# Energy Supply – Production of Fuel from Agricultural and Animal Waste

## Final Report

**Prepared By:**
**Society for Energy and Environmental Research (SEER)**
**Dr. Gabriel Miller**
**Executive Director**

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## 1.0 Introduction

The Society for Energy and Environmental Research (SEER) was funded in March 2004 by the Department of Energy, under grant DE-FG-36-04GO14268, to produce a study, and oversee construction and implementation, for the thermo-chemical production of fuel from agricultural and animal waste. The grant focuses on the Changing World Technologies (CWT) of West Hempstead, NY, thermal conversion process (TCP), which converts animal residues and industrial food processing bi-products into fuels, and as an additional product, fertilizers.

A commercial plant was designed and built by CWT, partially using grant funds, in Carthage, Missouri, to process animal residues from a nearby turkey processing plant. The DOE sponsored program consisted of four tasks. These were:

Task 1- Optimization of the CWT Plant in Carthage
This task focused on advancing and optimizing the process plant operated by CWT that converts organic waste to fuel and energy.

Task 2- Characterize and Validate Fuels Produced by CWT
This task focused on testing of bio-derived hydrocarbon fuels from the Carthage plant in power generating equipment to determine the regulatory compliance of emissions and overall performance of the fuel.

Task 3- Characterize Mixed Waste Streams
This task focused on studies performed at Princeton University to better characterize mixed waste incoming streams from animal and vegetable residues.

Task 4- Fundamental Research in Waste Processing Technologies
This task focused on studies performed at the Massachusetts Institute of Technology (MIT) on the chemical reformation reaction of agricultural biomass compounds in a hydrothermal medium.

Many of the challenges to optimize, improve and perfect the technology, equipment and processes in order to provide an economically viable means of creating sustainable energy were identified in the DOE Stage Gate Review, whose summary report was issued on July 30, 2004. This summary report appears herein as Appendix 1, and the findings of the report formed the basis for much of the subsequent work under the grant.

In the following sections, an explanation of the process is presented as well as the completed work on the four tasks.

## 2.0 The CWT Process

### 2.1 Background

The production of liquid petroleum products from foods and agricultural wastes, particularly those products referred to as bio-fuels, have been studied extensively since attempts at large scale production occurred during World War II. In this regard, studies have examined both the conversion of waste materials high in cellulose content (where the main conversion mechanism is cellulose to glucose to fuels) and the conversion of animal processing wastes high in fat and protein content (where the major conversion mechanism is fats to fatty acids to fuels). In both cases, studies have centered on hydrolysis processes (some involving acids or bases, either acting as reactants or catalysts, enzymes, and/or emulsifiers), at intermediate to high temperature and pressure. The major thrusts have been to understand the reaction kinetics, in order to find routes to high conversion rates to useful products, while minimizing: non-useful byproducts; energy losses; and significant expenditures on capital equipment and maintenance.

Hydrolysis reactions have been an important option for many years in the processing of oils and fats for the oleo-chemical industry. The original paper on the Colgate-Emery process (Allen, H. D., et. al.) was published in 1947. The original studies and processes, Colgate-Emery and Twitchell (Sonntag) were conducting at relatively low temperatures and pressures. In fact, the Colgate- Emery process studies were conducted at conditions similar to those of sub-critical water (250 C and 50 MPa), but because the oil to water ratio was 2-1, the process is more a steam based hydrolysis then a sub-critical one. More recent studies (for example Holliday, et. al.) have therefore centered on the hydrolysis of, for example vegetable oils, under sub-and super-critical water conditions, where the density of water is more liquid-like (greater than 0.5 g/cc) than gas-like.

Simplistically, fat splitting is represented as a reversible chemical reaction where adding water to a glyceride at elevated temperature will result in the production of glycerin and three moles of fatty acids. Fat hydrolysis, however, is not simple. One can consider a stepwise hydrolysis from triglycerides to diglycerides to monoglycerides and then to fatty acids plus glycerol. The fats splitting reactions are based on the fact that water is increasingly soluble in di-and monoglycerides and in fatty acids when compared to the original triglycerides, and this increase in solubility allows for the increased rate of hydrolysis at higher temperatures and pressures. These reactions are slow to start, but reaction rates increase markedly in the middle stages, and then decrease as glycerol concentration increases (which, of course, is a positive factor in controlling glycerol production).

Holliday, et. al. examined the dependence of conversion of triglycerides to fatty acids (greater than 97%) on time and temperature in a batch reactor, for four different vegetable oils, at a water density of 0.7 g/cc. Depending on feedstock, the temperature ranged from 260C to 289 C, and the reaction time from 15 minutes to 69 minutes (the linseed oil reached 97% conversion at 260 C in 69 minutes, but reached 97% conversion at 280 C in 20 minutes). This indicates the sensitivity of conversion rates on feedstock type, temperature and time.

### 2.2 The TCP Technology

There are a number of technologies that are being investigated to turn fat based products, such as oils and food based waste materials, to fuels (including bio-diesel, or methyl esters, and bio-distillates, or bio-fuels). A report describing the field is available (Tyson, et. al.). The process which is the focus of this grant is the technology developed by Changing World Technologies Inc. (the CWT TDP process), described by Adams, et. al., and by Adams, in the literature.

In Adams, et. al., the CWT Process utilizes turkey offal as the feedstock, and the paper describes the mechanisms for turning the waste material into three useful separate streams. These are: an essentially clean hydrocarbon gas; an organic liquid, the first stage oil being a fatty acid stream; and solid products which can be used, for example, as fertilizer.

Working with the heterogeneous water laden waste stream described in that paper, and operating in a continuous mode, the process has kinetics that is consistent with the studies described above. Operation centers on temperatures in the range below 250 C and 500 psi, or in the sub-critical regime. Operation above this temperature range is avoided to reduce the possibility of the formation of deaminates during protein breakdown to amino acids. This can lead to emulsions containing ammonia. Operation is therefore held at approximately 250 C, which leads to approximately 95% fat splitting, without emulsions, at a residence time, determined for this feedstock, of 15 minutes. The pH is adjusted and under optimum conditions is determined to be 4.5.

In this way, CWT produces a bio-fuel whose kinetics and processing is consistent with the studies in the literature and therefore one would expect that scale-up to commercial operation would be possible. The proof of concept is the Carthage plant operation, funded by this grant, as described herein.

### 2.3 The Carthage, Plant

In 2005, after construction completion, the Carthage plant began taking 100% of the waste generated by the ConAgra Butterball turkey processing plant nearby. In the third quarter of 2005, the Carthage plant was deemed commercial and has continued to operate without major disruption to this day. The plant is described in detail here.

Utilizing funds provided by this grant, the TCP facility was designed to utilize the thermal process to produce fuel and industrial chemicals from mixed organic wastes in Carthage, Missouri. The goal was to utilize waste and produce renewable fuel and industrial chemicals in an environmentally friendly manner. The objectives were to establish the new facility and process, with the goal of optimizing, improving, and perfecting the technology, equipment, and processes in order to provide an economically viable means to creating sustainable energy.

As a starting point, the Carthage plant was in its early days, an operational plant with comprehensive environmental and other operating permits. It became clear that shortfalls in initial engineering and design needed to be corrected. Modifications to the process at the facility were for expenses related to the operational improvement and optimization of the plant, including new equipment. These modifications required no new environmental permits and no amendments or revisions to any of the existing environmental permits held by the Carthage plant. The goal was to make improvements which would result in lower operating costs, and help in determining the quality of the fuel products and their markets.

## 3.0 The DOE Sponsored Program

The DOE program (DE-FG-36-04GO14268) encompassed four tasks. Each is described in the sub-sections here.

### 3.1 Task 1- Optimization of the CWT Carthage Plant

#### Overview

A commercial plant was designed and built by Changing World Technologies, Inc. (CWT) in Carthage, Missouri, to use the proprietary Thermal Conversion Process (TCP) to convert animal residues from a nearby turkey processing plant into fuels and commodity chemicals. The goal was to utilize waste and produce renewable fuel and industrial chemicals in an environmentally friendly manner. The objective was to establish a new demonstration facility with the goal of optimizing, improving, and perfecting the technology, equipment, and processes in order to provide an economically viable means to creating sustainable energy. The funds were thus used for testing and optimization of the facility as it moved toward full commercial operations in February 2005.

The Carthage plant was designed as a first-of-its-kind manufacturing plant with comprehensive environmental and other operating permits. It became clear that shortfalls in initial engineering and design needed to be corrected. Modifications to the process at the facility were for expenses related to the operational improvement and optimization of the plant, including new equipment. These modifications required no new environmental permits and no amendments or revisions to any of the existing environmental permits held by the Carthage plant. The goal was to make improvements which would result in lower operating costs, and help in determining the quality of the fuel products and their markets.

The funds were used for optimization activities that included the purchase of equipment and operation of the Carthage, Missouri facility from March 1, 2004 and ending February 28, 2005 to test process modifications. While CWT had determined that the TCP was technologically and economically viable, there were still several issues that needed to be evaluated to prove the commercial value of the technology. This included the overall optimization of the facility with regards to operations, equipment upgrades, and feedstock sourcing.

