operation has been fortunate to have gained experience with RDO produced exclusively from trap and other waste greases this year in Carthage, Missouri. Some Facts are noteworthy:

- Missouri plant operating costs should ultimately be approximately $1.00 per gallon at full capacity.
- Feedstock cost varies from $0/gallon to greater than $3/gallon. Many wastes are still legally or illegally entering the animal feeding market and thus holding a “value” above what is traditionally considered to be waste depending upon these feedstock’s water content, contaminants, rancidity, solids content or free fatty acid content. These wastes are typically indexed off of the Jacobsen Index that track fats and oils trading.
- CWT has recently qualified under EPA RFS 2 at its Carthage facility for processing wastes of the nature discussed in this project. This qualification is based upon many things including life cycle (energy and material balances) and sustainability of feedstock material.

Task 8.0 Facility Design for Upgrading to a Specification Biodiesel

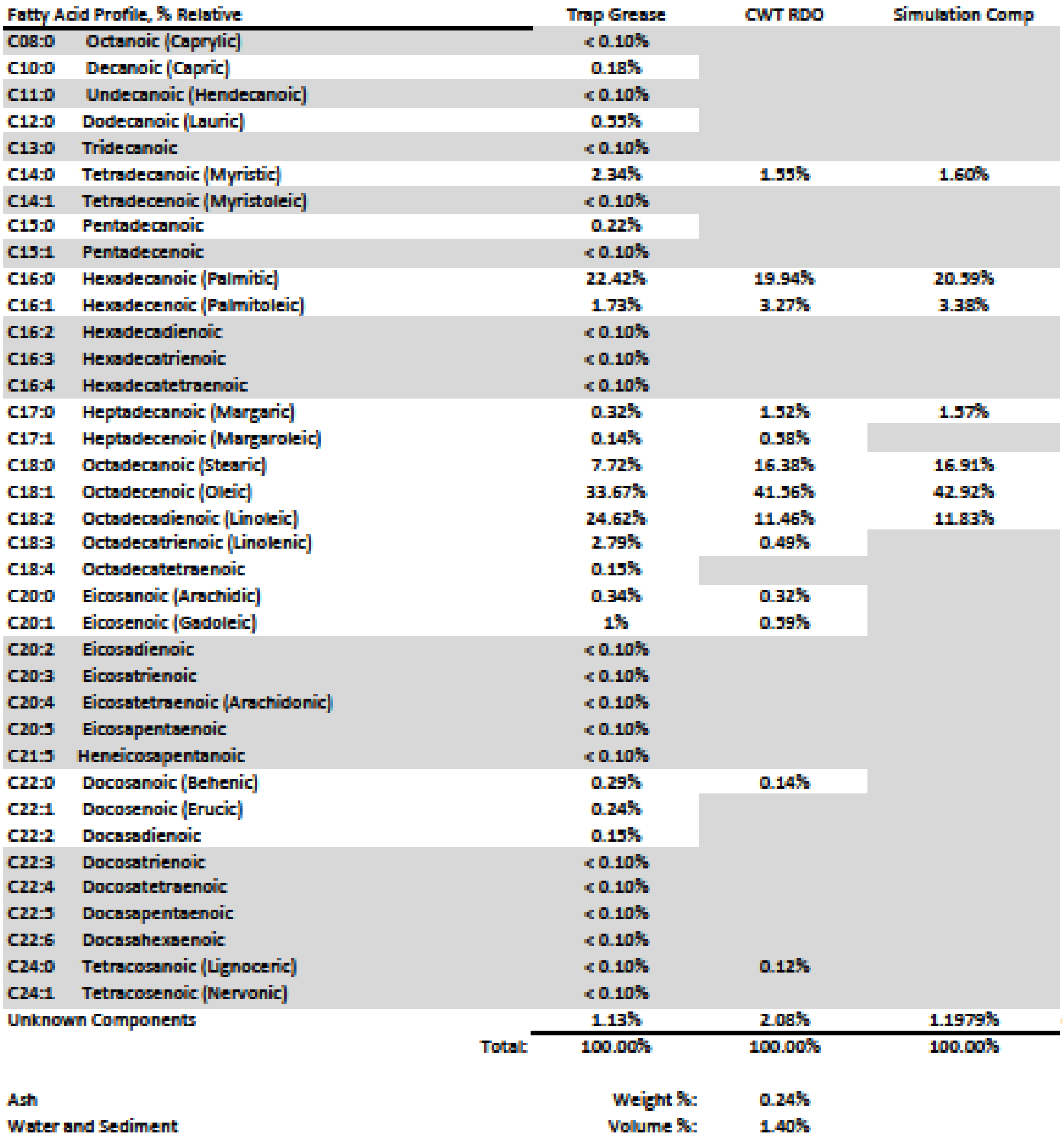
In line with the developments and results of Task 4, significant time and effort was allocated to the preliminary design of a biodiesel production facility using RDO as a feedstock. This work was done in parallel with Task 4 as there was belief among the investigators that an on-spec biodiesel could be produced from RDO made from low quality wastes such as trap grease. At the conclusion of Task 4, investigators were unable to identify a cost competitive series of unit processes that could make biodiesel from RDO and work under Task 8 was terminated before a complete estimate was obtained.

As discussed throughout this report, the conceptual design for Biodiesel production and bench work associated with it in tasks 4 and 8 was based on acid esterification. It was hypothesized that acid esterififcation on its own with little further treatment could be a reasonable add-on to TCP technology to provide an alternate end product for commercial distribution of liquid fuels. Literature selections from Canakci et. al. and others was the basis of the initial work as discussed in Task 4.

Investigators worked closely on this design assignment with outside engineering assistance provided by Thermal Kinetics (TKE) a Buffalo, New York area process engineering company. A production basis of 15,000,000 gallons/year renewable diesel oil (RDO) was chosen as the annual production rate to tie into other project economics being investigated in this study (see Task 7).

RDO characteristics such as fatty acid profile, moisture, ash, etc. were gathered from data obtained during the project's earlier tasks as well as properties of raw trap grease. Previous commercial characterizations of RDO from CWT were also used to validate the composition. Table 11 below is the simulated RDO composition used for the biodiesel facility design. Components making up a de minimus portion of the composition were left out for design purposes as seen in the table and rather than tracking each individual fatty acid, a composite average molecular weight was used in preparing mass balances.

Table 11: Simulation Composition of RDO



Fatty Acid Profile, % Relative		Trap Grease	CWT RDO	Simulation Comp
C08:0	Octanoic (Caprylic)	< 0.10%		
C10:0	Decanoic (Capric)	0.18%		
C11:0	Undecanoic (Hendecanoic)	< 0.10%		
C12:0	Dodecanoic (Lauric)	0.55%		
C13:0	Tridecanoic	< 0.10%		
C14:0	Tetradecanoic (Myristic)	2.34%	1.55%	1.60%
C14:1	Tetradecenoic (Myristoleic)	< 0.10%		
C15:0	Pentadecanoic	0.22%		
C15:1	Pentadecenoic	< 0.10%		
C16:0	Hexadecanoic (Palmitic)	22.42%	19.94%	20.59%
C16:1	Hexadecenoic (Palmitoleic)	1.73%	3.27%	3.38%
C16:2	Hexadecadienoic	< 0.10%		
C16:3	Hexadecatrienoic	< 0.10%		
C16:4	Hexadecatetraenoic	< 0.10%		
C17:0	Heptadecanoic (Margaric)	0.32%	1.52%	1.57%
C17:1	Heptadecenoic (Margaroleic)	0.14%	0.58%	
C18:0	Octadecanoic (Stearic)	7.72%	16.38%	16.91%
C18:1	Octadecenoic (Oleic)	33.67%	41.56%	42.92%
C18:2	Octadecadienoic (Linoleic)	24.62%	11.46%	11.83%
C18:3	Octadecatrienoic (Linolenic)	2.79%	0.49%	
C18:4	Octadecatetraenoic	0.15%		
C20:0	Eicosanoic (Arachidic)	0.34%	0.32%	
C20:1	Eicosenoic (Gadoleic)	1%	0.59%	
C20:2	Eicosadienoic	< 0.10%		
C20:3	Eicosatrienoic	< 0.10%		
C20:4	Eicosatetraenoic (Arachidonic)	< 0.10%		
C20:5	Eicosapentaenoic	< 0.10%		
C21:5	Heneicosapentanoic	< 0.10%		
C22:0	Docosanoic (Behenic)	0.29%	0.14%	
C22:1	Docosenoic (Erucic)	0.24%		
C22:2	Docasadienoic	0.15%		
C22:3	Docosatrienoic	< 0.10%		
C22:4	Docosatetraenoic	< 0.10%		
C22:5	Docasapentaenoic	< 0.10%		
C22:6	Docasahexaenoic	< 0.10%		
C24:0	Tetracosanoic (Lignoceric)	< 0.10%	0.12%	
C24:1	Tetracosenoic (Nervonic)	< 0.10%		
Unknown Components		1.13%	2.08%	1.1979%
	Total:	100.00%	100.00%	100.00%
Ash		Weight %:	0.24%	
Water and Sediment		Volume %:	1.40%	

Based on compositional information on the RDO, the average MW of fatty acid was 280.08. The final composition derived from discussions and used for the front end engineering was:

- 98.2 wt% FFA (avg MW = 280.08)
- 1.5 wt% water
- wt% ash
- 0.25 wt% triglycerides

This information was used to complete a simple balance. Metallurgy decisions were than addressed for the purpose of equipment selection. Since the methanol/water phase from each of the two reaction steps in acid esterification would have ~5% H2SO4 in solution, it was determined that 316L SS would not be adequate since operating temperatures would exceed 60 °C based upon bench work. This meant that major process equipment around the reaction would have to be manufactured with plastic liners, FRP, or other composites. As for further processing of the methanol/water phase to recycle methanol, it was determined that it would be best to neutralize with NaOH or Ca(OH)2 for example to avoid the use of graphite or Hastelloy C heat exchange equipment and expensive columns/vessels. Ultimately is was decided that Ca(OH)2 would be the best choice to neutralize because then solids from neutralization could be filtered or centrifuged before further processing and the liquid sent to evaporation/distillation for separation from the biodiesel.

Conversions were developed through theoretical methods as well as the results provided by Brookhaven National Laboratory experimentation. The first stage reactor was assumed to provide a 98% conversion to esters. The second stage only results in a 46% conversion of the remaining unconverted carboxylics and was restricted based to higher efficiency based upon the water in the reaction. Most of the water in the second reactor would be from water in the methanol itself (1%). Investigators believed that this reaction may go further if a lower moisture methanol is used in this step (increases the cost of). In summary, a two stage acid esterification would then either meet the biodiesel standard or more than likely would not (based upon the bench data the investigators were developing) or a polishing step(s) would be required after these primary reactions. The balances and the simulations are discussed in greater detail in earlier quarterly reports.

Looking to some of the side loops then, the preferred distillation method for methanol recovery appeared to be simple single column with cold feed using considerable energy to recover 99.5% w/w methanol. A molecular sieve integration was looked at to minimize energy, but it did not appear to offer any significant energy savings and is far more capital intensive.

Having settled on a basic balance, unit process requirements and metallurgy, equipment options were reviewed by the investigators. The main option to consider was whether to operate a batch or continuous system. Although a continuous system was preferred, a batch system was also considered. Nevertheless, the batch scenario offered the following problems:

- Two reactors for each reaction step would be needed
- Feed and discharge rates would be 2 to 4 times average flow rates impacting heat exchangers and pumps.
- If a gravity decanter vessel is used, then two would be needed for each reactor to allow sufficient settling time.
- If centrifugal decanters are used, they would need to be sized for some higher flow than average.
- Additional tanks would be needed to interface with continuous downstream operations such as distillation.

Ultimately, a continuous operation was selected. An important issue arose at this point in the design relating to bench-scale observations both at Brookhaven and in Philadelphia and that was the ease of separation of organic and aqueous phases after reaction. Biodiesel will have a density of close to 0.88 gm/cc and methanol/water/H2SO4 mixtures were not much different. In practice the investigators concluded that it might be necessary to adjust acid strength and/or add water to aid in phase separation.

At this juncture in the preliminary design of the biodiesel plant, the biodiesel results from South West Research Institute were issued from the large scale bench runs performed at the Philadelphia TDP facility. These results called into question that feasibility of actually achieving the ASTM D6751 specification using such low quality feedstocks.

In retrospect, there have been many attempts to produce biodiesel from very low quality fatty materials with limited success, typically occurring through dilution strategies with better quality feedstocks such as soybean oil or even distillation strategies to attempt to remove column bottoms (unsaponifiables and other impurities for example) that make meeting the biodiesel spec nearly impossible. The CWT TCP process does not appear to offer any real advantage to the biodiesel industry as a pretreatment in dealing with these issues that they face.

Task 9.0 Facility Design for Upgrading to an ASTM Specification Diesel

In Task 5 much bench work was conducted at both Brookhaven National Laboratory, Stony Brook University and at TDP in Philadelphia to find a non-traditional means to catalyze decarboxylation of CWT's RDO fuel oil product. The investigators agreed that there was no pathway that showed enough promise to justify looking at a plant design. Work on this task was terminated as a result.