**Objectives**

The primary objectives for conducting these activities were:

- Enhance documentation of the operational and maintenance (O&M) requirements for the equipment and systems included
- Coordinate repair and maintenance with engineering for increased reliability
- Document baseline operating conditions through trending of performance measurements
- Optimize control systems through calibration of critical sensors, review metered data and trend logs, and functional equipment testing
- Specify new equipment to correct design faults and/or enhance throughput or reliability
- Identify operational and maintenance enhancements that result in improvements in energy efficiency, odor control, and/or quality control.
- Increased inventory and spare parts management
- Identify O&M staff training needs

Full-scale plant operation leaves little time to document the hour by hour performance of the process as the operators are needed to keep the plant running. Therefore, to assure that the proper data and history about plant performance were recorded, extra plant personnel we added on short term assignments to assist in the process monitoring and evaluation. They were given very specific instructions as to what they were to inspect and record and what laboratory work they were to conduct during the runs to help get a bigger picture on plant performance.

**Project Steps- Overview**

The following summarizes the project steps used to evaluate the setting of capital projects and the identification of the process areas to optimize, which are detailed in Appendix 3.

1. Review existing systems and related documentation
2. Develop Plant Commissioning Manual
3. Perform calibration and maintenance checks
4. Implement diagnostic monitoring / trending
5. Perform functional run tests to gauge process bottlenecks
6. Analyze the monitoring / trending and test data
7. Assess and document the current operating strategies and sequences of operation for all systems and equipment included
8. Document O&M improvement opportunities
9. Calculate energy impacts and develop implementation cost estimates for O&M opportunities

10. Issue Final Carthage Plant Commissioning Report

Grant funding was used to support the capital and operating expenses during plant optimization (a breakout is found in Appendix 3)

**Project Steps-Detailed Optimization**

The RES Carthage optimization activities added to the current knowledge of converting organic waste to fuel and energy in four main areas:

(1) Improved understanding of high temperature chemistry and mineral/organic interactions under acid and basic reactor conditions.
(2) Determination of the pH changes observed during the hydrothermal treatment and their influence in yields, product distribution and metallurgical choices.
(3) Correlation of feed uniformity vs. residence time (of plant on stream) on product yield and product quality.
(4) Knowledge of the nature and origin of fouling of heat exchangers prior to hydrothermal treatment that resulted in extensive scaling that required high pressure washing to remove.

The following details each of the project steps to complete this task:

**Review Existing Systems & Documentation**

- Interviewed plant administrative support staff and review the existing building documentation to determine the original specifications, design intent, and their relevance to current operator/user requirements. The following lists the documentation that was gathered and reviewed:
  - → Sub-metered utility data and energy bill (electric and gas) information for at least 12 months along with rate schedules
  - → Drawings and specifications relevant to the systems scheduled for commissioning, especially control drawings and sequences of operation
  - → Existing control points list for each building
  - → Operating strategies programmed into the Motor Control Center (MCC)
  - → Equipment list with nameplate information for equipment controlled by the MCC
  - → Existing O&M and system manuals for equipment
  - → Operator reports; plant commissioning procedures; equipment calibration documentation

**Develop Plant Commissioning Manual**

Developed a Plant Commissioning Manual for testing and reporting on the pertinent systems, including documentation strategies. The Manual includes the following:

- Equipment, systems, or specific measures to be included, or selection criteria for inclusion
- Plan for reviewing existing systems and related documentation
- Define current operational requirements from original design documents and interviews with plant technical personnel
- Detailed plan for equipment calibrations, including calibration forms
- Maintenance checks to be performed
- Detailed plan for diagnostic monitoring / trending, including data archival
- Functional tests and operational runs to be performed
- Methods to be used in analyzing the monitored / trended data
- Plan to assess and document the current operating strategies and sequences of operation for all systems and equipment included
- Strategies to be used in calculating energy impacts and implementation cost estimates for opportunities identified
- Implementation schedule

**Perform Calibration and Maintenance Checks**

A list of instruments, sensors and actuators for calibration was developed following a points list review. The appropriate amount of calibration work depended on the level of confidence in the existing equipment and the history of problems with the controls equipment at an individual site. The calibration plan included a compressive list of instruments and critical equipment to be evaluated. Appropriate calibration procedures and required documentation were included in the Plant Commissioning Manual.

.Using forms and procedures developed by the CWT Engineering Dept, the group investigated, documented, and remedied many of the maintenance issues and performed some of the calibrations as specified in the Commissioning Manual. Successful completion of the calibrations was required prior to starting any monitoring, trending, and functional testing. This option was the least cost, but its viability depends on the level of expertise of RES Carthage staff as well as their availability. This option provided the highest assurance of quality control and helped educate staff.

## Implemented Diagnostic Monitoring and Testing

CWT provided a detailed request for the required trend logs from the MCC to the RES Carthage staff. If data loggers are required, the commissioning provider (ESCO) will provide and program the data loggers, which will be installed with the assistance of the facility staff. Facility staff may also be responsible for removing the sensors and data loggers, packaging them and sending them back to the provider for analysis after the end of the monitoring period.

## Functional Testing

CWT oversaw the execution of functional performance runs on selected equipment as specified in the Commissioning Plan, with the assistance of facility staff and the Equipment Manufacturer as required. Functional tests were comprised of changing parameters, set-points or conditions and observing and documenting the actual system or equipment response through various modes and conditions (both simulated and real). Tests were developed on a case-by-case basis to ensure functionality across normal operating conditions and to identify any process bottlenecks.

For equipment that is being monitored with sufficient points, manual testing may be accomplished by changing the parameters, etc. during the monitored period. The monitored data is then examined and used to document and verify correct or incorrect operation. Visual verification of equipment functionality was required in instances that feedback from the MCC system was not available.

## Analyzed Monitoring and Testing Data

Once the data was gathered from monitoring and testing, CWT analyzed the findings by comparing actual equipment operation to appropriate operation and to the existing process sequences. Issues and potential improvements were identified and documented.

## Assessed and Documented Current Operating Strategies

CWT worked with the RES Carthage staff to develop a comprehensive building operations plan for the equipment and systems included in this scope of work, based on the original building specifications and current operational needs of the site.

## Documented and Analyzed O&M Improvements

RES Carthage documented the improvement opportunities identified. For the most promising measures, energy impacts were calculated and implementation cost estimates were developed for Capital Improvement Projects (CIP).

### Energy Impacts and Implementation Cost Estimates

Energy calculations were performed for those operational measures that appeared to have the most impact on separations, energy conservation, or product quality. Implementation costs for the measures were estimated.

**Developed Final Carthage Plant Optimization Report**

The Final Carthage Plant Optimization Report was issued once commissioning scoping activities were completed. This report is detailed in this document, highlighting the actions specified herein.

The Final Carthage Plant Optimization Report includes the following information:

- Overview of activities conducted
- Project Objectives
- Commissioning Process Steps
- Grant Funding Breakdown
- Scope of the Commissioning Project
- Details of all potential improvements identified and other findings, including:
    - Documentation of equipment conditions
    - Identify any needed facility staff training
    - Missing critical documentation
- The estimated implementation costs and the description for each improvement (operations, feedstock, product quality, miscellaneous)
- Cost-effective measures in final accounting, along with other opportunities identified during commissioning period

**Plant Reliability**

Many improvements have been made in the Carthage plant in the area of material handling including: (1) heat exchanger designs, (2) piping designs, (3) valve and pump designs, (4) feedstock homogenizing, (5) product separation, (6) depolymerization process, (7) low density solids separation, and (8) mineral separation.

**Heat Exchanger Design**
The combination of a bone removal system prior to the heat exchangers and minor process changes were shown to limit the scaling of hot surfaces, enabling the heat exchangers to be operated at their design condition for longer periods of time.

**Feedstock Mixing**
A new motor and gear box were installed on the main reactor mixer to increase the horsepower and speed of the agitator.  A new rake designed by Ekato was also added to increase chances of obtaining a well mixed feed for the plant.

**Hydrolysis Prep-Acid Addition**
A new quill design was manufactured using silicon carbide.  Further investigation of quill options has been assigned to outside mechanical engineer.

**Depolymerization Solids Retention**
A deck screen was designed and installed to retain all particulate matter greater than 0.06 inches blown down from the screen chamber.  This project softened bone fragments and separated them from the main process feed going to the hydrolysis prep vessel.  The softened bones and small stones go directly to mineral separation and bypass the hydrolysis process completely.

**Depolymerization Solids Diversion**
This project diverted bones from depolymerization reactor directly to a new centrifuge via a small flash tank and star valve.

**Separated-Solids Removal and Dryness**
A new decanter was installed beneath the existing decanters.  The new decanter dried the minerals and allowed reduced moisture of the minerals from the existing decanters.  This increased the cleanliness of the water and oil going to the separators and kept the existing decanters from becoming packed with mineral cake.

- Allocated starters and VFDS for 1HP, 5HP, and 30HP motors.
- Fabricated supports and effluent tank.
- Allocated effluent recirculation pump.

**Centrifuge Bowl Skirt and Seal**
Bowl skirts have been re-engineered and installed.  Improved decanter performance with less solids carryover to the separators helped with this issue also.

**Enhanced Odor Control**

In addition to material handling improvements, numerous modifications to the plant have been made to greatly reduce the potential to emit odors. The following modifications were installed: (1) tarps and covers for all trailers, dumpsters and roll offs, (2) a larger thermal oxidizer with excess capacity and enough residence time to destroy all odor-causing vapors from process vessels and storage tanks, (3) higher efficiency packing to allow for better gas-to-liquid oxidant contacting in both wet gas scrubbers, (4) ozone generation in conjunction with chlorine dioxide generation has been successfully used as a combined oxidant for odor destruction in the wet gas scrubbers, and (5) a taller wet-gas scrubber exhaust stack to allow for more residence time and better mixing. The foregoing equipment was installed after consulting with engineers and the Missouri Department of Natural Resources, the agency responsible for oversight. RES has taken numerous actions to improve the generation and containment of any odors that may be generated from the process. This includes, but is not limited to:

1. Conducted Third Party odor expert review of facility. Utilized expert information to install new thermal oxidizer.
2. Expansion of collection of system for process and storage vapors.
3. Installed additional odor control blowers for collection of vapors and separated collection system into two parts. Relocated blowers to improve operation.
4. Installed carbon canisters on conservation vents for storage tanks in the event of a release during over pressure situation caused by blockage of normal vent line.
5. Conducted assessment of odor control chemicals with technical experts from suppliers. Installed addition equipment based upon assessment.
6. Installed building enclosure for separation centrifuge to collect fugitive vapors.
7. Installed building enclosure for liquid fertilizer processing area.
8. Replaced roof on receiving building to assure capture of vapors in area. Increased ventilation rate of receiving building and piped vapors to wet scrubber.
9. Installed new wet scrubber on process building ventilation to capture vapors during maintenance operations and/or process vapors.
10. Installed new thermal oxidizer on small process stream with higher control efficiency than original thermal oxidizer.
11. Conservation vents on storage tanks connected to scrubber as redundant control.
12. Removed bio-filter and installed larger scrubber to eliminate any potential breakdown in biofilter medium or odor emissions during replacement.
13. Installed new building around receiving and staging area to prevent odor emission from material trailers waiting to be processed
14. Installed new Ozone Generator to serve as primary feed to the Scrubber systems to reduce odor and a new Chlorine Dioxide system to serve as a back-up.
15. Installed taller wet-gas scrubber exhaust stack to allow for more residence time and better mixing
16. Tarps and covers for all trailers, dumpsters and roll offs

In addition to the specific equipment and upgrades mentioned above, RES has enacted best management practices to further prevent odor emissions.

**Equipment Upgrades**

In an effort to improve the process efficiency and reduce maintenance costs, new equipment was installed. Central to this effort was the installation of: (1) a new pre-breaker and grinder that eliminated the use of pulping equipment, (2) a new style high-pressure feed pump, and (3) a new style reactor let-down valve. The new equipment showed a reduction in maintenance expenses and energy consumption.

**Pre-Breaker / Large Grinder**
This process modification improved the plant's ability to process feathers, bones and meat in the receiving area. The project consists of two parts: (1) installation of a pre-breaker and special sliding vane pump below the pulper auger to reduce the feedstock to an average size of one inch or smaller and then transfer the pre-broken feedstock to the pulpers already installed; and (2) installation of a large meat grinder that we would pump into instead of pumping from the pre-breaker to the pulpers. The grinder unit worked well and replaced the pulpers at much lower horsepower and lower maintenance cost.

**High Pressure Pumping**
Two manufacturers of similarly engineered diaphragm pumps were evaluated as alternative designs for the original progressive cavity pumps. The new diaphragm pumps were capable of high pressures and higher levels of reliability. The required $NPSH_R$ was addressed by feedstock conditioning ahead of the pump. This project included:

- Piping changes to cascade non-condensable gases from depolymerization reactor to hydrolysis prep tank.
- Flow meter dry-run protection.
- Establish effectiveness of external check valves vs. internal valves.

**High Pressure Let-Down Valve**

- Let-down valve installed.
- Inspected internals after first month for wear.
- High suction trial from hydrolysis reactor.

**Separators Run in Parallel**
The two separators were originally run in series by using the smaller one to polish the water stream from the first unit. This allowed for a very clean oil product. Piping changes were made so that both separators could run in parallel and thus increase hydraulic throughput without sacrificing product quality.

**Stainless Steel Upgrades**
A replacement vessel was secured at a local fabrication shop to change out the original depolymerization reactor. Primary reason for replacement was corrosion. New vessel was constructed of 316 SS. Additionally, a few minor design changes have been incorporated into the new vessel. These include depolymerization screening system and solids rake steady bearing. The finished oil tanks had carbon

steel heating coils and thief hatches that appeared to be corroding and were also replaced with 316 SS.

**Product Quality Control**

Many of the reasons for inconsistencies in product quality were eliminated to a certain degree through process mechanical changes during the commissioning period. These variations in process conditions included erratic pH control, reactor residence time fluctuations, pressure fluctuations, temperature gradients, over-pressuring on the oil and water discharges to the separators, and the inability to get good recirculation through the exchangers, decanters, etc.

CWT documented why and by how much the process deviated from target product qualities throughout the course of weekly runs. Capital expenditures were made to enhance the process to get cleaner minerals, cleaner oil or cleaner produced water.

**Tertiary Dehydration**

The original dehydration system was designed to remove clean water from oil (not laden with dissolved solids). Therefore, higher temperatures were needed to get the moisture to release from the TCP oil. A design change was also made to provide proper pressure in the heat exchangers and maintain flow through to the dehydration system. The finished oil currently has moisture content between 2% to 3%. Commercial technologies are available that can reduce this moisture to less than 1%. This project included:

- Hot oil as an alternative to waste steam was explored with HX manufacturer
- Vacuum pump feasibility for dehydration system was also explored
- Piping and pump analysis showed that 30 psig back pressure on exchanger with current configuration was satisfactory.

**Concentration of Process Water**

Evaporation of produced water will reduce truck traffic and resulting cost. A vapor recompressions system (“Vacom”) was operated to remove the maximum amount of organics from the effluent so that process wastewater can be discharged to the city and to thicken the concentrate as much as possible to produce a high quality liquid fertilizer. The Vacom required minor mechanical repairs due to the unit sitting idle for nearly a year. pH probes and new pressure transducers were installed. This project included:

- Replacing rotometers.
- Diaphragm transfer pump from evaporator to T-860.
- Re-route concentrate discharge through E-850 before entering T-860 to reduce concentrate temperature.

**Oil Filtration**

After much R&D work on oil filtration, it became evident that ash and other particulate solids which can cause filter element fouling were best removed after dehydration and oil cooling (around 100 F). CWT experimented with filter bags in the plant at commercial scale, prior to full dehydration and prior to oil cooling, and found that solids removal was incomplete. The plant therefore installed a trim cooler after dehydration along with a filter prior to storage tanks for finished product refinement.

**Mineral Disposal / Utilization**

A draft mineral utilization plan was developed jointly with a local agricultural concern. They intended to market and sell the TCP solid fertilizer byproduct for a fixed fee per wet ton. The plan would generate a net positive profit to CWT, after trucking and fees to the agricultural company.

## Feedstock Sourcing

In February 2005, the CWT Carthage plant began taking 100% of the waste and low-value materials generated at the ConAgra Butterball turkey processing plant. To process this material, the facility only needed to operate twenty-four hours a day for 3 or 4 days per week as the Butterball facility does not operate on weekends. In order to further extend the operating hours of the plant to establish steady state operations and improve the overall utilization of the facility, the plant initiated discussions with suppliers in the local area to supplement the Butterball feedstock with animal fats, spent hens, and other food processing wastes.

Beyond the increased capital expenditures associated with the addition of the equipment mentioned above, these additions also result in an increase in maintenance, utility, and chemical expenditures necessary to operate the equipment. Recognizing the financial impact on RES and future TCP plants, CWT has investigated the ability to utilize different feedstock sources to improve product yields and gross margin. Through testing, RES has learned that utilizing varying portions of used animal fats, vegetable oils, waste greases and other agricultural byproducts mixed in with our traditional feedstocks of slaughterhouse waste and spent egg-layers both improves operations acting as a natural lubricant supporting specific processes and improves oil yields as the composition of these greases & oils has a high level of fat.

## Miscellaneous Process Improvements

**Grease Storage and Delivery Upgrades**

An expansion of grease storage and feeding capacity was undertaken to allow for more than one tanker load of grease to be stored on-site at once. It was determined that one of the existing raw product storage tanks would be retrofitted with heat and a pump for grease storage and transfer.

**Low Pressure Steam System Upgrades**

The low pressure steam system was constructed initially using carbon steel. This was selected given the initial belief that the overhead vapor from the TCP process would have a relatively high pH. This was the case generally until the ratio of fat to protein started to increase, which caused the overhead vapor pH profile to drop significantly. Much of this system was replaced with 316 SS piping and fittings. Also, in thinking through the low pressure steam system issue, abandoned and over-designed piping runs were eliminated (which there were a few).