Task 10: Review of Natural Resources

Early in the development of this project the investigators developed a report to identify municipal waste streams in commercial quantities that can be converted into a diesel fuel substitute, RDO. Multiple feedstocks have been identified including, brown grease, dissolved air floatation (DAF) sludge, soap stocks, unrefined restaurant greases, trap grease, corn condensed distillers solubles (CDS), fatty acids, oleo wastes and wastewater skimmings. These wastes all have similar properties as they all contain a percentage of water, fat and in some instances a solids component.

Brown grease is defined as a 100% vegetable oil or animal fat not exceeding a free fatty acid content of 50%, but being in excess of 15% free fatty acid. Moisture content is low, usually less than 0.5%.

Dissolved air floatation (DAF) sludge is fat-containing by-product from a water treatment process where dissolved air floatation is utilized as a means to extract fat/oil from a waste water stream.

Soap stock is a by-product generated in large quantities by soybean, canola, and sunflower oil refiners during the oil purification process. Soap stock will generally contain 50% oil/derivatives and 50% water to maintain flow ability.

Unrefined restaurant greases are about 65% oil, remainder water (25%) and some solids (10%).

Trap grease is a waste product generated by the servicing of wastewater grease traps and runs about 8 to 10% oil/grease, 20% solids, remainder (70%) water.

Reclaimed fats/oils, fatty acids, oleo waste and wastewater skimming are waste streams that are commonly generated by vegetable oil processors/refiners that produce these waste oil streams from tanker/railcar cleaning, margarine and/or salad dressing production, specialty bakery products, and wastewater treatment decanters.

Corn condensed distillers solubles (CDS) is a term generally used to refer to the evaporated co-products of the grain fermentation industry.

The report has identified 10 different feedstock options that are available in commercial size quantities that meet the criteria of municipal waste streams. All of these products can be combined into a single waste stream and converted into a fuel.

The concept of combining the above feedstocks/waste streams has been recently proven at commercial scale this calendar year at CWT's Carthage, Missouri production facility. CWT in it restart of commercial operation has been fortunate to have gained experience with purchasing or otherwise acquiring wastes from many of the sources identified above and have been able to successfully convert commercial quantities into saleable RDO.

Task 11.0 Pilot Scale Thermal Depolymerization Runs to a Non-Standard Product

Introduction

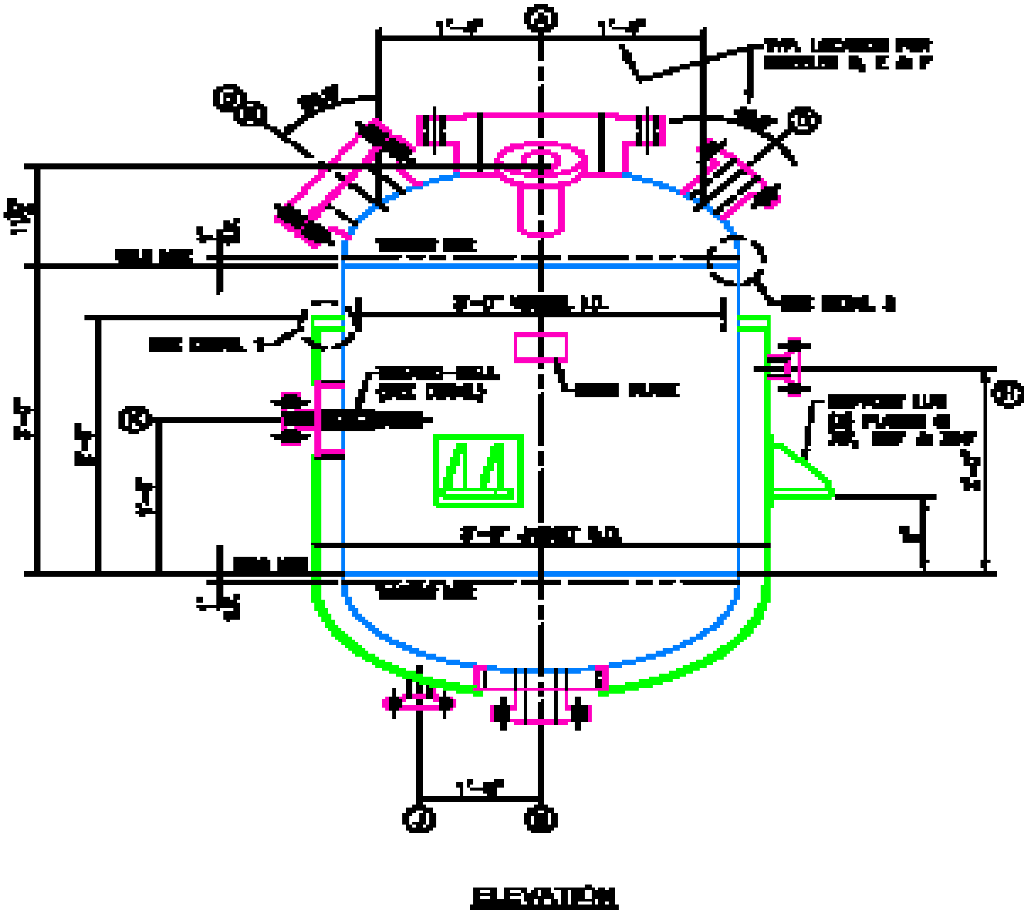
CWT successfully converted greasy food waste (i.e. grease trap waste) into Renewable Diesel Fuel Oil (RDO) in the company's new pilot reactor located in Philadelphia, PA. The company used several hundred gallons of high moisture, low quality waste to produce approximately 170 gallons of RDO. The quantity manufactured was in line with the project's goals for combustion testing to be done at the Brookhaven National Laboratory (BNL) (see next section). Two 55 gallon drums of RDO from the pilot runs have since been shipped from the Philadelphia plant (along with product from CWT's recently re-commissioned commercial facility in Carthage, Missouri) to BNL for their use in the combustion testing (see Task 12).

Prior to shipping RDO to BNL, product quality was closely evaluated internally and externally at the Philadelphia plant and compared it to relevant standards and to what is now produced in the facility in Missouri. The mixture of low quality waste properly converted to RDO as was expected.

Pilot Construction

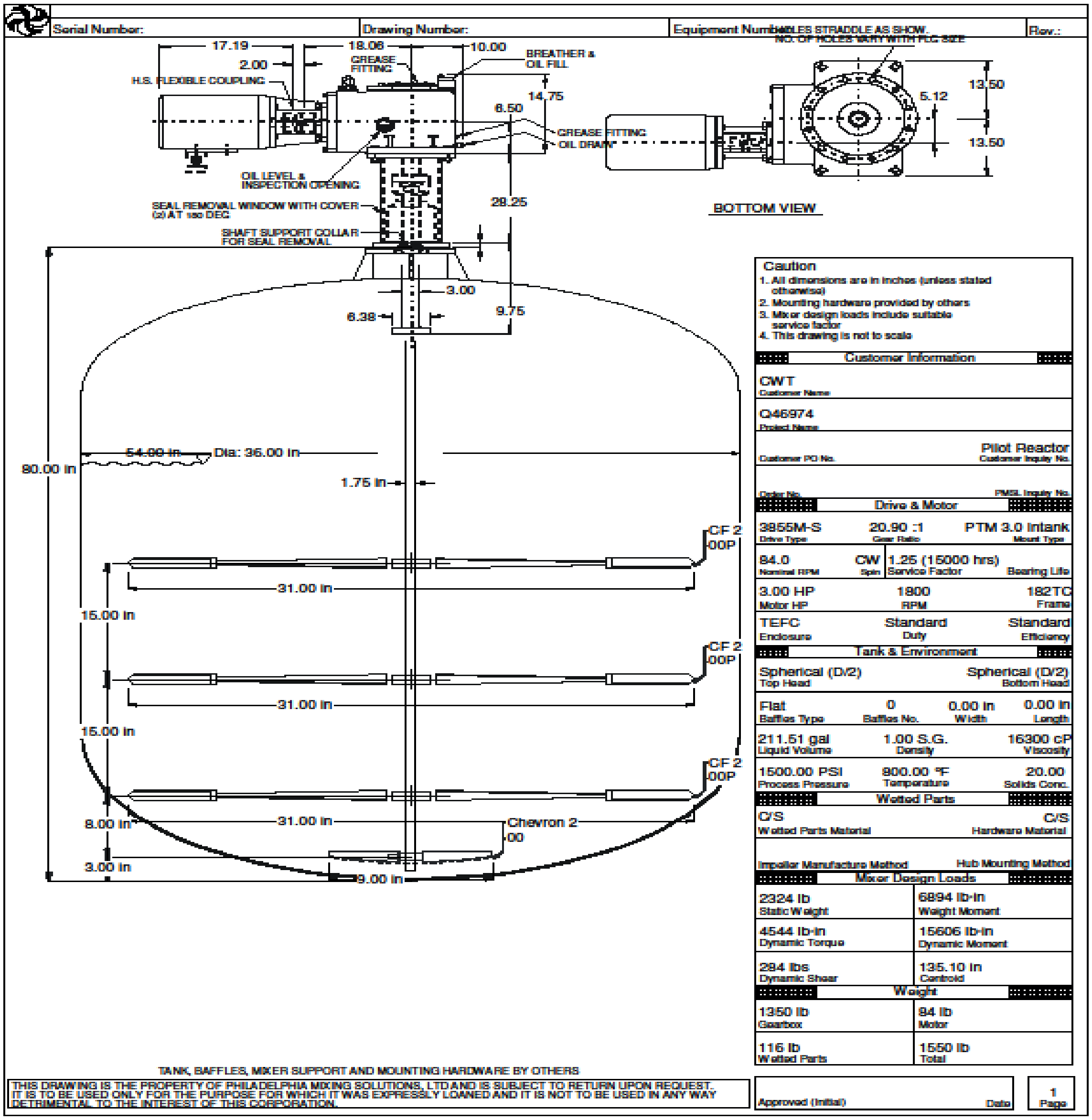
The pilot trials in Philadelphia utilized a new 210 gallon jacketed reactor that was manufactured at Gasport Welding (ASME Vessel Manufacturer), near Buffalo, NY, whose quote was selected out of 5 fabricators that bid the job. The reactor was designed by the project investigators in conjunction with a mechanical engineering company, Thermal Kinetics (TKE) located near Buffalo, NY as well.   The reactor was designed to be used in conjunction with an existing hot oil thermal system already in service in Philadelphia. Figure 1 below, shows a fabrication drawing for the reactor that was ultimately constructed for the project.

Figure 1: 160 gallon reactor drawing



As is discussed in several earlier reports issues for this project, many options for reactor mixing were investigated. One such option was to repurpose a Philadelphia Mixer for the reactor. A design of the option follows as Figure 2.

Figure 2: Proposed reactor and mixer configuration



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Caution
1. All dimensions are in inches (unless stated otherwise)
2. Mounting hardware provided by others
3. Mixer design loads include suitable service factor
4. This drawing is not to scale

Customer Information

CWT
Customer Name

Q46974
Project Name

Customer PO No.
Pilot Reactor
Customer Inquiry No.

Order No.
PMSL Inquiry No.

Drive & Motor

3855M-S Drive Type	20.90 :1 Gear Ratio	PTM 3.0 Intank Mount Type
84.0 Nominal RPM	CW Spin	1.25 (15000 hrs) Service Factor / Bearing Life
3.00 HP Motor HP	1800 RPM	182TC Frame
TEFC Enclosure	Standard Duty	Standard Efficiency

Tank & Environment

Spherical (D/2) Top Head			Spherical (D/2) Bottom Head
Flat Baffles Type	0 Baffles No.	0.00 in Width	0.00 in Length
211.51 gal Liquid Volume	1.00 S.G. Density		16300 cP Viscosity
1500.00 PSI Process Pressure	900.00 °F Temperature		20.00 Solids Conc.

Wetted Parts

C/S Wetted Parts Material	C/S Hardware Material
Impeller Manufacture Method	Hub Mounting Method

Mixer Design Loads

2324 lb Static Weight	6894 lb-in Weight Moment
4544 lb-in Dynamic Torque	15606 lb-in Dynamic Moment
284 lbs Dynamic Shear	135.10 in Centroid

Weight

1350 lb Gearbox	84 lb Motor
116 lb Wetted Parts	1550 lb Total

Approved (Initial) Date

1
Page

After much debate about the physical characteristics of the feedstocks that were being evaluated in this project, the investigators opted for an alternate mixing design. A seal-less high pressure high temperature magnetic drive pump by Kontro was rebuilt and repurposed for the application. This ump was successfully used to re-circulate and mix reactor feedstock during the reaction period.

After all new and repurposed components were ordered, reconfigured and received , the TDP facility staff completed cleanouts, mechanical, electrical and instrumentation connections, and commissioning of all equipment including applicable tanks, pumps, centrifuges and piping.

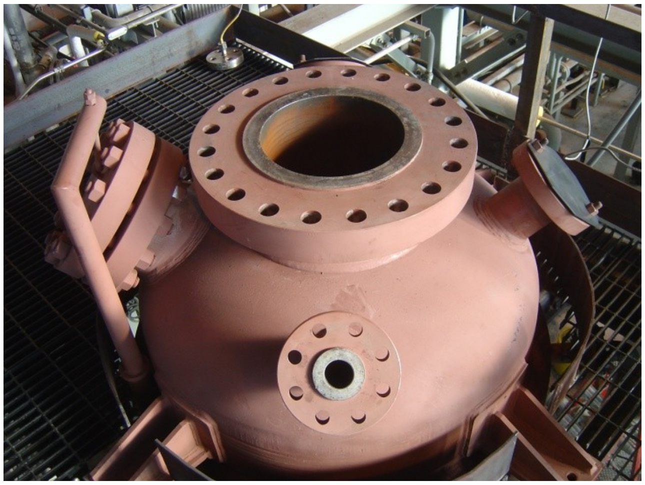
Based upon process design, the trials were all run in a batch environment, with temperature and pressure reduction occurring after each reaction was complete.