**Electrical Declassifying Process**

Declassifying the TCP process from an electrical code standpoint (explosion proof rating) will provide for decreased costs in the purchase of replacement parts such as motors. A local engineering company has been contacted to ensure compliance with local codes pertaining to declassification.

**Rail to Facility**

The rail siding was upgraded (new ties, ballast and leveling) and the platform and pans were purchased and delivered to the site (held in storage). No decision was made to install and pipe the system so this project is on-hold at present.

Other miscellaneous projects that are slated for near term completion include:

- ✓ V-275 discharge basket filters as a low cost operational change to be compared with Sweco unit (may be a low cost alternative to maintenance and upkeep of Sweco).
- ✓ Blood / DAF transfer line to T-120A from receiving pumps (improved throughput in receiving).
- ✓ Phosphoric acid trial with totes. Cut in required in containment wall and suction piping at high pressure acid pumps for trial (process improvement).
- ✓ Coker modifications (E-535 replacement, P-580 replacements and higher pressure ratings between P-430 pumps and R-470).
- ✓ Trailer modifications
- ✓ Trailer parking area drainage system
- ✓ Lungs blending with blood and feathers blending with offal at Butterball

### 3.1.1 Oil Characterization and Boiler Emissions Analysis

The fuel produced by the plant has been used 100% neat in boilers (B100). The fuel produced from waste is similar to many of the characteristics of the American Society for Testing and Materials ASTM D-396, except the fuel is derived from a renewable source. The D-396 specification covers grades of fuel intended for use in various types of fuel-oil burning equipment. The heating content of renewable diesel is ~126,000 Btu/gal, which is slightly below standard heating oil.

Steam boilers firing fuel oil or natural gas are the most commonly and widely used equipment to produce process steam and other heat energy. Boilers already configured to burn fuel oils can burn renewable fuel oil with simple replacement of select components of the fuel delivery system (e.g. pumps, meters, and nozzles). Natural gas fired boilers require more extensive modifications and additions, such as the installation of fuel storage tanks and liquid fuel delivery systems. One-time costs for converting a typical boiler burning fuel oil and a boiler burning natural gas to burn renewable fuel oil, represent less than 1% and 2%  of a typical first year's value of fuel consumption respectively.

The fuel oil has been sold locally for medium sized industrial boilers and an emission test was completed in 2007. It was also necessary to determine if the fuel could be used in larger boilers, and fuel oil samples were sent to Keyspan Energy's Hicksville laboratory for analysis. Keyspan is a large NY energy company that has generating plants of over 1,000 megawatts.   The analysis revealed a combustible oil fuel, which could be used in large boilers equipped to combust fuel oil.  This was further confirmed in an extensive study by Brookhaven National Laboratory.

A review and analysis of an Emission Test Report by Air Source Technologies for the renewable diesel fuel oil (RDF) produced by the facility, was performed based on testing at a medium sized commercial boiler at an industrial cheese manufacturing facility in Monett, MO.  The tests were performed on March 7, 2007, to determine criteria pollutant emission levels using a 100% renewable fuel from the plant.  These tests establish pollutant levels to obtain operating permits to burn the fuel at targeted facilities.

The table below presents the results of the three tests (including the $O_2$ level in the exhaust), and the AP42 emission levels for natural gas, #2 oil and #6 oil, for each of the pollutants.  Note first that the NOx level from the three tests tracks directly with the level of $O_2$ in the exhaust, as expected.  What is significant with respect to NOx, is that the level is only slightly above the NOx level for #2 oil, and when the $O_2$ level in the exhaust was below 5%, the NOx level was essentially the same as for the #2 oil.

This is significant, as there has been much written about the fuel bound nitrogen level in such bio-fuels, which can yield increased levels of NOx.  For this renewable fuel oil, the nitrogen in the fuel is in the amine form, similar to the structure of ammonia, with less than 10% of the bound nitrogen in heterocyclic rings.  Amine forms of nitrogen in fuels convert to NOx at a much lower reaction rate, because amine nitrogen (like ammonia) and NOx can convert to $N_2$ under proper conditions in the combustion chamber (similar to selective non-catalytic reduction, or SNCR). Therefore, it is not surprising that by properly controlling conditions in the combustion zone, NOx levels similar to a #2 oil can be achieved.

Attention should also be given to the other criteria pollutants.  Note, for example, the sulfur dioxide results.  The $SO_2$ levels with the renewable fuel oil are similar to that of a #2 fuel oil with an extremely low level of sulfur (0.2%).  Particulate levels are in line with the oil emission values, with the levels of carbon monoxide somewhat higher (except for the Test 3 case), more in line with the CO level for natural gas. Levels of volatile organic compounds and hazardous air pollutants are below those for the fossil fuels.

**TABLE 1: FACILITY EMISSIONS SUMMARY (1)**

| Emission | RDF Fuel Test 1 | RDF Fuel Test 2 | RDF Fuel Test 3 | RDF Fuel Average | Natural Gas | #2 Fuel Oil | #6 Fuel Oil |
|---|---|---|---|---|---|---|---|
| Particulate (lb/mmbtu) | 0.092 | 0.092 | 0.103 | 0.095 | 0.008 | 0.08 | 0.08 |
| Sulfur Dioxide (lb/mmbtu) | 0.216 | 0.216 | 0.210 | 0.216 | 0.0006 | 0.20 (2) | 0.32 (3) |
| Oxides of Nitrogen (lb/mmbtu) | 0.153 | 0.252 | 0.231 | 0.210 | 0.10 | 0.14 | 0.50 |
| Carbon Monoxide (lb/mmbtu) | 0.195 | 0.084 | 0.042 | 0.105 | 0.084 | 0.04 | 0.04 |
| Oxygen (%) | 4.5 | 6.58 | 5.22 | 5.44 | | | |
| VOCs (lb/mmbtu) | ND | ND | ND | ND | 0.006 | 0.002 | 0.009 |
| HAPs (4) (lb/mmbtu) | ND | ND | ND | ND | 0.006 | 0.002 | 0.009 |

(1) RDF data from emissions test. Emission levels of natural gas, #2 oil and #6 oil from AP42.
(2) Based on a #2 fuel oil with sulfur content of 0.2%.
(3) Based on a #6 fuel oil with sulfur content of 0.3%.
(4) Total HAPs taken equal to total VOCs.

In conclusion, it has been determined that the renewable diesel fuel oil has the potential to have emission levels consistent with a low sulfur #2 fuel oil. While these were boiler rather than engine tests, the fuel may also be an excellent replacement for low sulfur diesel oil.

With the success of the boiler testing applications, it is feasible to enter into additional fuel markets. The results below indicate that the fuel could be upgraded at a refinery with minor refinery modifications.

## CRUDE PRODUCTS

| PROPERTY | Renewable Diesel | TEXAS SOUR | HEAVY CRUDE |
|---|---|---|---|
| GASOLINE, wt% Dry | 13 | 29 | 2 |
| DIESEL, wt% Dry | 41 | 29 | 26 |
| TOPPED CRUDE, wt% Dry | 46 | 41 | 74 |

## CRUDE PROPERTIES

| PROPERTY | Renewable Diesel | TEXAS SOUR | HEAVY CRUDE |
|---|---|---|---|
| API GRAVITY | 20.5 | 32.3 | 13.3 |
| SULFUR (WT. %) | 0.2 | 1.67 | 1.23 |
| TAN | 113* | 0.5 | 1.8 |

## TOPPED CRUDE PROPERTIES

| PROPERTY | Renewable Diesel | TEXAS SOUR | HEAVY CRUDE |
|---|---|---|---|
| API GRAVITY | 20.5* | 15.2 | 7.9 |
| CARBON RESIDUE, wt% | 4.0 | 6-8 | 9-11 |
| METALS (PPM) | >200** | ~10 | >300 |

*TAN= Carboxylic Acids
**Metals = Calcium and P2O5
API = 20 minimum

The overall conclusion for this task is that the Carthage plant has been a success at meeting its program objectives. Through December 2007, the renewable diesel production from program onset was nearly seven million gallons, and mineral fertilizer production exceeded eight thousand tons.

### 3.2 Task 2- Characterize and Validate Fuels Produced by CWT in Power Generating Equipment

The success and confirmation of renewable diesel testing in boilers indicates that using these fuels in a diesel engine or turbine would be the next logical step in expanding applications. Both diesel fuel and TCP fuel consist of mixtures of hydrocarbons. The range of carbon chain lengths for diesel fuel is from about 10 to 30, with a small portion falling outside this range. Cetane, with a carbon chain length of 16, is used as a standard for diesel combustion characteristics. Cetane would be referred to as a C-16 hydrocarbon. TCP fuel, and other bio-derived fuels such as bio-diesel, typically have shorter chain lengths and a narrower range of chain lengths. The dominant carbon chain lengths of bio-derived fuels are between 15 and 19, with only a very small portion above C-20. This difference in carbon chain lengths results in some differences in combustion characteristics that can actually translate into improvements in combustion pollutant emissions.

**TYPICAL DIESEL COMBUSTION ENGINE**

When comparing petroleum-derived diesel and bio-derived diesel fuels, it is typical that under identical combustion conditions in a diesel engine, the bio-derived fuel produces less soot and more $NO_x$ than the petroleum-derived fuel. Given the differences in the compositions of these fuels and the mechanism of formation outlined above, this is reasonable. It also suggests that if the combustion conditions were optimized for both fuels, the bio-derived fuel would produce lower soot and perhaps lower $NO_x$ emissions.

During combustion of a liquid fuel, the products of incomplete combustion are due to incomplete mixing of the air with the fuel, due to either insufficient turbulence, late evaporation of the fuel, or improper fuel/air ratios. Liquid fuels, such as diesel, evaporate before they burn. The liquid droplets are sprayed into a hot combustion environment, evaporate into the gas phase, mix with the combustion air and burn in the gas phase. The portion of the fuel that is slow to evaporate will burn last in an oxygen-depleted condition. At this point, unless mixing is very intense, incomplete combustion occurs which forms the products of incomplete combustion, including soot.

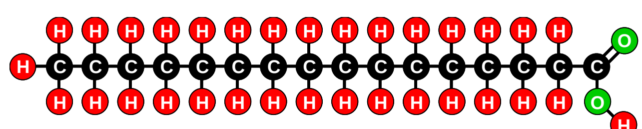
Bio-derived fuels typically don't contain the longer carbon chain lengths that are associated with the heavy end of petroleum diesel fuels, and bio-derived fuels are also richer in hydrogen. As a result, less of the bio-derived fuels will be in the range that produces most of the products of incomplete combustion. All practical tests of soot formation with the two types of diesel fuel show this advantage for the bio-derived fuels.

The flip side of the improved liquid spray combustion characteristics with bio-derived fuels is that they can burn hotter than the petroleum-derived fuels, thus generating more thermal-$NO_x$. Rapid evaporation leads to rapid fuel-air mixing, which leads to more intense combustion and higher temperatures. A larger portion of the petroleum-derived fuel is in the longer carbon chain lengths that are slower to burn. This delay, or lower combustion intensity, is the cause of the higher volumes of products of incomplete combustion, but it also tempers the overall combustion intensity and reduces the formation of thermal $NO_x$.

The apparent advantage of $NO_x$ formation in petroleum-derived fuels over the bio-derived fuels, under identical combustion conditions, can be turned into an advantage for the bio-derived fuels. If the combustion condition for each fuel is optimized for that fuel, then $NO_x$ can be, perhaps, lower for the bio-derived fuel. This is why there is conflicting data from various sources, which show better $NO_x$ emissions for one or the other fuel, depending on which fuel the test engine is optimized for. In general, the shorter carbon chain lengths of bio-derived fuels allow a greater range of conditions for combustion with low levels of the products of incomplete combustion. Optimization of $NO_x$ should be, therefore, easier with bio-derived fuels such as TCP-40 (a 40% blend with TCP).

### 3.2.1 Chemistry of TCP Fuel Oils

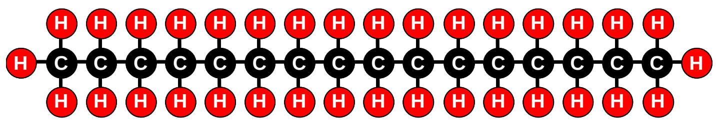
There are many theories to explain the formation of crude oils. One widely accepted theory suggests the subduction and cooking of plants and animals in the earth over thousands of years. One reason for this is that the structures of plants and animals (organic material) are similar to the structures of crude oil. This should give comfort and making it obvious that the process can produce a renewable diesel fuel oil. A simplified explanation of the chemistry, as illustrated below, can be made by using just one component that is common to both plants and animals - fatty acids. Plant and animal fats consist of triglycerides, molecules composed of a glycerol backbone with three attached fatty acids. One typical fatty acid is Palmitic acid:



Palmitic Acid

The Palmitic acid molecule consists of a long chain of carbon atoms with attached hydrogen atoms. At one end is a group consisting of one carbon, two oxygen, and one hydrogen. This is called a “carboxyl” group [-COOH]; it gives the molecule its acidic character. Palmitic acid contains sixteen carbon atoms, so it is designated a C16 fatty acid. Triglyceride fats consist of three fatty acids that are similar to Palmitic acid, although some have more carbon atoms than Palmitic acid.

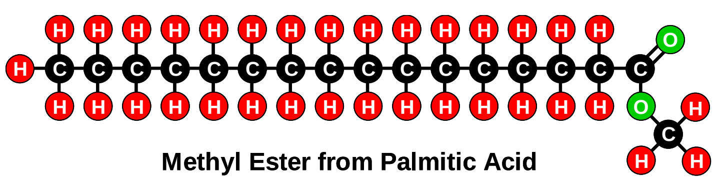
Setting aside the carboxyl group, the Palmitic acid molecular structure looks like a hydrocarbon molecule with sixteen carbon atoms. Petroleum fuels (fossil fuels) are mixtures of long and short-chain hydrocarbons. Cetane is often used as a characteristic molecule of the mid-range of diesel fuels. Its molecular structure is:



**Cetane**

### 3.2.2 Applicability

Biodiesel fuels can also be made from fatty acids by substituting a [-$CH_3$] group for the hydrogen atom [-H] in the carboxyl group on the fatty acid. The process of adding an ester to a fatty acid is called “transesterfication.” The simplest fatty ester that could be formed from Palmitic acid is:



**Methyl Ester from Palmitic Acid**

There are some disadvantages of converting the fatty acid to an ester, aside from cost, including storage, solubility, and thermal NOx issues. Alcohol tends to burn hotter, increasing NOx; and by adding an ester to the fatty acid, it limits refinery uses since alcohols tend to create operational issues.  Renewable diesel does not contain esters.

It is therefore concluded that with proper equipment modification, the TCP fuel can be used efficiently in power generating equipment. It is not expected that combustion of this fuel in an engine or turbine will yield significant emission problems (particularly with respect to NOx) and combustion of this fuel, perhaps at levels approaching 100% in a blend, will be able to meet emission standards, including those deemed MACT (Maximum Achievable Control Technology) standards for such equipment.

### 3.3 Task 3- Characterize Mixed Waste Streams (Princeton University)

#### 3.3.1 Background

A key element in the success of the TCP process is producing valuable products from mixed-waste streams. The CWT plant at Carthage, MO accepts a mixture of turkey offal, blood, feathers, bones, and grease to produce two fertilizers, oil, and a hydrocarbon in clean, concentrated streams. Product separation is of critical importance not only to TCP but to many different energy conversion technologies. Indeed, the economic viability of virtually any waste processing plant counts on the separation of mixed inputs into valuable, clean products. Improving our understanding and characterization of "product separations" will result in greater efficiencies and energy outputs of many waste-to-energy technologies, with substantial benefits to society.

Waste streams typically contain combinations of materials from various major chemical categories: proteins, fats, carbohydrates, hydrocarbons, carbons, metals, minerals, and water. Various break-down products from these categories can interact during processing to form emulsions, gels, sols and solutions, complicating separation of the final products and requiring substantial treatments to obtain clean separation of the components. This is true of any process that produces solid or liquid products such as bio-diesel or ethanol plants, as well as a TCP plant.

Information on treatment or avoidance of difficult-to-separate combinations has been developed in various industries over the course of years. This information needs to be summarized for ready application by developers of new waste-to-energy technologies. As well, practical testing of product combinations typical of waste-to-energy processes would find immediate practical application and form the basis for more fundamental efforts to maximize the value of waste-to-energy product streams.

During hydrothermal treatment at temperatures above 150°C, proteins break down into amino acids, and fats break down into fatty acids. In aqueous environments the amino acids dissolve in the water or the fatty oil depending on their relative solubility. This should result in a very easy separation of fatty oil and water. However, some of the amino acids can break down further into amines. In mixtures that also contain carbohydrates and minerals, undesirable combinations such as emulsions and mineral-laden greases can be formed, most likely as a result of the amines combining with the carbohydrate and mineral components. This is a problem in simple fat splitting and in waste-grease processing to bio-diesel, as well as in the TCP process.

Princeton University developed a project to address this type of issue. The initial work examined separation techniques with a focus on the types of chemical and physical combinations that are likely to occur with waste materials. The second phase of this work was to catalog the interaction of various combinations of wastes under a variety of typical operating conditions.

### 3.3.2 Research Goals and Results

The research aimed to first roughly characterize the feed. It was also important to determine how those items decomposed and reacted with other compounds present, in order to understand the likely products

#### 3.3.2.1 Animal Studies

A rough compositional analysis of the main components of animal offal is given below. The overall composition of the feed will depend on the ratio of the main components, i.e. bone to feathers to organs, etc. The three primary components are water, protein and lipids (mostly natural animal fat).