In order to accommodate the 210 gallon reactor, TDP removed an existing pulping system at the Philadelphia facility. They then did structural steel calculations and this rigged the reactor to be suspended in the area of the plant where the pulper had once been. The aforementioned hot oil heater and other components that were available for the pilot on-site were moved into position as well. The site under construction can be seen in **Figure 13** below (hot oil system is on right side of photo).

Figure 13: Reactor location where prior pulping system has been removed

Figure 14, below shows the reactor prior to insulating and cladding the reactor is supported by a modified structure that previously housed a pulper system.

Figure 14: Pilot Reactor



P&IDs for the Philadelphia pilot process and other technical data have been presented through the course of the project and are not duplicated here to keep report focused.

Commissioning and Production Runs

The feedstock used was a mixture of trap grease and yellow grease in order to simulate a commercial process. Trap Grease was received from Long Island, NY and St. Louis, MO. Yellow grease was also acquired to create a low value blend of waste products for the trials. Inbound feedstock was screened using a duplex basket strainer.

Commissioning was commenced and completed for the following plant systems:

- hot oil system
- plant air system
- utility steam,
- electrical system,
- reactor recirculation mixing pump loop,
- non-condensable gas system,
- waste steam condenser,
- cooling water system

Water trials were then completed on the whole process to test the thermal fluid system, pressure check the process, and check for leaks. The water trials also allowed TDP personnel to further configure and test parameters set up to be recorded and trended in the DCS system. Considerable effort was made to configure the recirculation pump to operate acceptably within process guidelines. The aim was to run the pump at the maximum rate possible without any adverse effects. This proved to require a number of trials with the pump manufacturer's representative as the pump must be set to shut off under a low or high load reliably. Ultimately, a representative for the pump controller manufacturer (Emotron) configured the controls while TDP personnel ran a trial using a representative feedstock of grease and water.

Training of plant staff to properly and safely run the new high pressure reactor were completed in conjunction with the aforementioned water trials as well.

As mentioned previously, TDP received totes of low quality grease trap waste from two waste management companies. Higher quality (lower moisture) grease was also obtained from a Pennsylvania firm. The trap grease that was ultimately processed came from Long Island and from an Eastern Missouri pumping company. The Investigators evaluated the quality of the mixture of greases used in the pilot stage of Task 11 and confirmed that it was a realistic commercial mix of the products available in the market from actual waste processes. Data on product qualities of these very low quality non-food products have been presented in several prior reports and are not duplicated here.

Bench scale Parr reactor runs were performed on both of the selected trap grease feedstocks. These preliminary batch reactions were used to validate use of the feedstocks in the pilot plant. The feedstocks were combined with the higher quality grease and water in the following ratio: 25% trap grease, 25% yellow/brown grease, 50% water. Visual and quantitative analysis showed that both feedstocks proved to convert effectively. After feedstocks were blended as indicated above, raw feed characteristics were obtained and another Parr reactor run was performed similar to the first two but instead using the mixed trap grease feedstock. Once again visual and quantitative analysis showed an effective conversion, and this ratio was used for the pilot trials. As has been discussed elsewhere in this report, the premise for using a mix of trap grease and higher quality grease is based on previous market studies under the project that demonstrated commercial availabilities could preclude a production plant from running only trap grease. It was also learned previously that using the mixed feedstock would also allow the plant to run most optimally based on the availability of waste greases.

For the larger scale pilot runs, the mixed waste was pumped through the duplex strainer once more on its way to charge the reactor. The reactor contents were heated and held at desired temperature and pressure set points. The pump functioned properly and no problems were experienced. Upon completion of the heating, the thermal fluid system heaters were turned off and the reaction was flashed through a condensing heat exchanger. The resulting contents of the reactor runs converted and separated well indicating a successful trial with the waste mix. Water and solids from the reactor were decanted while the mixture was still hot. The resulting lower density (floating oil was then pumped through filters (cloth – 3 microns) to a mobile jacketed storage tank. Samples were taken on all cuts of the reaction. Preliminary numbers showed the oil would need to be further dewatered as no liquid/liquid centrifugation or separation had yet been performed on the oil fraction. Further gravity decanting and dehydration were conducted to produce a final RDO product.

This task has provided valuable data and insight into value adding waste into a renewable fuel. Although funding from the grant has ended, CWT is continuing with further evaluation and analysis on completing some areas of interest. Of particular interest are the subtle perturbations in characteristics of waste feedstock and the impact on RDO fuel quality and ultimately what needs to be considered in a next generation RD plant specifically for low value waste grease.

Task 12.0 Combustion Tests of Non-Standard Fuel Product in Boiler Applications

Preparation

Preparations for the 100 hour fuel combustion test that is now underway at Brookhaven National Laboratory were conducted over the course of several months. Samples of RDO produced at the pilot facility in Philadelphia and at the recently re-commissioned commercial TCP plant in Carthage, Missouri were sent in advance before a final shipment was made to assure that the properties of the fuel were in line with the equipment selected by the investigators for the test. Issues such as the following were discussed and evaluated:

- No filter clogging issues
    - filtration specifications
    - pour point / preheat expectations
- Ignition capability
    - Using No 2 oil to fire off
    - Using 100% RDO on cold boiler (successful)
- Nozzle temp
- Atomization pressures (not using steam or air atomization with the burner that was selected for the test)

With a strong preliminary understanding of the fuel and its anticipated performance, the 100 hour test was scheduled. Of special note, the fuel that is being used in the 100 hour test was ultimately manufactured in a commercial setting in Missouri providing real time analysis of the waste grease markets that are targeted by this study. The pilot facility in Philadelphia was built and operated in accordance with this project's scope but it was believed that since Carthage, Missouri was recently restarted (in part with lessons learned in the pilot in Philadelphia) it was advantageous to use a stream from a commercial plant with the specific focus of processing trap grease, dissolved air floatation skimmings and other low grade greases that a production plant data set would be more valuable to the reader than would pilot scale data.

General Goals of the 100 hour test

The long term combustion test underway has a firing rate of approximately 0.75 gallons per hour and is being run to look at issues such as the following:

- Emissions profile vs. excess air
    - Optimal tuning for smoke, NO_x, CO, O_2
- PM 2.5 measurements at optimal tuning
    - Compare fine particulates with other fuels
- Net energy comparison between No.2 fuel and CWT's RDO
    - Calorific value determination without bomb calorimetry
- Cad Cell resistance plot vs. O_2
- Cyclical and steady state operation
- Retention head carbon buildup, gumming and/or varnishes
- Nozzle plugging and coking
- Boiler ash deposits
- Ignition reliability
- Emissions stability

As of this submission, the 100 hour test is well underway. Data collected on September 22, 20011 follows.

Test Conditions

Parameter		Renewable Diesel (RDO)	No. 2 Heating Oil (Baseline on Same Burner)
Nozzle Temperature		275 °F	115 °F
Fuel Tank Temp		135 °F	Ambient
Boiler Temp 140 °F		140 °F	140 °F
Burner start time (ULSD)		9/22/11 8:30 AM	Morning of Sept 27th
Burner switched to RDO		9/22/11 9:00 AM	NA
Burner Shut down Time		9/22/11 3:30 PM	4 hour combustion runtime
Smoke number		3	0

Comparison RDO to No 2 Oil

Parameter	Average RDO Values	Average No 2 Oil Values
Stack Temp	355.0	335.5
Oxygen %	6.3	6.08
CO2 %	11.0	11.15
CO ppm	2.6	2
NO ppm	178.2	92.8
NO2 ppm	2.1	0
Nox ppm	180.2	92.8
SO2 ppm	30.5	40
Excess Air %	39.8	36.8

Un-Averaged Data

Run 1 RDO	**Duration 96 min**									
Time		9:20	9:23	9:36	9:51	10:03	10:31	10:46	10:53	AVG
Stack Temp		352.9	357.8	355.1	355.5	355.1	353.3	354	355.2	354.9
Oxygen %		6.39	6.63	6.47	6.42	6.45	6.3	6.59	6.47	6.47
CO2 %		10.91	10.73	10.85	10.88	10.86	10.98	10.76	10.85	10.85
CO ppm		4	4	4	3	3	2	2	3	3
NO ppm		175.7	173.9	177.4	174.7	179.3	176.7	175.6	175.6	176.1
NO2 ppm		1.4	1.8	2.2	1.8	1.6	2.2	2.2	2	1.9
Nox ppm		177.1	175.7	179.6	176.5	180.9	178.9	177.7	177.6	178.0
SO2 ppm		23	33	33	31	31	28	30	30	30
Excess Air %		40.5	42.7	41.2	40.8	41	39.6	42.3	41.2	41.2

Un-Averaged Data

Run 2 RDO	**Duration 96 min**									
Time		11:09	11:12	11:26	11:41	11:55	12:16	12:31	12:45	AVG
Stack Temp		357.9	358.5	354.1	355.3	354.4	356.1	353.8	355.1	355.7
Oxygen %		6.15	6.53	6.56	6.38	6.9	6.34	6.53	6.31	6.46
CO2 %		11.09	10.8	10.78	10.91	10.52	10.95	10.8	10.97	10.85
CO ppm		3	2	2	2	3	2	2	2	2
NO ppm		178.4	178.4	177.3	175.7	176	176.1	175.1	173.6	176.3
NO2 ppm		2.2	1.8	2	2.2	1.4	2.2	2	2.4	2.025
Nox ppm		180.5	180.1	179.3	177.8	177.4	178.3	177	175.9	178.3
SO2 ppm		30	33	32	28	33	29	30	30	31
Excess Air %		38.3	41.8	42	40.4	45.3	40	41.8	39.7	41.2

Un-Averaged Data

Run 3 RDO	**Duration 96 min**								
Time	2:06	2:14	2:28	2:36	2:44	2:59	3:16	3:22	AVG
Stack Temp	355.6	358.6	351.8	352.2	350.6	357.4	355.6	353.7	354.4
Oxygen %	6.24	6.3	6.41	6.34	6.09	5.37	5.54	5.64	5.99
CO2 %	11.02	10.98	10.9	10.95	11.13	11.67	11.54	11.47	11.21
CO ppm	2	3	2	2	3	3	2	3	3
NO ppm	181.3	185	180.6	178.9	178.8	194.9	182	175.9	182.2
NO2 ppm	2.6	2.7	2.2	2.2	2.2	2	2.2	1.8	2.2375
Nox ppm	183.8	188	182.8	181.1	181	196.9	184.2	177.7	184.4
SO2 ppm	30	32	31	31	27	35	32	29	31
Excess Air %	39.2	39.6	40.6	40	37.8	31.8	33.2	34	37.0

Test Commentary on the 100 hour Combustion Test to-date

Combustion testing of a large sample of fuel received from CWT was performed at Brookhaven National Laboratory with the goal of evaluating basic performance and air pollutant emissions over a 100 hour (cumulative) run time period. The burner used for these tests is typical of the construction used in small, oil-fired boilers and includes a pressure atomized, swirl nozzle operating at a pressure of 250 psig. This specific burner has been modified to incorporate a nozzle/line heater at the firing end of the fuel line. This heater enables close control of the adjustment of the temperature of the fired fuel. The fuel system includes a close-coupled, heated storage drum, heated fuel transfer line and 90 micron in-line fuel filter. Firing rate for all tests was .75 gallons fuel/hr.

The burner and nozzle/heater assembly was provided to this project by Carlin Combustion Technologies, Inc.. This is a very recent development by this company currently in field trials/early market deployment. This heater assembly has been designed for low surface heat flux which provides fuel heating without high local internal temperatures which can lead to fuel coke formation. The heater is being used in a modulating, pressure atomized burner in which both pressure and temperature are being used to control firing rate while maintaining a high atomization quality over a 2/1 burner turndown ratio. As used in this test the nozzle heater was coupled with a temperature controller and fuel pressure was fixed. For these tests the burner was fired in a typical small boiler with a horizontal combustion chamber, 10 inches in diameter.

This chamber is steel with a thin (1/2” wall) refractory liner approximately half of the 18 inch length. This refractory liner is standard with #2 oil firing (Thermodynamic Co. Model LM-75).