**Composition of main offal components, given in percent**

| | Blood Plasma | Bone | Feathers | Internal Organs |
|---|---|---|---|---|
| Water | 92 | -- | 67 | 70-80 |
| Protein | 6-8 | -- | 33 | 16-22 |
| Lipids | 0.6 | -- | -- | 3-10 |
| Cholesterol | -- | -- | -- | 0.5 |
| Salts/Minerals | 0.8 | -- | -- | 0.5 |
| $Ca_{10}(PO_4)_6(OH)_2$ | -- | 65-70 | -- | -- |
| Collagen | -- | 30-35 | -- | -- |

At high temperatures, and in the presence of an acid, proteins will undergo hydrolysis to give their constituent amino acids. Standard protein hydrolysis for purposes of amino acid analysis uses 6N HCl for 24 hours at 110°C. However, tryptophan, cysteine, threonine and serine are destroyed by acid hydrolysis and are not recovered. Asparagine and glutamine are converted to aspartic acid and glutamic acid and methionine is partially oxidized during hydrolysis.

Solid amino acids in air begin to decompose at temperatures between 178°C (cysteine) and 344°C (tyrosine). The main process of fragmentation for valine, leucine and isoleucine is the loss of the carboxyl group followed by the loss of the aminic group. Glycine also loses the carboxyl group. Threonine fragments into a stabilized ion by water loss and cyclization. Desulphydration, deamination and decarboxylation occur simultaneously in cysteine. Methionine fragments to $CH_3SCH_2^+$ and $CH_2=CHCH^+NH_2$ (obtained by the loss of $CH_3SH$) and the amine fragment with the loss of a carboxyl group. The presence of a heteroatom in the side chain, favors the breakage of the side chain causing a greater difficulty in losing the carboxyl group and increasing the decomposition temperature. Longer chains decrease the initial decomposition temperature; the $RCH^+NH2$ product obtained by the loss of the carboxyl group undergoes further decomposition.

In general, dipeptides are less stable than the single component amino acids. The first fragment of decomposition is usually carboxyl groups followed by amine groups or functional groups. Dipeptides decompose in one to four stages.

When heating amino acids and proteins in water, hydrolysis and decomposition compete. The rates of hydrolysis and decomposition are primarily dependent on temperature; pressure has no significant effect. Below 150°C neither hydrolysis nor decomposition occurs at a significant rate. Optimal production of amino acids through hydrolysis occurs at 250°C hydrolysis. At temperatures over 300°C decomposition is favored and amino acids cannot be recovered. However, maximum recovery of amino acids from proteins occurred at 300°C for very short reaction times, less than 2 minutes. Pressure was found to have a minimal effect on the overall amount of amino acids recovered during hydrolysis; however the composition changes suggesting that changing pressure affects the production of specific amino acids.

Natural animal fat is a blend of mixed triglycerides composed primarily of five fatty acids, which are listed below with their chemical formulas. The approximate compositional analysis of natural animal fat is also given below. While the composition of animal fat varies between animal and source, natural fats tend to be composed of roughly 50% saturated and 50% unsaturated fatty acids.

Composition of natural animal fat

| | | |
|---|---|---|
| Myristic | $CH_3(CH_2)_{12}COOH$ | 1-5% |
| Palmitic | $CH_3(CH_2)_{14}COOH$ | 20-30% |
| Stearic | $CH_3(CH_2)_{16}COOH$ | 10-15% |
| Oleic | $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ | 40-50% |
| Linoleic | $CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$ | 5-10% |
| Linolenic | $CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$ | 0-3% |

Triglycerides can be broken down into hydrocarbons and aromatics through intermediate radicals by pyrolysis cracking. It has been found that in the presence of metal oxides and salts the pyrolysis of free fatty acids leads to the formation of long mid-chain ketones. Above temperatures of 300°C fatty acids begin to decompose at a significant rate.

Triglycerides will react with an alcohol in the presence of a catalyst to form fatty acid esters and glycerol, with diglycerides and monoglycerides formed as intermediates. Alkyl halides may interact with the anions of fatty acid salts to form esters as well. The use of an alkali catalyst in the presence of water or free fatty acids leads to the formation of soaps; the soaps formed from the fatty acids present are borderline soluble/insoluble in water (chains longer than 18 tend to be insoluble in water). Acids can also be used to catalyze esterification.

Fats in the presence of water and an acid catalyst will be hydrolyzed to free acids, known as fat splitting. This occurs as a homogenous reaction between fats and water dissolved in the oil phase. Three methods are commonly used. Hydrolysis in the presence of sulfonate long chain alkylbenzenes runs for 24-48 hours at 100°C. In the presence of Zn, Mg, or Ca oxides which act in part as emulsifying agents and in part as catalyst, hydrolysis takes 2-3 hours at 250°C and 50 bar. High pressure uncatalyzed hydrolysis is run at 20-60 bar and 250°C. Fat splitting with water is

believed to occur through radial intermediates. The rate of hydrolysis increases with temperature and degree of hydration.
Free glycerol has been found to limit the degree of hydrolysis; at 25% glycerol hydrolysis is limited to 80%. The solubility of water in fat was found to affect hydrolysis completion and rates. The fatty acids from animal fat have solubilities in water on the order of $10^{-2}$ mol/kg$H_2O$ at 230°C and the oil phase will contain about 2% water at 300°C; both solubilities increase with increasing temperature. Emulsions have been shown to slow hydrolysis, and other phase structures present also affect the rate of hydrolysis.

Sulfuric acid will also react with the double bond in unsaturated triglycerides (the sulfonic group is joined to the carbon chain) to form an emulsifying agent. Monoglycerides, which are formed as intermediates, are an additional emulsifying agent present.

Lipids have several liquid-crystalline structures formed upon heating or in the presence of water. A lamellar lipid-water structure is formed with water layers alternating with lipid bi-layers. Two hexagonal structures, termed hexagonal I and hexagonal II are also common and generally exist in solutions that are 40-70% amphiphile. The hexagonal I phase consists of infinite cylinders of lipid molecules with polar groups exposed on the surface and a core of hydrocarbon chains in disordered liquid like conformation. The hexagonal II phase is the inverse. A third liquid-crystalline structure is the cubic phase which takes several forms. L2 is used to denote the liquid phase of water aggregates in a continuous hydrocarbon-chain medium, considered a microemulsion.

For chain lengths above $C_8$ the L2 phase is formed at high temperatures. At water levels greater than 50% the L2 phase is present alongside water. Increasing chain length strongly increases the hydrophobicity, which drastically lowers the critical micelle concentration and tends to favor the formation of non lamellar phases. The lamellar-hexagonal transition temperature falls steeply with increasing chain length.

In binary systems of lipids soluble as micelles in water (such as fatty acid salts), when lipid concentration in the micellar solution is increased, the spherical micelles are transformed into rod-shaped micelles and at higher concentrations the cylinders are hexagonally arranged (hexagonal I phase). At temperatures above 300°C spherical micellar solution is formed.

Ternary systems of water, monoglycerides and triglycerides are complex. At low monoglyceride levels oil, water and L2 phases are present.

Adding a salt or lowering the pH, reduces the hydrophilic interaction and the optimal interface. The ions in solution reduce the repulsive interactions between groups, reducing the radius of curvature which makes the molecules more likely to form bilayers or inverse micelles. The addition of fatty acids does not give rise to instability of oil and water emulsions. However, the addition of amines and alcohols decrease stability.

#### 3.3.2.2 Plant Studies

The work centered on characterizing plant-related biomass, its decomposition under conditions specified by TCP.

On the whole, the main three components of plant wastes are cellulose, hemicellulose and lignin. Since these lignocellulosic molecules are the main precursors of the CWT process, using them as starting points seemed to make the most sense. In lignocellulosic material, the carbohydrate polymers are tightly bound to lignin mainly by hydrogen bonds but also by some covalent bonds.

Cellulose is an insoluble polymer of varying degree of polymerization. The glucose residues bound by b-1,4-linkages are extremely crystalline in nature and extensive hydrogen bonding makes a network of cellulose very rigid, strong and resistant to hydrolysis. Hemicelluloses are composed of many to all of the pentoses (though xylose is the most prominent). In contrast to cellulose, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base. Lignins are by far the most complicated of the three major components. Lignin is formed by removal of water from sugars to create aromatic structures in irreversible reactions. The building blocks of lignin are believed to be a three carbon chain attached to rings of six carbon atoms, called phenyl-propanes. Extensive polymerization and cross-linking make lignin an even more complex molecule. There are many tables of the elemental composition contribution of each of these three molecules to the total lignocellulosic material, but on average the breakdown seems to be: cellulose (40-60%); hemicellulose (20-40%) and lignin (10-25%). All other material fall under extractives which refer to a large variety of different chemicals produced by the plant for a variety of reasons (protection, food storage, formation of membranes, color, etc.). This is not to say however, that nothing else comprises plant matter. There are a number of fatty acids, oils, proteins and molecules such as waxes, terpenes, carotenes, and rubbers that are present in plants. However, most of these macromolecules are either found in negligible amounts or are different from their animal analogs by the placement of a double bond or varying amino acid composition.