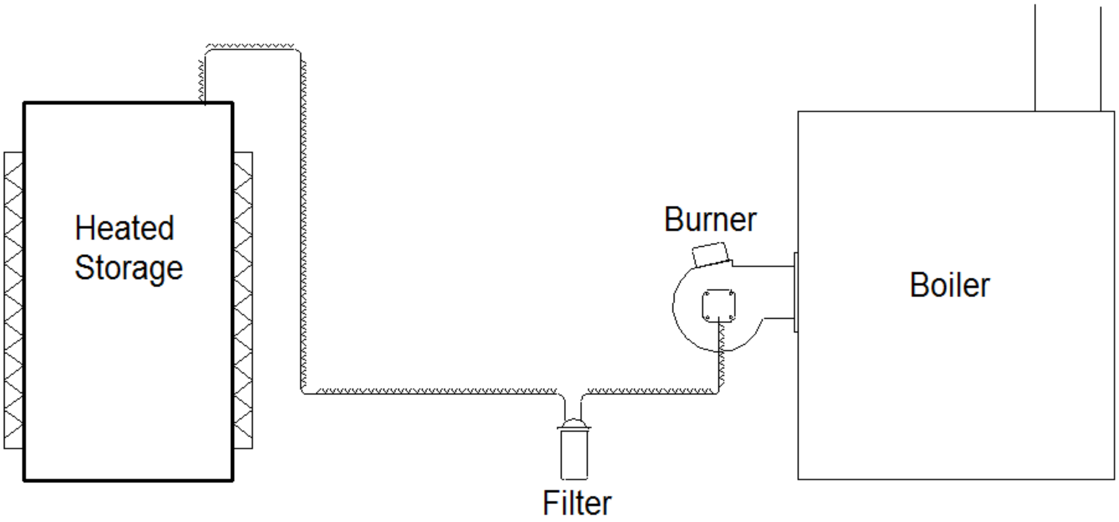


Figure 1. Illustration of Boiler Combustion Test Arrangement

For the 100 hour combustion testing the burner is operated daily in steady state for roughly 8 hours. The fuel sample tested is not a liquid at room temperatures and must be heated to a minimum of 110 F. For this reason the burner fuel line is purged after every run period with #2 heating oil. It has been demonstrated, however, that the boiler can be started from cold, with the CWT fuel using the heated nozzle.

Flue gas composition during these tests has been measured using an integrated analyzer with wet cell sensors (Testo Model 350). Flue gas smoke number was measured using a manual Bacharach filter scale.

As compared to conventional #2 oil firing the fuel tested here has higher NOx emissions (180 vs ~ 93 ppm) and a higher smoke number (4 vs. ~0). Flame appearance and stability were found to be excellent during all tests. As of the present time, the planned 100 hours of combustion testing is 50% completed. The full 100 hours will be completed by the end of Sept. 2011.

In addition to combustion testing in the boiler some combustion tests were also conducted using a special quartz combustion chamber. This chamber is frequently used at BNL for simple whole-flame evaluation. Like the test boiler the chamber is a horizontal cylinder with a 10 inch diameter and 16 inch length. Figures 2 and 3 provide a comparison of the flame with #2 oil and the CWT fuel. In both cases excellent retention of the flame on the burner head can be noted as well as a similar flame length.

Figure 2. Image of a#2 oil flame in quartz combustion chamber

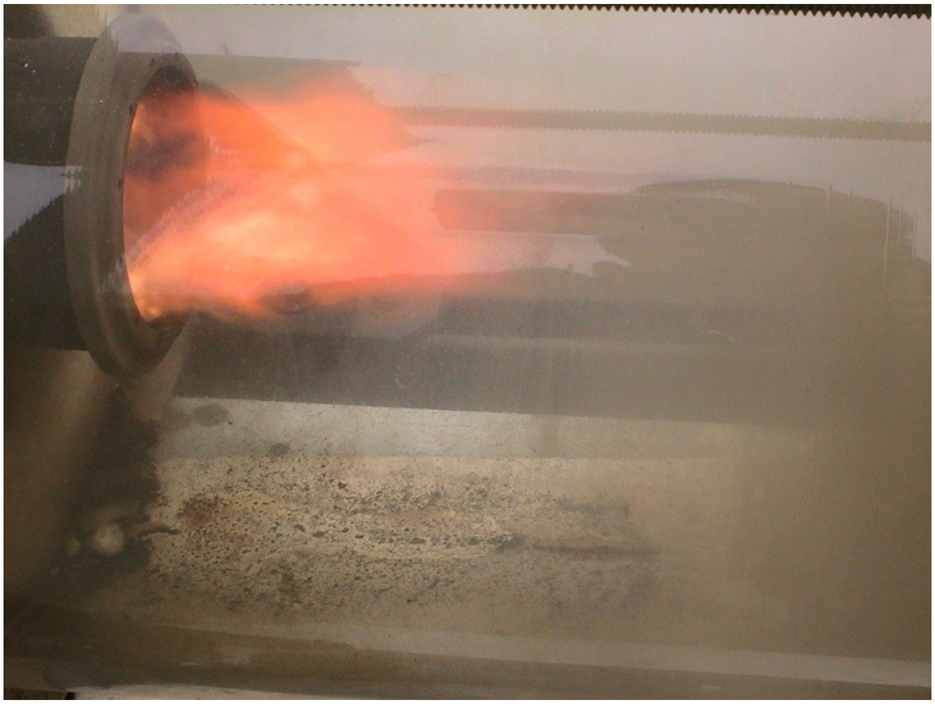


Figure 3. Image of CWT fuel flame in quartz combustion chamber

Task 13.0 Comparison of the Economic and Technical Factors Associated with End Product Targets

Three end product targets were investigated in this study:

4. The production of Renewable Diesel Oil (RDO) as a stand-alone fuel,
5. The production of RDO as a platform for the further manufacture of Biodiesel utilizing acid esterification and
6. The production of RDO as a platform for the manufacture of an ASTM Diesel Fuel using one or more catalysts to effect a decarboxylation of the carboxylics present in RDO

These product targets were carefully studied and are discussed at length in this report (see Tasks 4,5,6,7,8,9 and 12). The cumulative result of these investigations found that the manufacture of Biodiesel and ASTM Diesel from very low quality waste grease was impractical. Neither the optimized bench-scale studies conducted using acid esterification for biodiesel production nor in-situ or stand-alone catalytic decarboxylation for the production of ASTM Diesel turned out to meet requisite product specifications for those product targets.

Although the results were inconclusive in finding ways to utilize RDO technology, in effect, as a pretreatment for commonly discussed technologies such as Biodiesel and ASTM Diesel, this study does shed much light on the properties, performance and cost of utilizing waste greases directly as a retail liquid fuel (RDO). Details about RDO are already reported at length in many sections of this report and are not repeated here. (see Tasks 3,6,7,11 and 12).

Appendices:

A. Site Selection Report Colorado

B. Biodiesel Production from Trap-Grease

C. Development of Upgrade Processes to Convert to ASTM Diesel

D. RDO Plant Cost Estimate Summary

APPENDIX A

Table of Contents

INTRODUCTION:

Between June 23 and June 25, 2003, Paul Halberstadt, Jim Freiss and Bill Powell conducted visits to two potential sites for construction of a CWT-TP facility in Colorado.

One site is adjacent to the ConAgra turkey plant in Longmont. The other site is located on a ConAgra turkey farm approximately 20 miles away from the Longmont plant.

Visits were also conducted to the Swift beef plant in Greeley and the ConAgra turkey plant in Longmont to discuss with managers current and/or future feedstocks that may be available for the CWT-TP plant.

Finally, a brief meeting with Weld County Planning and Zoning was conducted (anonymously) in order to better understand zoning issues for the Evergreen site.

Bill Powell remained in Colorado for June 24 and 25th to investigate engineering and code requirements and to attempt to locate qualified contractors for the construction of the CWT-TP plant.

An outline of the three-day trip is enclosed as an appendix to this report (***Appendix 1***). The remainder of the narrative is organized as follows:

Site Reconnaissance
  A. Evergreen property
  B. Longmont property

Feedstock Investigations
  A. Greeley
  B. Longmont

Recommendations and required actions for project execution.

SITE RECONNAISSANCE

The Evergreen Property

The Evergreen Farm is a ConAgra property that houses approximately 33,000 finisher turkeys making it the smallest of the finisher farms in the Longmont Complex. The site is located approximately 23 miles from the Longmont Turkey plant and about 20 miles from the Swift plants in Greeley. A general site map showing the Evergreen farm in relation to Longmont and Greeley is attached as ***Exhibit 1***.

The property is one half mile wide by one mile long (320 acres). The Northern most quarter of the property (about 80 acres) that abuts the paved road is occupied by the turkey farm. The remaining three-quarters (about 240 acres) are undeveloped with the exception of oil and gas wells and associated collection tanks and piping (Petina Oil and Gas Corp.).

The turkey farm was constructed in the 1970's. The improvements identified on the property by the county assessors office (available on the county [Weld County] website) is attached as ***Exhibit 2***. An appraisal performed for ConAgra for the property is also attached as ***Exhibit 3***. The current appraised value is $ _______ *(To de obtained at a later date and will be forwarded at that time.).*

The property is surrounded mainly by agricultural entities. A sketch of area property usage is provided as ***Exhibit 4***. To the north are pastures and a very large dairy farm. To the south is irrigated cropland. To the east are industrial/commercial entities which include auto salvage (junkyard) and a tire disposal site (aptly named "Tire Mountain"). Site photographs are also provided with the area usage sketch (***Exhibit 4***). The nearest neighbors to the site are to the southwest of the property (see ***Exhibit 4***).

The utilities near the Evergreen property appear substantial. A rough sketch (no capacity, pressure or line sizes are known at present) is provided as ***Exhibit 5***. Road access to the property is limited to the frontage near the turkey barns (to the north) and to a non-maintained deeply rutted dirt road on the west side of the tract. Natural gas and electricity are nearby as shown on the drawing (Greeley Gas Company (800) 922-1987 and United Power – no phone number noted). No wastewater facilities are located in this area although the adjacent dairy farm does have a permitted irrigation system for liquid agricultural wastes. The dairy, operated by John Moser, provided us with a drawing of their farm and associated irrigation areas (*See* ***Exhibit 6***) [Morwai Dairy 19999 WCR28 Hudson, Colorado 80642]. Potable water has been brought to the area (by the dairy) although the ability to get capacity on this line appears to be very costly (Northern Colorado Conservancy District) and time consuming. There are ground water wells located near the turkey barns which are permitted for commercial use.

Soils on the Evergreen property are identified on ***Exhibit 7***. The exhibit includes the site soil map and report prepared by the Soil Conservation Service (SCS). Excerpts from the soil survey report include:

1. Soil map
2. Soil descriptions
3. Engineering properties
4. Physical and chemical properties
5. Soil and water features
6. Typical soils horizons
7. Area rainfall and temperature data
8. Freeze dates
9. Soil fertility
10. Tables relating to constructability, etc.

In general, the soils are gently sloping and well drained (very sandy with quite a few fines). This report should be helpful in understanding soil engineering in general terms,

A topographic map from the USGS is provided for Evergreen as ***Exhibit 8***.

After careful onsite review, we developed a preliminary siting scenario for the RES plant if we were to pursue this farm. First, we would want to be located as far away from the turkey farm to alleviate any concerns ConAgra would have relative to bio-security. Second, we would want to locate the facility as far away as is practical from residences and third, we would want to locate on high ground as close as possible to existing utilities and paved roads. The best preliminary location is shown on ***Exhibit 8***. We should consider acquiring acreage not just for the current proposed tonnage but for future expansion. Possibly a parcel of about 40 acres would be suggested. After receiving feedback from utility companies and the road department, we have prepared a more detailed sketch of this parcel with proposed utility runs (see ***Exhibit 8A***).

Aerials of the property from the USGS and from a private flyover are provided as ***Exhibit 9***. What appear to be roadways in the undeveloped portion of the farm are the roadways between well heads (the well heads are seen as tiny circles at the end of each roadway). The gas and oil collection tanks are located at two points along the western boundary of the property. These points can also be seen on the aerial. At present we assume that the piping is buried along or under the roadways (this needs to be verified).

Given the initial siting scenario described above (see ***Exhibit 8***) only one well head appears to be within the proposed area.

The deed for the property is attached as ***Exhibit 10***.

The well water withdraw permit is provided as ***Exhibit 11***. An analysis of the well water for nitrates and fecal chloroform is included with the permit (no detection of either contaminate noted in 2000). The two wells (one is in service and one is not in service – both located close to the turkey barns in the northwest corner of the property) are supposedly drilled into the Fox Hills Aquifer (good soft water). John Moser (Morwai dairy farm owner) said that although the site has a withdraw permit of 35 gpm (gallons per minute), he rarely has seen a well in the Fox Hills Aquifer that would yield more than about 15 gpm on a sustained basis. New wells into the Fox Hills formation he believed would cost about $ 20 – 25,000 each fully installed. Doug Pennock said that he knew of a pump test where the well yielded 40 gpm. This may not have been on a sustained basis though.

Both Doug Pennock (Longmont Farms) and John Moser recommended Mr. Kim Lawrence (telephone 970-356-9160) as the best local water attorney to help sort out allocation, use, etc. In discussion with Doug, he said that when turkeys are full grown (just before being sent to slaughter) that he believed the turkey farm used most of the well's capacity (maybe 30 gpm) during certain times of the day. He felt that there is a lot of excess capacity if storage were provided on site. Using a usage rate of 220 gallons per 1,000 full-grown Tom Turkeys per day (from Utah State University Extension Service Fact Sheet, August, 2000). The Evergreen Farm would have a worst case 24-hour usage of approximately 7,500 gallon. This would leave 35,700 gallons per day of permitted capacity.

We met with a county planner, Jacqueline Hatch, (anonymously) to discuss a hypothetical project in Weld County to be located on agricultural land. The planning office is located in Greeley (the county seat) near the Swift plant. We were advised that the County Planning Office conduct weekly staff meetings where they review projects that are potentially upcoming. They ask that a letter be written explaining the nature of the project. After their review (usually within one to two weeks), they respond with a proposed strategy for filing the project with the county. Weld County Zoning application forms that most likely apply to our proposed project are included as ***Exhibit 12***.