Most current day processes for conversion of lignocellulosic first requires deligninification to liberate cellulose and hemicellulose followed by the depolymerization of carbohydrate polymers. Deligninification is the rate-limiting step and the most difficult to be solved. One important area to consider is the cellulose/lignin ratio of the feed. The biodegradability of cellulose is much higher than that of lignin, but the cellulose is protected in a sheath-like manner by the lignin. For the production of ethanol for example, a biomass feedstock with a high, cellulose/hemi-cellulose content is needed to provide a high, l/t, yield. While the lignin content represents a potentially large energy source, current techniques involving hydrolysis/enzymatic systems cannot convert the lignin. To illustrate the effect of cellulose content on yield, up to 280l/t of ethanol can be produced from switchgrass (5-20% lignin, 30-50% cellulose), compared with 205l/t from wood (27-30% lignin, 35-40% cellulose), an effect largely due to the increased proportion of lignin. The general pattern concerning the thermal degradation of these three molecules seems to be:

Hemicellulose > cellulose >>>> lignin

The next direction that was taken was a survey of conversion technologies that are related to the CWT-TCP process. Though not completely related to the TCP process, an investigation of not only the processes themselves but the chemistry and chemical breakdown of the three above mentioned materials by pyrolysis gave a good background and intellectual grounding into the breakdown of these molecules and what one might be able to expect to happen. The products of various chemical pathways are simple sugars, simple acids, gases (such as CO, $CO_2$), aldehydes, ketones and alcohols. Conditions such as those for pyrolysis to occur, in little to no oxygen at temperatures between 262$^{o}$C to 502$^{o}$C, are more extreme than those for the CWT-TDP in water process.

A closer examination of literature on conversion techniques closer to conditions of the TCP process was the next step. Of primary interest were the conditions under which the various experiments were conducted and as close an understanding to the kinetics and chemical pathways of the degradation of lignocellulosics as possible. Incidentally, water has a $P_c$ = 22.1 MPa and $T_c$ = 374$^{o}$C and behaves more like an acid at or above the critical point. It seems the largest effect of supercritical water to subcritical water is the rate at which products are converted from larger macromolecules to simpler, component molecules.

In supercritical water (400$^{o}$C, 25MPa), cellulose breakdown products are mostly cellulose hydrolysis products (glucose, fructose, oligomers such as cellobiose, cellotriose, etc.). At temperatures below the critical point (350$^{o}$C, 25MPa) aqueous degradation products and pyrolysis products are formed (erythrose, glyceraldehydes, dihydroxyacetone, pyruvaldehyde, 1,6-anhydroglucose, 5-HMF, furfural and acids.

Below 350$^{o}$C, glucose or cellobiose (oligomer) decomposition rates are much faster than that of the cellulose hydrolysis rates. Even if cellulose hydrolysis products are formed below 350$^{o}$C, they are immediately decomposed to glucose decomposition products. At 350$^{o}$C, cellulose hydrolysis decomposition rate changes drastically and upon comparison of Arrhenius plots of cellulose decomposition rates to oligomer decomposition rates, one sees a change in the reaction rate of more than an order which suggests that cellulose hydrolysis takes place on the cellulose crystal surface at lower temperatures. At higher temperatures above 350$^{o}$C, homogeneous hydrolysis proceeded after the dissolution of cellulose. To further complicate things, hydrolysis products such as glucose are subject to further degradation to glucose decomposition products such as glyceraldehydes, etc. which makes attention to residence time another process concern to take into consideration. The key consideration here seems to be the interplay and balancing of effects of cellulose hydrolysis at the surface and its dissolution and whether it proceeds in a heterogeneous or homogeneous fashion. In a heterogenous fashion one is more likely to obtain glucose decomposition products, in contrast to cellulose hydrolysis products from homogenous hydrolysis. And depending on what products are useful and what selectivity is desired, one has certain experimental parameters; for example, if one wants to get more oligomeric and cellulose in the aqueous solution and avoid the glucose decomposition products, the temperature of the reaction should be above 350$^{o}$C and at the appropriate residence times. This shows the level of complexity and detail that must go into process considerations.

Other literature reported that at 300 $^{o}$C and 8.9MPa cellulosic biomass when subjected to subcritical water converts into HMF (hydroxymethyl furfural), 2-FA (furaldehyde) and lactic acid among other products. The initial decomposition products were glucose and cellulose. Further degradation of fructose, glyceraldehydes, dihydroxyacetone, and pyruvaldehyde all yield among other things primarily lactic acid.

One of the first main foci of this project was to see if there could be an educated guess at what is present in the product streams, the "sludge", after the first reactor heating stage. Initial solubility investigations show that simple carbohydrates are in the majority water soluble due to their proclivity to forming hydrogen bonds with water while lignin and complexed sugars such as cellulose are not very soluble. Closer examination of lignin and cellulose chemistry yields not only more about the chemistry but also key properties such as solubility which may have an impact on the composition of the "sludge" being investigated. Other avenues of investigation such as rheological and mechanical properties of suspensions of lignocellulosic materials may be of interest. Effective pre-treatment, whether by dilute acids or other means, or other means by which the breakdown of the super-structure of the lignocellulosic material is achieved may also be of interest.

### 3.4 Task 4- Fundamental Research in Waste Processing Technologies (MIT)

Accelerated development of industries that convert biomass to liquid fuels and other petroleum substitutes would provide new markets for farmers and stimulate rural economic development in the U.S. and throughout the world. The project at MIT focused on the production of liquid fuels from waste biomass by means of TCP technology, with emphasis on understanding and modeling of the chemistry of the hydrothermal conversion. Specifically, the project studied the kinetics of chemical reactions which occur in the conversion, with particular emphasis on the deleterious effects of the so-called Maillard reaction, which is a polymer-producing reaction between carbohydrates and amino acids.

The work sought to: validate the reaction mechanisms using glucose and glycine as the model compounds; develop procedures and operations protocols from existing Maillard reaction literature; perform, if possible, bench-scale testing using reactors with short residence times to determine reaction intermediates and reaction rates; explore further process development initiatives (i.e. use of acid catalyst to increase rates of reaction), as required.

The results of the program were presented as two papers. The first tiled "Turkey Processing Wastes to Diesel Oil- Investigating the Environmental Performance of a Hydrothermal Process for Transferring Food Industry Waste into Useful Products" was presented at the 9$^{th}$ European Biosolids and Biowaste Conference in November

2004. The second titled “Hydrothermal Processing in Biorefineries-A Case Study of the Environmental Performance was presented at the 7th World Congress of Chemical Engineering in July 2005. In both papers the CWT process was established as a viable hydrothermal process for consideration. Both papers appear herein as Appendix 2.

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**APPENDIX 1**

**Stage Gate Review – Colorado SEER Project**
**July 30, 2004**
**Summary Report**

**The Society for Energy and Environmental Research (SEER) obtained a $2.5 million earmark in the FY 2003 Energy & Water Development Conference Report to develop a $21 million, 250 ton per day demonstration biorefinery in Weld County, Colorado. SEER, a wholly owned, non-profit subsidiary of Changing World Technologies, Inc. (CWT), plans to utilize the patented Thermal-Depolymerization technology (TDP) process to produce fuel, power, and industrial chemicals from turkey and other organic wastes. As part of the project plans, SEER was required to participate in a Stage Gate Review with DOE. This report documents the results of the Stage Gate Review held on July 30, 2004.**

**Current Status of the Project: The project is in the engineering design stage. The implementation of the Colorado plant is dependent on the resolution of operational issues at the Carthage, Missouri plant, CWT's first demonstration plant. A $12.4 million DOE earmark was approved in FY04 to support and address the Carthage plant technical issues. The Carthage plant optimization may last into 2005. The Colorado plant technical status is that the Process and Instrument Drawings have moved from 60% completion to 70%. Air and waste water permits are 50% complete. In addition, DOE is required to perform an Environmental Assessment (EA) as part of NEPA compliance. A draft EA was released to the public for comment on August 12, 2004. Responses and comments are due back to DOE by September 15, 2004. To date SEER has invoiced for $273,281 under this award and documented $33,979 in cost share.**

## Review Objectives:

Overall, the review was designed to help both the performers and DOE understand the current stage of development of the Colorado SEER project and the key issues being addressed as the project moves into the validation stage.

The specific objectives were as follows:

1. Review historical basis and efforts for current work including:
    a. technical feasibility and risks, and identification of key barriers to demonstrating the technology
    b. the competitive advantage of technology over competing technologies
2. Examine the business and technical assessment information that lead to the determination of technical goals
    a. Progress to date on meeting technical goals
    b. Progress to date on meeting economic, manufacturing, and business goals
3. Review the technical, health, safety, economic and environmental issues
4. Assess the market and business plans including customer relationships
5. Assess critical success factors and showstoppers
6. Assess plans to proceed

## DOE Review Team Participants:

Esteban Chornet Enerkem

| | |
|---|---|
| Douglas Elliott | Battelle, PNNL |
| Paul Grabowski | DOE Office of the Biomass Program |
| Ralph Overend | National Renewable Energy Laboratory |
| Jeff Tester | MIT |
| Frank Baumgardt | DOE Golden Field Office – IRT/McNeil |
| Jim Spaeth | DOE Golden Field Office |

A report of the results follows:

**Historical Perspective And Technical Status, Feasibility And Risks:**

History: The company has been in existence for about 7 years, started by the inventor of the process, Paul Baskis. Paul holds 3 patents on the process. Brian Appel bought into the company in 1997. CWT and the inventor have since effectively parted company. CWT has been financed from private sources and has developed the process further in bench scale autoclaves and the construction of a nominal 7 ton per day pilot plant located in the Philadelphia Naval Shipyard. CWT has many active and evolving collaborative arrangements with a number of large industrial groups, from ConAgra to major energy and auto and tire manufacturing companies.