We received a recommendation by John Moser that we might want to use AgPro, an environmental consulting group in the City of Longmont, for wastewater planning purposes at the Evergreen site. Tom Heron is the owner of AgPro and Moser believed he has done a great job managing Moser's environmental affairs. Moser plans to ask Tom Heron what requirements would RES and John Moser need to meet to use Moser's waste management facilities for either excess clean water from a Vacom-type system or for nitrogen ladened produced water if we did not use a Vacom-type system. (This may or may not be a simple process. We should not count on this one.)

As a result of our meeting at the farm Doug Pennock began making contacts with local utility providers (he did this as a ConAgra land owner, he did not tell anyone the type of project that is being contemplated other than asking for enough electricity and gas to meet RES' needs).

- He will provide us with specification requirements and possible locations for a roadway to the proposed site. (He is calling public works regarding road access to the back of the property.) ***Exhibit 8A*** shows likely alignment on an existing county right-of-way. Road specifications will be obtained as soon as practical.

- He found out from the company that has the mineral rights (Petina Oil and Gas Corp.) that the piping network on the farm is not on a map but should be mapped within the next year. We will need to do a *line locate* if we get serious about this site. Gathering lines are small and even if they need to be moved, this would not be a costly expense.

- Doug has been told by the gas and electric companies that 20,000,000 Btu/Hr of gas and 3 megawatts connected power is not a problem for his turkey farm site. Both companies will be providing Doug with rough estimates for service connection costs.

- Doug mentioned that his last turkey farm that he constructed in Weld County where he needed to rezone *agricultura*l land to *special use* (commercial) took 8 months.

- Doug should be getting follow-up information from John Moser relative to the use of water produced by RES on Moser's Dairy Farm.

The Longmont Property

The Longmont site is located adjacent to ConAgra's turkey processing facility in downtown Longmont. Longmont is about 30 miles to the southwest of the Swift plant in Greeley. A general site map showing the Longmont location in relation to Greeley is shown on ***Exhibit 1***.

The property is approximately 19 acres in size. Approximately 1,100 feet of the property abuts the paved street to the north (1st Ave.). The property is mostly undeveloped. ConAgra currently is using only about 3 acres for truck parking. The truck facility is a fenced area along the north edge of the property and utilizes about 700 feet of the available frontage. The site is otherwise undeveloped with only piles of construction debris (i.e. concrete, asphalt) noted throughout the vacant lot. Site photographs are provided as ***Exhibit 13***.

An appraisal performed for ConAgra for the property is attached as ***Exhibit 14***. The current appraised value for the property is $ _________ *(to be obtained at a later date and will be forwarded at that time)*.

The property is surrounded by city land and other industrial and commercial entities. An aerial photograph (***Exhibit 15***) provides a description of land usage in the area. To the North is a rail yard and to the South are old ponds which were presumably part of the city's wastewater treatment operation at some point in the past. The land use to the East includes a firemen's training facility and the city wastewater treatment facilities. To the West is the turkey plant and other commercial and light industrial businesses. About one city block further west is Main Street. There is very substantial development work being done directly south of the site where a new highway is being constructed (See ***Exhibit 15).***

Exhibit 16 is a USGS topographic map of the site area for reference purposes.

There was not adequate time on this trip to visit the City of Boulder in order to perform due diligence on zoning. [Please see Kevin Saxon's comments in Section 3 (Feedstock

Investigations), Part B.] The city appears to be very interested in non-industrial endeavors (apparently so is the county of Boulder).

FEEDSTOCK INVESTIGATIONS

Greeley

We visited Swift's corporate office in Greeley on Monday, June 23. We first met with Tom Siegrist of Swift. He is the environmental engineering manager for Swift. He informed us of Greeley's current plan to contract for land application services for all of their products that they do not regularly render. (This has been a piece meal service in the past with multiple contractors.)

We then went to the Greeley beef plant and met with Ben Duran. Ben is the manager of the beef plant's environmental systems and rendering plant.

Ben provided us with a tour of the rendering plant plus a tour of the collection areas for the residues that are part of the RFP for land application. Specifically we toured the paunch processing and load-out area, the plant wastewater screening area, the primary DAF sludge treatment area, the secondary DAF sludge treatment area (primary sludge is grease and protein harvested from wastewater exiting the kill plant, secondary sludge is sludge harvested from aerobically treated wastewater before the wastewater is discharges to the city treatment plant) and the grit removal area.

The paunch, screenings, primary and secondary DAF sludges and grit are all land applied either regularly or at specific times by Greeley. They are trying to arrange for a single contract from a land application company to manage these products. The RFP is attached as ***Exhibit 17*** (*to be provided as soon as it is obtained*).

Production rates for Greeley residuals were described by Ben Duran as follows:

- **Grit:** Mostly fiber and ash, about 10 tons per day 5.5 days per week.
- **Secondary DAF Skimmings:** About 10% solids (with 2% being fat), 200 tons per day with about 50% volatile solids content, 5.5 days per week.
- **Primary DAF Skimmings:** These are part of *Inedible Tallow Sales* (they use tricantor centrifuges to separate solids which go to rendering, water which goes to wastewater and fat which goes directly to the Inedible Tallow tanks).
- **Paunch:** Paunch is not pressed. They produce 10-20% solids content, about 110 tons per day, 5.5 days per week. The paunch is removed from the stomach by slitting. From observing the paunch collection area there appeared to be only a limited amount of animal tissue entrained with the paunch. At present, most of the paunch is shipped to feedyards for refeeding. With the proposed RFP they see this stopping.
- **Wastewater Screenings:** These screenings are made up of some paunch and protein and fat (animal parts that are washed down the drain). The solids content is around 25% and they produce about 50 tons per day, 5.5 days per week (There can be some plastics entrained in the screenings from such items as cow's ear tags, etc. but this appears to be much less than 1%).

Production rates for Greeley rendered byproducts were described by Ben Duran as follows:

- **Inedible Meat and Bone Meal**: ~ 500,000 lbs per day, 5.5 days per week (70% is exported from the US to primarily Asia).
- **Inedible Tallow:** ~ 500,000 lbs per day, 5.5 days per week.
- **Edible Tallow:** ~ 375,000 lbs per day, 5.5 days per week.

- **Pet Foods (raw harvest):** 30,000 lbs per day, 5.5 days per week.
- **Gelatin/Bone:** 80,000 lbs. per day, 5.5 days per week.
- **Blood Meal** (this includes the blood from the Swift lamb plant and the ConAgra Longmont turkey plant): 50,000 lbs, 5.5 days per week.

Ben Duran explained that the Swift lamb processing plant in Greeley sends its byproducts to National Byproducts in Denver (same as the Longmont Turkey operation). Ben said that due to concerns over scrapie that the lamb offal has not been allowed to enter the beef rendering facility. (He also said that due to feathers, they have no plans to ever process Longmont turkey offal and feathers).

Ben provided us with his understanding of the lamb plant raw offal production (please note that Ben is not responsible for the lamb facility so his numbers need to be carefully checked)

The lamb plant kills 7,000 daily, 5.5 days per week. Offal yield should be about 35 lbs. per head (not including blood, DAF skimmings, mortalities, etc.). Ben believed that moisture on lamb runs at about 30%! (This seems hard to believe -- we need to verify). Based upon the above, we could look at this source as 96 tons per day, seven days per week for offal alone. We have requested settlement sheets for this plant from Swift through Mike Walters.

Longmont Turkey Plant

On Tuesday, June 24 we met with Kevin Saxon, Longmont Turkey Company Manager, (he has the responsibility for the farms, the feedmill, the hatchery and the processing plant) and with Larry Hatcher, manager of live bird production. We met the two at the Longmont processing plant.

Saxon provided us with the following information:

- The plant is killing 4.2 million birds per year with a total live weight of 172 million pounds or an average live weight per bird of 41 lbs. The average daily kill is about 16,500 birds. [Note: This compares to Carthage's reported kill of 35,000 birds per day or 250 – 260 million live pounds of poultry per year.]

- Saxon believes that his kill numbers will not increase over the next few years. He believes that his production will be flat. Saxon explained that Longmont is an unbranded plant (not part of Butterball). His finished goods are fed into the food services group of ConAgra.

- Saxon indicated that he felt construction in the City of Longmont or for that matter construction anywhere in Boulder County would be much more politically challenging than in Weld County. Weld County is very proactive toward agriculture. He explained that Longmont is an extension of Boulder and is rapidly developing into a high tech city and frowns on business such as his turkey processing plant. Saxon indicated that several years ago that Longmont rendered in the basement of the processing plant. The odor issues are remembered to this day by the city fathers and he felt that this would further complicate local community support for RES.

- Saxon was very receptive to getting the RES project done for the good of the industry and he said that he would be strongly supportive in helping us at whichever site we select.

- We explained to Saxon that there may be advantages to building next to the turkey plant from a state permitting perspective

- In a separate discussion with Larry Hatcher we sorted out the turkey litter composting economics. The turkey farms produce about 150,000 yards of litter compost per year (there are about 2 yards / ton so they produce about 75,000 tons of litter per year).

  They work with a composting company called ABS. Hatcher figures that ConAgra has about $2 per ton of cost in composting the litter. ABS has additional cost of their own (Hatcher does not know their costs). When the compost is sold (Typically $6/ton FOB turkey farm) 40% of the revenue goes to ABS while 60%

goes to ConAgra. This means that ConAgra nets $1.60/ton on average.

Turkey composting water usage is about 10 – 15 gallons per yard placed. Hatcher estimates that they use about 20,000 gallons per day, 5 days per week year round.

Hatcher thinks turkey compost demand on the Colorado front range is growing rapidly since organic farmers are staying away from municipal sewage sludge.

RECOMMENDATIONS AND REQUIRED ACTIONS FOR FINAL SITE SELECTION AND PROJECT EXECUTION

Based upon the information collected before, during and after this site selection trip it is clear that the Evergreen site has many ***advantages*** to RES. These advantages include:

- Weld County appears much more receptive to industrial (and especially agricultural) expansion than does Boulder County or the City of Longmont.

- The Evergreen site is much larger and much more isolated from area businesses and residences. This should be advantageous especially when RES expands its Colorado holdings to handle all byproducts from area ConAgra and Swift plants.

- The valuation of the Evergreen site is much less than the Longmont property. This should be an overall project cost advantage.

- The Evergreen site is located about equidistant from Longmont and the City of Greeley. By being closer to Greeley, RES is in a better long-term freighting position as the RES Colorado holdings grow.

- Although not confirmed with the State of Colorado, it appears that Boulder County is a non-attainment area for air. Although RES will not have any significant air emissions, the Weld site again would seem to be the better initial choice from air permit timing.

The ***disadvantages*** of Evergreen are as follows:

- The Longmont site could most likely be sewered and provided with potable water by the city. We will have to carefully investigate both aspects of the Evergreen site from a water law standpoint and from a wastewater permitting perspective. Neither of these issues appear to be that difficult to overcome given the information collected so far from the site.
- There may or may not be an inherent benefit in permitting the Longmont property due to it being contiguous to the Longmont turkey plant. This point may be moot though if from a city and county zoning standpoint RES is not a welcomed addition to the City of Longmont.

Looking at the advantages and disadvantages above, it is recommended that we prioritize the Evergreen site and determine the time frame and costs that would be necessary to complete the RES facility at the site. The following items require resolution or further investigation.

Areas to address:

1. **Solid Waste Exemption** – Prepare exemption set up meeting with appropriate state people who will support our project.
2. **Zoning Requirements** – Examine existing zoning and establish a plan for changing if necessary. Set up meeting with appropriate county officials who will support our project.

3. **Apply for Inducement Resolution** – This will be done with Weld County after we have applied formally for the zoning change,

4. **Air Permit** – Begin preparation and discuss this during state meeting (similar kick off like Carthage).

5. **Siting** -- Agree on site to be parceled or leased to RES. [See attached drawing.]

6. **Potable Water** – Evaluate rights and most expedient way to obtain supply of about 10 – 20,000 gpd. Investigate water well yields and whether additional wells will need to be drilled. Also investigate current withdrawal records to verify adequate supply (35 gpm, 24 hours per day) with storage.

   Initial indication is that the turkey farm uses only a small percentage of their total allocation. There has been a pump test which indicates the existing well yields in excess of 40 gpm. This may not be on a sustained basis though. At 33,000 birds (farm population) and using arid turkey farming data (Utah) which indicates a usage for full grown "Toms" of 220 gallon per 1,000 head per day, maximum usage is around 7,500 gallons. Total farm use should be less than 10,000 gallons per day. Based upon 35 gallons per minute (50,000 gallons per day) there is excess permitted capacity of 40,000 gallons per day.

7. **Process Water** – Establish disposal options and begin permit process. This may be complicated by the fact that the existing property use is CAFO (*confined animal feed operation*). This means the site has a zero discharge requirement. Options and permit requirements may be limited.

8. **Electricity** – Complete discussion and cost estimate for 3 megawatts from United Power.

9. **Gas** – Complete discussions and cost estimate for 20,000,000 Btu/Hr gas supply (15 psig at meter).

10. **Roadways** – Obtain specifications (county) for road construction. Obtain preliminary cost for site access.

11. **Domestic Sewage** – Obtain approximate cost for septic system for 40 employees. Prepare preliminary design for system and establish permit requirements

12. **Property Acquisition** – Obtain property appraisal and conduct any additional due diligence to negotiate land purchase or lease from ConAgra.

13. **Feedstock Sourcing** – Obtain settlement sheets from lamb plant and RFP from Greeley. Also begin discussion with large grease haulers.

14. **Boundary Survey and Topographical Survey** – Obtain quotes and establish schedule.

15. **Geotechnical Borings** – Prepare site layout and establish boring requirements. Obtain quotes and establish schedule.

APPENDIX B

1. Introduction

The goal of this study was to develop and evaluate the experimental conditions for producing biodiesel from waste products derived from regional waste streams, especially trap-grease and waste cooking oils. Commonly, biodiesel refers to methyl esters of long-chain fatty acids (Fatty acid Methyl esters, FAMEs) derived from vegetable oils and/or animal fats. It has viscosity close to that of No.2 diesel oil and can be used as a pure fuel or blended with petroleum in any percentage. ASTM Standard D6751 stipulates the specifications of biodiesel as a fuel product.

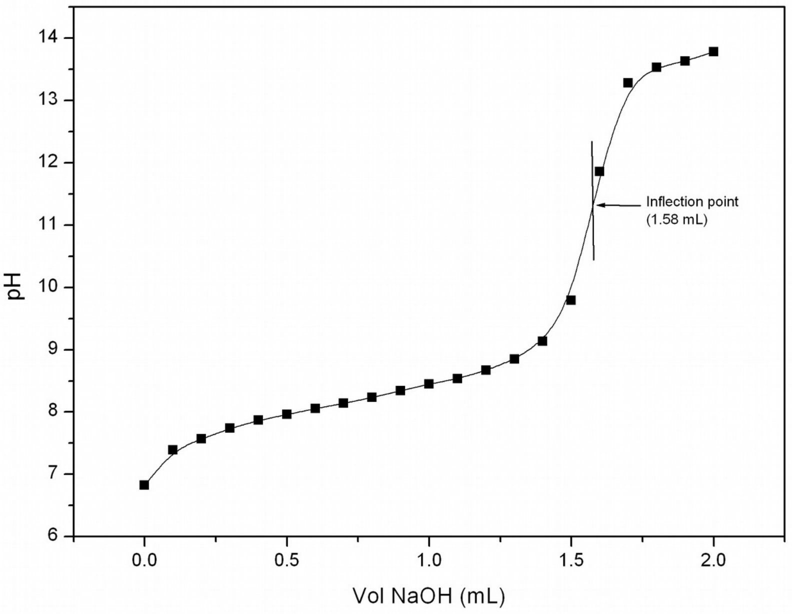
While raw oils and fats mainly are composed of the triglycerides of fatty acids, waste cooking oils and trap-grease contain a significant fraction of free fatty acids (FFA's) generated through hydrolysis during cooking. Thus, it is a heterogeneous product containing triglycerides, FFAs, and a variety of other food derived biochemicals. Therefore, the first step in the process was to convert this heterogeneous product into a feedstock of more uniform composition. We accomplished this mainly through thermal depolymerization that hydrolyzes the remaining triglycerides to fatty acids, and was conducted in collaboration with **Changing World Technologies** (CWT). In this process, carried out in two stages of separation and conversion, the trap-grease/waste cooking oil is treated in a closed batch reactor at about 250 ^{0}C and 50 atm to achieve thermal hydrolysis. The product, hereafter referred to as the **CWT Stage 2 product**, is nearly 100 % FFA, and essentially water free.

We quantified the total fatty acids in the product by titrating with an alkali (KOH) according to the ASTM Standard D 664-06, *Standard Test Method for Acid Number of Petroleum products by Potentiometric Titration*. In this method a 0.5 g sample was diluted to 10 mL in a titration solvent (~1:1 mixture of isopropanol and toluene), and 1 mL of the diluted sample was added to about 150 mL of the titration solvent and titrated against 0.1 M KOH in isopropanol. Figure 1 shows a typical potentiometric titration curve of our analysis. These results show 3.16 mmoles of titrable acidity in 1 g sample, and amounts to an acid number of 177.3 mg KOH/g.

Determination of Acid Number of the CWT Stage-2 Product (New batch)

(Method: ASTM D664)

0.5 g sample diluted to 10 mL in titration solvent and
1 mL used to titrate aganinst 0.1 M KOH in isopropanol



Results show 3.16 mmoles titrable acidity in 1 g sample

Acid number is 177.3 mg KOH/g

Figure 1. Potentiometric Titration Curve of the CWT Stage 2 product.

Conversion of CWT Stage 2 Product to Biodiesel.

Commonly, glycerides are converted to FAMEs by an alkaline-catalyzed trans-esterification reaction with methanol. Practically, acid catalysis is not possible in trans-esterification because kinetically it is very slow. However, acid catalysis using mineral acids, such as sulfuric acid, is the well-known approach to convert FFA's to FAMEs. Since the CWT Stage 2 product essentially contains FFAs, our approach was to use only the acid-catalyzed direct esterification to produce biodiesel.

Usually, a two-step process is employed, involving a sequential application of acid-catalyzed esterification, and an alkaline-catalyzed transesterification to convert feedstocks that contain considerable amounts of both FFAs and triglycerides to FAMEs. Thus, in earlier studies of biodiesel production with feedstocks containing a mixture of high levels of free fatty acids and triglycerides, including waste grease, Canakci and Van Gerpan (**1-3**) used a combination of acid-catalyzed esterification and alkaline-catalyzed transesterification to convert FFAs and triglycerides, respectively, to FAMEs. It is necessary to carry out direct esterification of FFAs before trans-esterification of triglycerides because FFAs form soap with alkalis (such as NaOH), which interferes in subsequent steps. Because the acid-catalyzed esterification is an equilibrium reaction, it does not give high yields in one single step when the product water remains in the reaction mixture. Therefore, to maximize yield, Canakci and Van Gerpen undertook a two-step conversion. After the first step, the ester layer containing residual FFA was separated from the methanol-water layer, and, in the second step, reacted again with acidified methanol. The first step employed 5% sulfuric acid and a 20:1 molar ratio of methanol, both based on the FFA content of the feedstock. In the second step, the sulfuric acid was 5%, and the molar ratio was 40:1, again based on the level of FFAs. The reaction temperature was 55 - 60 ^{0}C. This two-step treatment resulted in final product with less than 1 % FFAs.

Esterification Conditions used in this Study

The esterification reaction was conducted as a closed system reaction. The vessel was a thick-walled round bottom glass flask (500 mL) with a pressure rating of 60 PSI at 120 Deg C (Ace Glassware). The reaction conditions were largely based on earlier studies (e.g., Canakci and Van Gerpan, **1-3**) and include the following:

* An excess of methanol(typically 10x stoichiometric)

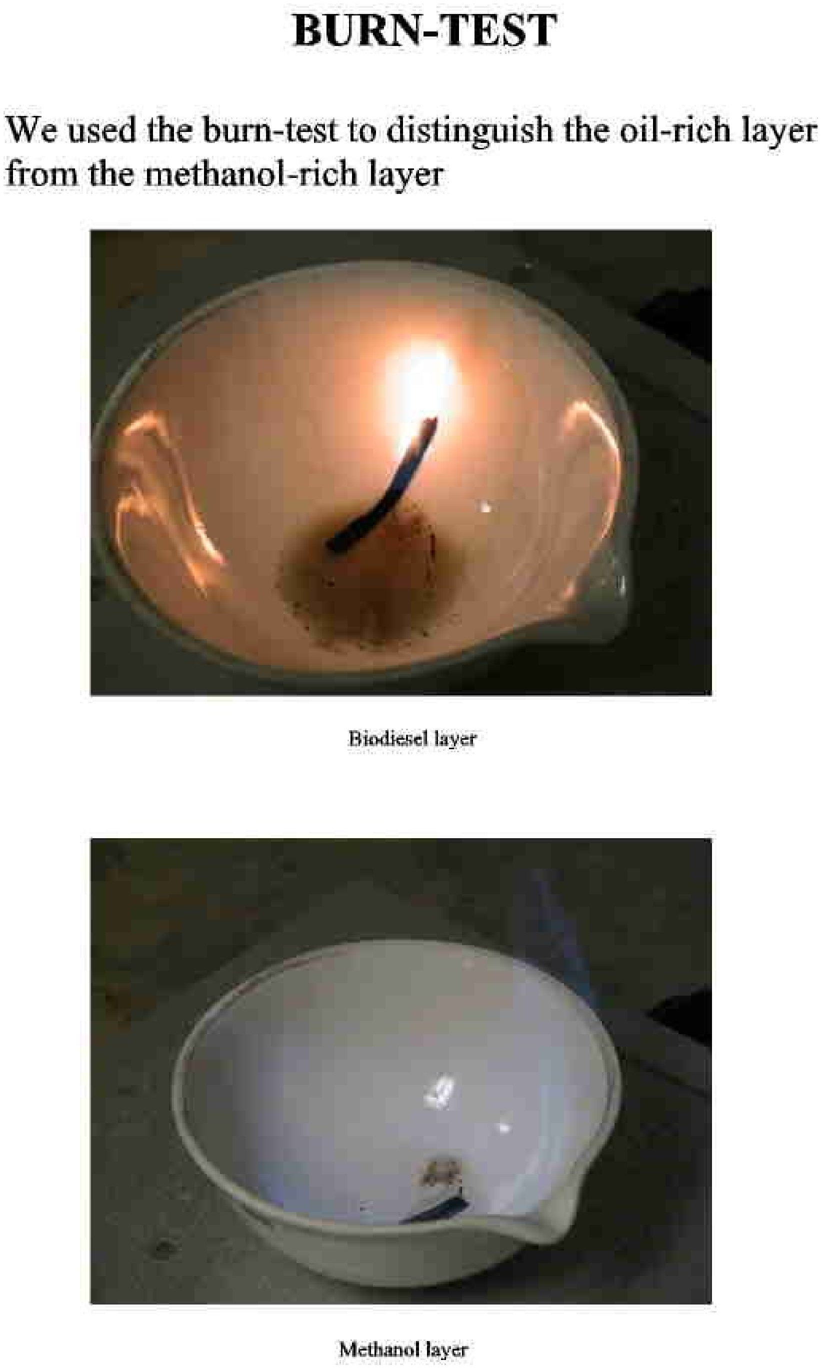
* A 5% solution of sulfuric acid in methanol

* Reaction temperature of 70 Deg C.

* Reaction time of approximately 1 hr.

We chose a higher reaction temperature of 70 ^{0}C than used in previous studies (60 ^{0}C) mainly to accelerate the kinetics of the reaction. It was necessary to use a pressure-rated vessel because this temperature was slightly above the boiling point of methanol (65 ^{0}C) and therefore some positive pressure could develop. Our preliminary studies showed that at 70 ^{0}C the esterification reached the maximum in about half an hour. However, to ensure maximum yield of esterification, the reaction time was extended to 1 hour. A thorough optimization of the kinetics was expected to be carried out under industrial conditions by our collaborators, Changing World Technologies.

At the end of the reaction time, the reaction mixture was transferred to a separatory funnel and allowed to stand to cool down and to get the layers separated. It was difficult to visually recognize the separation line between the two layers because the dark impurities originally present in the feedstock partitions both in the oil phase and the methanol/water phase. Thus, we used a flame-test to distinguish the oil-rich layer from the methanol/water layer. As shown in Figure 2, the biodiesel burns with a bright flame whereas the methanol layer burns as a light blue flame. In addition to the flame test, we used the differences in flow characteristics, to separate and isolate the biodiesel layer from the methanol/water layer. The biodiesel layer separated on top of the methanol/water layer. The biodiesel obtained this way had a dark brown/black color due to impurities originally present in the feedstock.



BURN-TEST

We used the burn-test to distinguish the oil-rich layer from the methanol-rich layer

Biodiesel layer

Methanol layer

Figure 2. Comparison of flames of biodiesel and the methanol layer.

We conducted preliminary studies using activated carbon (Aldrich Chemical Co.) to improve the color of the biodiesel by removing the dark colored impurities. In these experiments, activated carbon was added at a 5% level and mixed for about 5 min. Our results showed that treatment with activated carbon in fact improved the color. Figure 3 gives a comparison of biodiesel produced in this project, before and after carbon cleanup, with some commercial biodiesel fuels.

Our main goal in this study was to achieve a complete conversion of the FFAs in the CWT stage 2 product to methyl esters so that the FFA value of the generated biodiesel conforms to the ASTM D6751 limit of 0.5 max (mg KOH/g). Therefore, we carried the esterification reaction in two repetitions to maximize the yield. Figure 4 gives a flow diagram of the sequence of steps we used in this work. The stoichiometric amounts of the reactants are also given in this Figure. The acid number of the biodiesel was determined after each esterification step and our results are as follows:

Feedstock: 177.3 mg KOH/g (3.16 mmoles/g)

Biodiesel - 1st step: 3.53 mg KOH/g (0.063 mmoles/g)

Biodiesel - 2nd Step: 1.9 mg KOH/g (0.034 mmoles/g)

As these results show it was difficult to achieve acid number values of less than 0.5 mg KOH/g even with two stages of esterification. This is expected because of the nature of the reaction as an equilibrium reaction.

<u>Using a base to reduce the acid number</u>:

While a third stage of esterification could possibly bring down the acid number further, we chose to treat with a base to remove the remaining acids because of practical advantages.

Initially, we evaluated a KOH washing step to reduce the acid number to the limit value. However, this approach was not successful as it led to some emulsification of the biodiesel probably through reaction with some impurities in the biodiesel.

Subsequently, we studied treatment with calcium oxide (quick lime) and calcium hydroxide ($Ca(OH)_2$) to further reduce the acid number of the biodiesel. These were obtained as industrial grade powdered products from **Mississippi Lime Company**, MO. The products used were Petrocal OS100 Calcium Oxide and Petrocal HS Calcium Hydroxide. These were added at a 2% level. The results of these treatments were as follows:

With Calcium oxide: 0.7 mg KOH/g, 0.6 mg KOH/g (two sets)

With Calcium hydroxide: 0.28 mg KOH/g, 0.22 mg KOH/g

As these results show, calcium hydroxide was more effective in reducing the acid number to the limit value. However, treating with calcium oxide helped to slightly improve the color of the biodiesel through sorption of some of the dark impurities. Also the residue sedimented faster from the biodiesel. Therefore, we suggest that a combination of calcium oxide and calcium hydroxide could probably be a better choice for reducing the acid number to the limit value.

RESULTS

BIODIESEL MADE FROM CWT PRODUCT COMPARED WITH TWO OTHER TYPES OF BIODIESEL

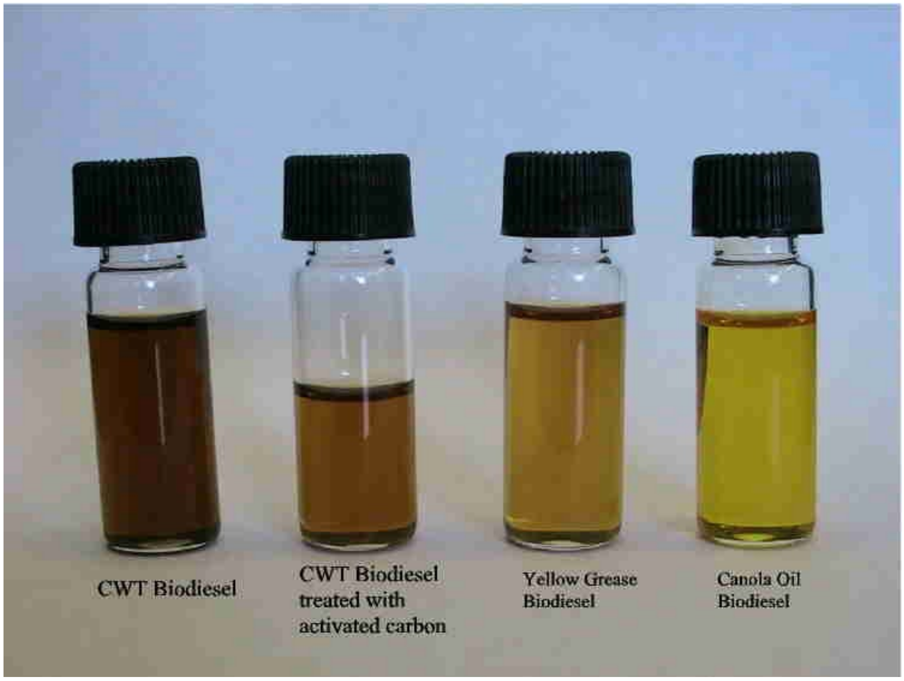


Figure 3. Comparison of biodiesel produced in this project with some commercial biodiesel fuel

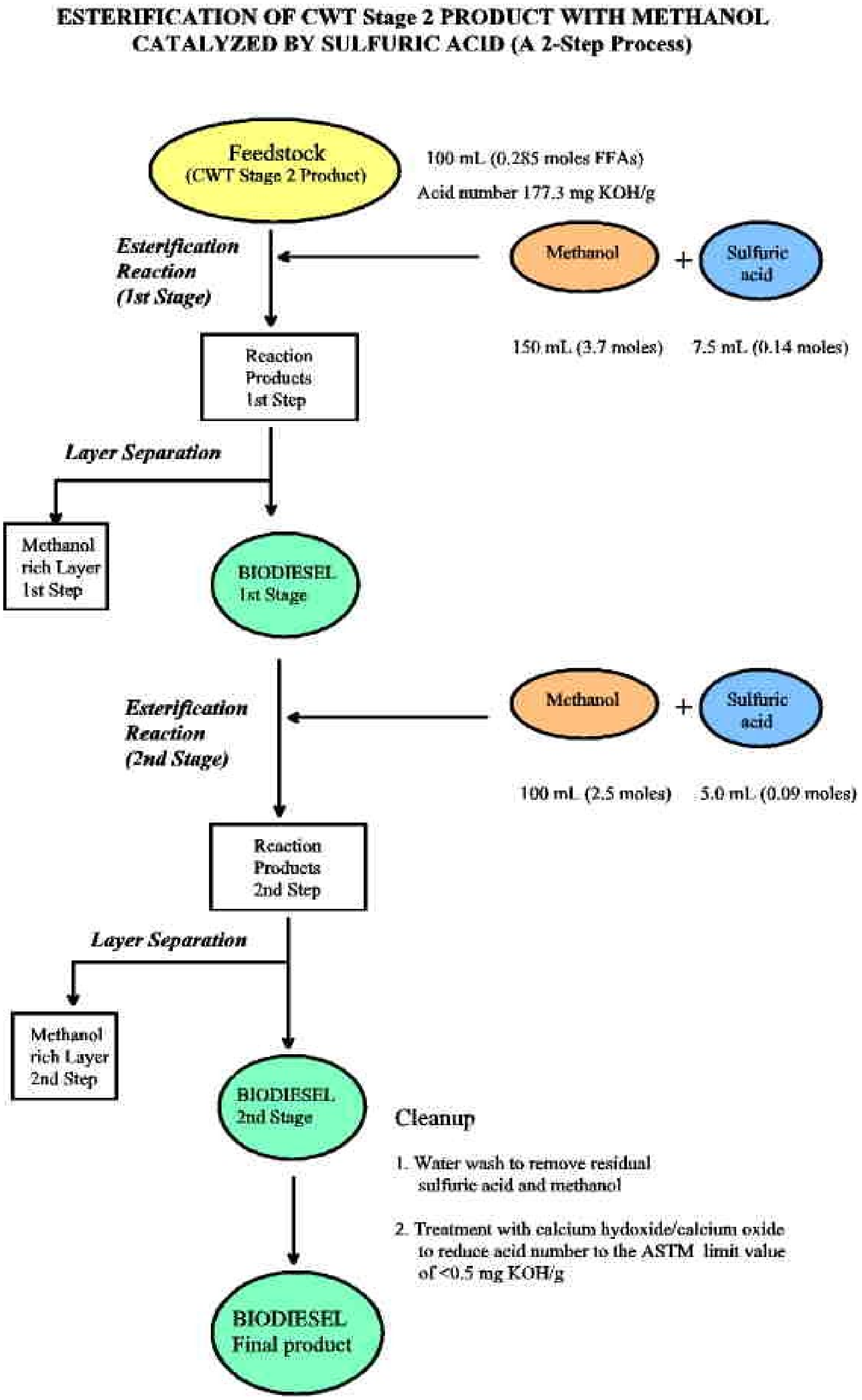


Figure 4. Schematic Flow Diagram of the Esterification Process for Biodiesel

Lterature Cited

(1) Canakei, M., and Van Gerpen J. (1999). Biodiesel Production Via Acid Catalysis. *Transactions of the American Society of Agricultural Engineers*, *42* (5), 1203-1210.

(2) Canakei, M., and Van Gerpen J.(2001). Biodiesel Production From Oils And Fats With High Free Fatty Acids. *Transactions of the American Society of Agricultural Engineers*, *44* (6), 1429-1436.

(3) Canakei, M., and Van Gerpen J. (2003). A Pilot Plant to Produce Biodiesel from High Free Fatty Acid Feedstocks. *Transactions of the American Society of Agricultural Engineers*, *4* (4), 945-954.

APPENDIX C

Since, oils, fats and greases primarily contain carbon chains between C16 – C18, an ideal process would decarboxylate these molecules to produce hydrocarbon products that fall within the diesel range. For catalytic decarboxylation, the use of Pd/C as a catalyst has been evaluated. For example, in a paper by Simakova et al. (Catalysis today, 2009), it is reported that decarboxylation of fatty acids of chain length between C17 and C22 was achieved at 300°C and 1.7 MPa pressure. The reported conversions were between 83% to 93% except for C19 and C22 fatty acids for which the conversion was about 20%. These conversion numbers were achieved in 2.5 hours.

A work plan was then prepared that BNL is pursuing to develop a technology to specifically convert trap grease, in which all mono- di- and triglycerides have been converted into fatty acids through the CWT process, into hydrocarbon fuels. It is realized that any developed catalyst must have the following features:

- Since C18 carbon chain is predominant in trap grease, oleic acid is a good starting FFA as a substrate.
- Under reaction conditions, H_2 for hydrogenation of the C-C double bond in oleic acid could be generated *in situ* via the water-gas-shift reaction(WGS). The CO needed for WGS would come from slight decomposition of the oleic acid during the reaction.
- The decarboxylation/hydrogenation reactions must be fast enough to be of commercial interest.

A successful development of this system would allow potential combining the decarboxylation step with Step 2 of the CWT process. Below we describe our preliminary results.

Catalytic Runs

The Unit

All runs are being carried out in a Parr batch unit (Series 4560) that consists of a 300 mL stirred reactor rated for operation up to 350°C and 14 MPa. The unit is fitted with liquid inlet/outlet and gas inlet/outlet valves, digital pressure readouts, thermocouple, and variable speed stirrer. A rupture disc is rated at 12 MPa for operational safety. Any potential catalysts will be a candidate for scale-up.

GAS ANALYSIS

Gas composition was measured as volume% (v/v) of total gas in the Parr pressure vessel headspace. The vessel at reaction temperature was allowed to cool to room temperature prior to gas sampling for analysis. The headspace was sampled using gas-tight syringes and assayed by gas chromatography using thermal conductivity detectors. The gas mass balance total was within ± 2% in each experiment. A Gow Mac series 580 gas chromatograph, operating under isothermal mode was fitted with a customized column, depending on the gas analyzed. The customized columns, Carbowax (9'L x 1/8"ID) and Molecualr Sieve (8'L x 1/8"ID), were used to analyze N_2, CO, CO_2, O_2, CH_4 and H_2. Helium was used as the carrier gas for all gases except for H_2 for which N_2 carrier gas was used.

LIQUID ANALYSIS

Gas chromatographic analysis was also carried out with a fully programmable HP series 5890 gas chromatograph equipped with a flame ionization detector (FID). GC separation was carried out on liquid samples obtained at the end of each experiments. Normally, the product was solid so it was dissolved in a solvent. For example, 0.3g solid product was dissolved in 10 ml dichloromethane and was injected in a DB-2887 10 meter long capillary column for analyzing saturated hydrocarbons C_5-C_{20}. Operating conditions were as follows: injector temperature 30˚C; detector temperature 250˚C; oven temperature 30˚C for 1 minute goes to 200˚C at ramp rate 15 degree/minute; carrier gas He; Injection volume was 1.0µl.

Screening Potential Hydrogenation Catalyst

The first step in the development of an integrated system is to identify a catalyst that can efficiently decarboxylate and hydrogenate oleic acid. The following constraints were imposed on the system under development: Three catalysts, Fe-based, Co-based and a Ni-based, were selected for initial evaluation under our conditions.

Catalytic reaction

<u>Runs with neat oleic acid</u>. The first series of runs consisted of 5 runs with γ-Al_2O_3, $Co_2(CO)_8$, $Fe(CO)_5$ and $NiCl_2$ and combination thereof in the presence of N_2 and H_2 gases at 280°C and 300°C. These runs were in neat oleic acid, i.e., no solvent was added. In a typical run,. 2g γ-Al_2O_3 and 100 ml oleic acid were mixed with 0.7 ml $Fe(CO)_5$ or 0.5 g $Co_2(CO)_8$ or 0.5 g $NiCl_2$ in the 300 mL reaction vessel. The reactor was flushed with N_2 gas a few times at room temperature then pressurized with N_2 and then with H_2, both gases totaling about 500 psig. The reaction vessel was heated to the desired temperature: 280°C for Run 1 & 2 and 300°C for Run 3, 4, 5 and stirring was initiated. At the end of each run, the vessel was cooled and brought to room temperature and gas and liquid compositions were measured. The run data are shown in Tables 1 and 2 and gas and liquid analysis data are shown in Tables 3 and 4.

The gas analysis data gives several clues on the mechanism of the catalyzed reactions with metals used in this study. The decarboxylation of oleic acid proceeds but the rates are slow with reaction times of several hours (up to 9 hours) and the decomposition of oleic acid, measured by %CO_2 in the final gas phase, to be less than 10%. The data from Runs 1-5 can be interpreted as follows:

- Oleic acid decomposition is achieved but slow.
- Decomposition: 3 - 9%. The reaction is complication due to water-gas-shift (WGS) reaction.
- The main product is C17 hydrocarbon though other products ranging from C6 – C20 are also observed.

It is clear that the reaction rates must be improved for the evaluated catalysts to be of interest.

Data of Decarboxylation of Oleic Acid Runs

Test Unit: 300 mL Parr batch reactor.

Analytical: Columns for hydrocarbon analysis

C5 – C20: Column: DB-2887 (10 m x 0.53 mm I.D., 3.0 µm)

C1 – C100: Column: DB-HT Sim Dis (5 m x 0.53 mm I.D., 0.15 µm)

Table 1. Summary of runs with various catalysts

Run #	Catalyst	Operation T oC	Pressure @RT(psig)	Pressure at T(psig)	Pressure increase(psi)	Run time (h)
1	$Fe(CO)_5$	280	492	936	26	1
2	$Fe(CO)_5$	280	516	931	0	6
3	$Fe(CO)_5$	300	508	969	5	5
4*	$Co_2(CO)_8$	300	485	910	2	9
5	$NiCl_2$	300	420	730	-10	9

Catalyst: $Fe(CO)_5$:0.7ml;γ-Al_2O_3:2g; substrate: Oleic Acid; reactor volume:300ml; substrate volume:100ml;Starting with N_2:446 psig H_2:44psig; At t=0 N_2:94%; H_2:7.9%;

*Catalyst: $Co_2(CO)_8$:0.5g;γ-Al_2O_3; N_2:462 psig H_2:52psig ; At t=0 N_2:90% H_2:10%

** Catalyst: $NiCl_2$:0.5g;γ-Al_2O_3; At t=0 N_2:86% H_2:15%

Table 2. Gas analysis of Runs 1-5.

Run #	N_2 %	CO (%	CO_2 (%)	H_2 (%)	CH_4 (%)
1	85	6.7	0	8.9	0
2	83.6	6.9	0.8	8	0
3	82.1	7.4	2.2	6.3	0
4*	84	0.1	3.6	9	0

5	82.1	7.4	2.2	6.3	0

Table 3. Liquid analysis of gas phase of Runs 3-5.

Run #	Catalyst	Pressure @RT(psig)	Pressure increase(psi)	Pressure increase(psi)	Saturated Hydrocarbon Products Detected
3	$Fe(CO)_5$	508	5	5	C_6, C_8, C_{10}, C_{12}, C_{16} C_6-C_{20}
4*	$Co_2(CO)_8$	485	2	2	C_5, C_8, C_{10}, C_{12}, C_{16} C_{17}-C_{20}
5**	$NiCl_2$	420	-10	-10	C_8, C_{10}, C_{12}, C_{16}, C_7-C_{20}

Runs with oleic acid in a solvent. The second series of runs are being conducted in the presence of a solvent. We noted that most reactions reported in literature, specifically those with Pd/C catalyst, were conducted in dodecane solvent (Simakova et al, 2009).

We, therefore, conducted a run (Run 6) with 5wt%Pd/γ-Al_2O_3 in ethylflo-164 (C30 hydrocarbon oil) solvent (90%) and oleic acid (10% by volume). The gas analysis data are shown below.

Gas Analysis of Run 6

Time, h	% H_2	% N_2	%CO	% CO_2
0	22	79	0	0
2.5	9	88	0.2	0
6.5	4.9	95	0.4	0

The data show that H_2 was consumed fairly fast indicating that the Pd catalyst is an effective hydrogenation catalyst. However, no CO was observed contrary to what was reported with the Pd/C catalyst. We plan to repeat the run with a commercial Pd/C (5 wt%, 1000 m^2/g) catalyst.

Planned Runs

All runs will be in solvent/oleic acid mixture. The ongoing and planned runs are:

Series 2

- 5 wt% Pd/C catalyst.
- Ni catalyst at various T
-

Series 3

- Select the best catalyst from Series 2.
- Repeat without H_2.

Series 4

- Runs with catalyst selected from Series 2 and 3 integrated with CWT Stage 2.

APPENDIX D

March 22, 2011

Mr. James H. Freiss, P.E.

Chief Operating Officer

Changing World Technologies, Inc.

460 Hempstead Avenue

West Hempstead, NY 11552

Dear Jim:

RE: RDO Grease Plant Design and Estimate

TKE Project Number 73598

Please find attached the site plan, PFD's, facility site layout, and cost estimate for the RDO project. Since a site location is yet to be specified, we assumed all utilites would be available at the boundary limits of the project. Also since environmental permits and soil conditions are dependent upon local conditions, we did not include a cost for these items. The accuracy of the cost estimate is +/- 25 per cent exclusive of these site related additions/modifications.

The following is a summary of the criteria and assumptions used to prepare the site plan and cost estimate for the RDO project.

Site Plan

- Based upon Tiperary site plan with solids processing removed
- Replaced MVR with the first effect evaporator skid, and a second effect evaporator skid from TKE
- Added the RDO Dehydrator skid from TKE
- Includes a 100 scfm RTO for eliminating VOC's
- Added T-120 (grease day tank)
- Reduced water concentrate and RDO storage capacity per PFD's
- Includes a 50 foot plant roadway around complete site
- Receipt of raw materials and delivery of product is only by truck. No rail facilities are provided

Equipment prices

- Major equipment was quoted on basis of Tiperary equipment specifications modified for the pressures, flowrates and sizes shown on the PFD's
- Steam boiler, RTO, Backup generator, Air Compressor prices were obtained from Internet and are in agreement with previous TKE estimates.
- Skid prices for 1st effect, 2nd effect, RDO Dehydration, and Hot oil were estimated by TKE on the basis of previous project estimates.
- Scrubber, V1000, T1300 estimated on basis of diameter from previous quotations of similar pressure vessels and tanks
- Building at $125/Square foot

Installation costs

- SNC Quebec used as basis for installation cost numbers
- Eliminated all items associated with processing of carcasses, buffer tanks, mineral dehydration,
- Removed installation of MVR and replaced it with piping between decanter and 1st effect evaporation skid and piping between 1st effect and second effect skid
- Added piping from decanter to RDO Dehydrator skid

- Eliminated storage ponds for fire protection water and nitrogen concentrate
- 8 inch concrete pads on 12 inch stone for all equipment foundations
- Includes spill containment for grease storage tanks, finished oil storage, concentrate storage, sulfuric acid tank, and caustic tank.

Utilities

- 500 KW - 3 Phase 480 volt power is available at property boundary

- Natural gas of sufficient quantity and reduced to commercial pressure at property boundary
- Water and Sewer of sufficient capacities are available at property boundary

Not Included

- Railroad access
- Environmental studies and permitting
- Access roads from highway to property boundaries
- Excessive site grading
- Land Acquisition

If you need more detailed information, please do not hesitate to call us.

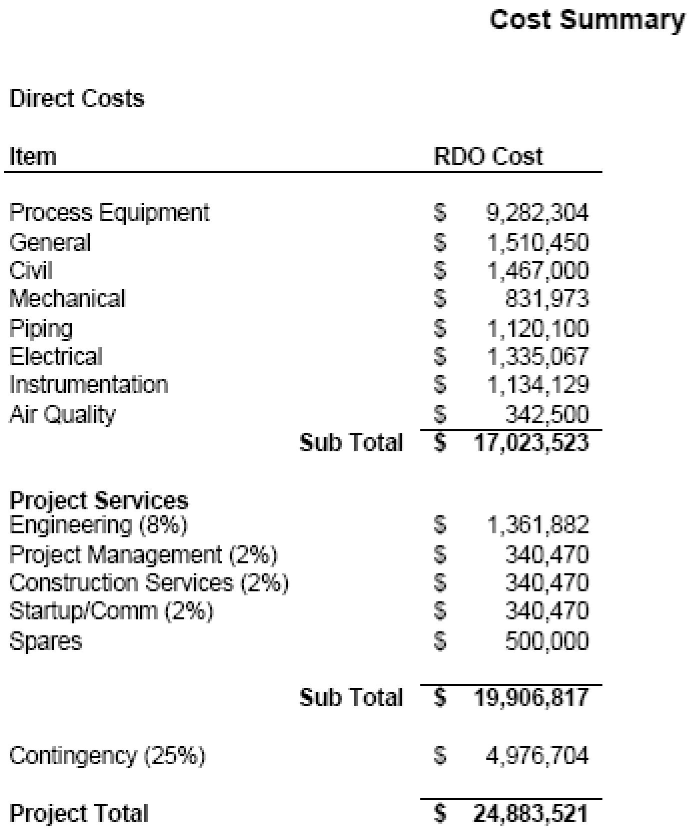
Sincerely,

Christopher J. Brown, P.E.

President

Thermal Kinetics Engineering, PLLC

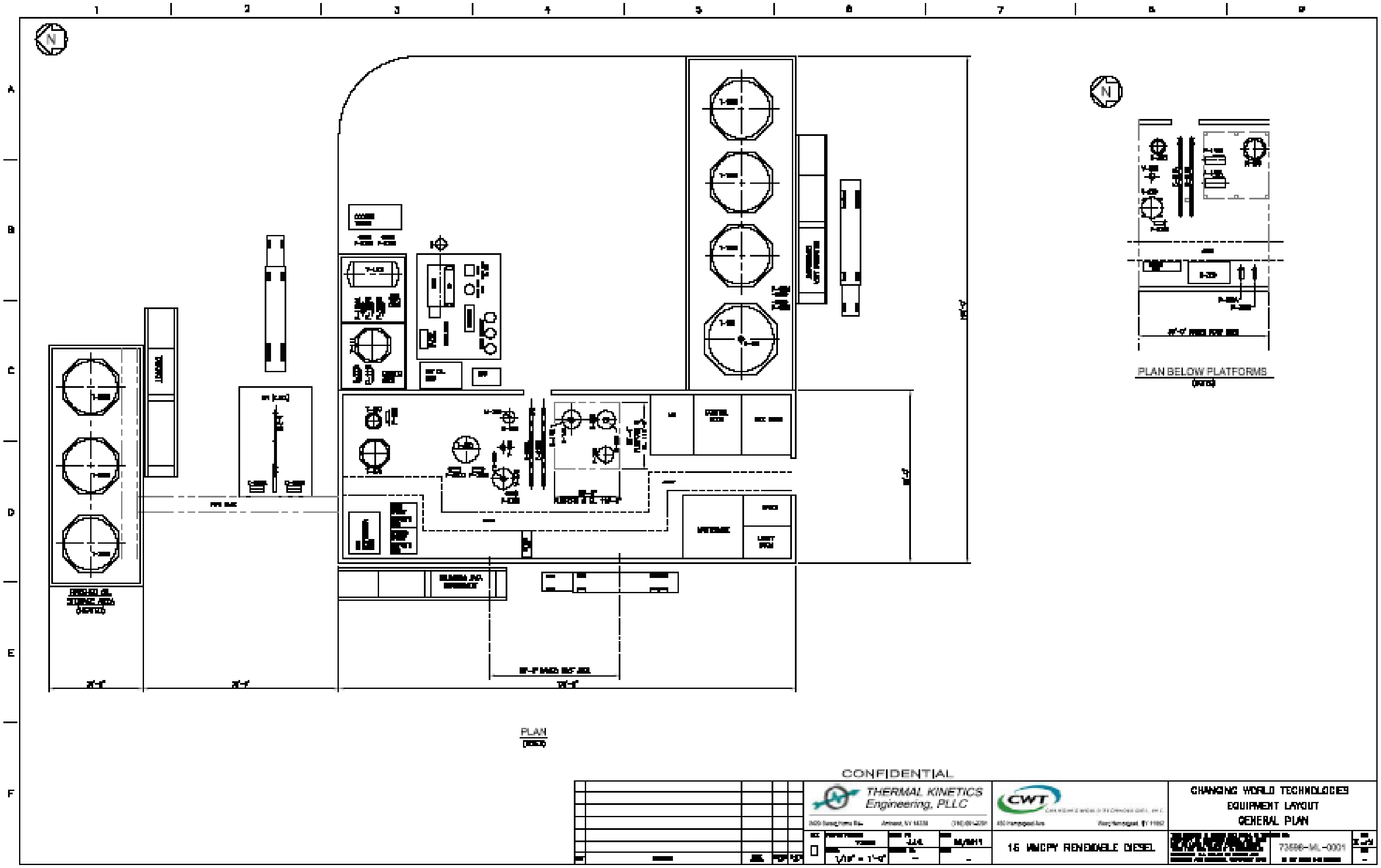
pc: Project file



Cost Summary

Direct Costs

Item		RDO Cost
Process Equipment		$ 9,282,304
General		$ 1,510,450
Civil		$ 1,467,000
Mechanical		$ 831,973
Piping		$ 1,120,100
Electrical		$ 1,335,067
Instrumentation		$ 1,134,129
Air Quality		$ 342,500
	Sub Total	**$ 17,023,523**
Project Services		
Engineering (8%)		$ 1,361,882
Project Management (2%)		$ 340,470
Construction Services (2%)		$ 340,470
Startup/Comm (2%)		$ 340,470
Spares		$ 500,000
	Sub Total	**$ 19,906,817**
Contingency (25%)		$ 4,976,704
Project Total		**$ 24,883,521**


PLAN BELOW PLATFORMS
PLAN
CONFIDENTIAL
THERMAL KINETICS Engineering, PLLC
CWT
CHANGING WORLD TECHNOLOGIES
EQUIPMENT LAYOUT
GENERAL PLAN
15 MMGPY RENEWABLE DIESEL
1/16" = 1'-0"
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