Technical Status: CWT's effort in the early stages of laboratory scale and pilot scale testing was focused on waste food processing feedstocks to establish a basis for the design of the Carthage facilty. Their current laboratory bench and pilot scale work includes development on plastics, tires, ASR (auto shredder refuse), sewage sludge and MSW. Much of this is financed by the potential clients and thus is proprietary data - the identity of the clients was withheld.

The autoclave data and pilot plant runs were used by Kvaerner Process Systems, their licencee and process implementation company, to develop the flow sheets and P&ID for the Carthage, Missouri plant. This plant is owned by Renewable Environmental Solutions, LLC. (RES), a joint venture between CWT and ConAgra. The cost of the plant was over $20 million with $5 million contributed through an FY01 EPA earmark. From a stage Gate perspective the Carthage plant which processes 200 tons per day of Butterball turkey residues is already at Gate 5 the *Commercial Launch Stage*.

The reviewers all recognized that in a one-day meeting, it was not possible to conduct a quantitative due diligence review of CWT's claims of performance. Nonetheless, based on the information presented regarding product selectivity and mass and energy balances, it appears that CWT has achieved reasonable closure of mass and energy balances in both its pilot plant and Carthage startup operations. The overall efficiency of their process was presented as approximately 85% or greater defined in terms of the outgoing fuel combustion heating values of all their products relative to the amount of total combustion energy content of the feedstock corrected for the energy input required in the process.

The plant in Carthage is currently still in a "shakedown" stage and has been in this stage since the fall of 2003. The plant has only run in test campaigns so far. The current process residue is assigned to a commercial renderer. The plan is for the contract to move from the renderer to the Carthage plant in September 2004. The testing so far in the startup phase has not revealed any technical "showstoppers" but has provided quantitative information on the performance of the entire system as well as individual process equipment. Nonetheless, the CWT process must be ready to function more or less continuously with very high reliability in September 2004. Based on the information presented to the review panel CWT is optimistic about meeting this objective and they have taken appropriate steps to attempt to preclude long-time outages. For example, from the flow sheet that was presented it appears that there is a high degree of redundancy of pumps and lines, and all major items such as centrifuges were available as spares on site.

Lessons Learned: CWT and its contractors have learned much from the construction and startup of Carthage and have employed a reasonable approach to documenting and utilizing that experience to improve performance. The site visit confirmed that CWT follows good laboratory practice in its operations, and uses a wide range of recognized and reputable analytical services in support of its sample analysis and data gathering. Such practice seems consistent with developing a rationale approach to assimilating its evolving know how into re-engineering and re-designing new plants as well as to enhancing performance of the Carthage plant as it moves towards continuous production.

The Carthage plant has processed materials that have been stockpiled resulting in runs of 3 or 4 days and about 500 tons processed per campaign. The Carthage plant is approximately 25 to 35 times larger in throughput capacity than the Philadelphia pilot facility. The results have been declared satisfactory though there have been challenging problems with pumps, sensors and controls which are part of the shakedown. Problems of this type are commonly encountered in startups of first-of-a-kind chemical plants based on such a large scale-up factor. They have been dealt with by CWT using normal engineering practice.

Other technological concerns and problems that were raised during the meeting and that require further elaboration by CWT include:

- pH changes during the hydrothermal treatment and their influence in yields, product distribution and metallurgical choices;
- uniformity vs. time (of plant on stream) of oil yield and oil quality;
- fouling of heat exchanger prior to hydrothermal treatment;
- accumulation of char/tar in the pyrolysis auger;
- need for microfiltration and/or distillation of the oil may be an issue;
- Nitrogen and Sulfur are distributed among the water phase, the oil phase and the gaseous phase. CWT should document better the Nitrogen and Sulfur carrying compounds present in these fractions.
- the water concentrate phase was presented as "full of amino-acids" yet no analytical evidence was provided other than verbal testimony related to impressive plant growth gained from the nutrients contained in the amino acid

mixture;

- waste water treatment facilities may need to be added to the process. This was discussed yet in no depth.

The reviewers also expressed concern about too rapid expansion of the technology into other non-lipid types of feedstock. The background information provided by CWT routinely implies that the technology can be applied to all wastes.

Environmental and Regulatory Issues: These issues do not appear to limit the deployment of CWT technology, although odor issues have been noted in the press at the Carthage plant.
It appears that CWT's TDP process would have some distinct environmental advantages over current practices such as rendering or land reuse of food wastes. For example, the high temperatures involved with their process would certainly destroy or sterilize any bio-toxins or pathogens – including proteins. The deploymerization of protein matter also has apparent advantages in producing amino acids for fertilizers.

This type of process - hydrothermal decomposition followed by phase separations and then delayed coking of the oil product - is very capital intensive. The materials of construction in the early stage require significant erosion and corrosion resistance and operate at high pressure. A plant handling biological material such as turkey residue must meet sanitary requirements for health and safety for the incoming feed; the basic conversion steps of the process and plant must meet all steam regulations in addition to the fire and explosion requirements of an oil refinery.

Economics: From the data provided, it was not possible to analyze the economics of the CWT process. Treatment of cash flows, estimates for costs of capital equipment, feed stocks supply costs, and product prices were not presented. The fact that ConAgra has invested significantly in the Carthage plant and is moving forward in a joint venture with CWT strongly suggests that there has been a detailed economic assessment of the feasibility of TDP technology for turkey and other meat processing wastes, at least at the scale of the current Carthage plant and the proposed Weld County, Colorado plant. Given the percentage of funding that the DOE is providing relative to current and planned investments by CWT and its partners, it seems unlikely that full disclosure of its economic analysis will be made.

The company is actively marketing in Europe where a public response to both "Mad Cow Disease" (BSE) and the foot and mouth epidemics, has effectively shut down the rendering industry as there can be no reuse of critical animal parts in either the feed or even industrial applications. This takes away the lower cost alternative processing for animal residues which is the CWT competition for animal residue feedstock in the US.

Risks: Initial testing of equipment at Carthage and at the CWT pilot plant have demonstrated that high quality fuel and fertilizer products can be produced. However, the long term durability of the process equipment has yet to be proven. An important result to date is that the basic chemical conversion pathways of hydrolysis and deploymerization of fats, proteins and carbohydrates appears well founded. CWT is also investigating a wide range of alternative feedstocks and despite some of the public pronouncements, CWT acknowledged that there is significant development effort required for lignocellulosics to produce significant oil yields (CWT's initial work shows extensive gas production).

Other technical issues that CWT is dealing with include: poor seals and welds, inadequate separation of partly emulsified oil and water product streams, char buildup, fouling of heat exchangers, and pump seal failure, and odor control. These types of technical challenges are to not unexpected given the approximate factor of 30 scale-up from the pilot plant to the Carthage plant. These problems are consistent with the normal "growing pains" of many plant startups of this magnitude. Although there is inherent risk, CWT and its partners have shown that they are committed to learning from their early operating experience at Carthage and will re-invest to modify equipment or change operating procedures to achieve acceptable levels of performance.

**Conclusions and Suggestions:**

CWT should pursue a means for more quantitatively comparing its technology for waste treatment and energy recovery with other competing technologies. Such a detailed comparative study would help clarify their position and the general attractiveness of TDP for bio-waste conversion application

Information on CWT's TDP process has begun appearing in the open literature. Two recently released papers are good examples of what CWT should be doing to increase its credibility and acceptance in peer-reviewed settings (Adams, Appel, Samson, and Roberts , "Converting turkey offal into bio-derived hydrocarbon oil and with the CWT thermal process," Power-Gen Conference, Las Vegas, NV (March 1-3, 2004), and Roberts, Williams, and Adams, "Animal waste to marketable products," Natural Gas Technologies Conference, Phoenix, AZ ( Feb 8-11, 2004)).

Though CWT presented the overall efficiency of their process as 85% or better, it is important for CWT to explore other ways of representing the efficiency of the TDP process. For example it would be valuable to see what a full life cycle assessment would yield. This will require that appropriate allocations be made for the total energy requirements needed to produce their food waste feedstocks as well as the energy content of its products.

The limitations of a one-day review did not make it possible for the panel to evaluate several important details or claims including: verification of the composition and suitability of its liquid fuel and mixed amino acid product streams; validation of the energy and mass balances; and review of critical economic elements and plant performance factors. Without suitable ways of protecting its intellectual property, it seems unlikely that CWT will be able to disclose further proprietary information and know how to the DOE for review and analysis.

## Appendix 2- MIT Papers

**HYDROTHERMAL PROCESSING IN BIOREFINERIES – A CASE STUDY OF THE ENVIRONMENTAL PERFORMANCE**

**Morgan Fröling [1,2] Andrew Peterson[2] and Jefferson W Tester [1,2]**

**[1] Laboratory for Energy and the Environment, Massachusetts Institute of Technology,**

**[2] Department of Chemical Engineering, Massachusetts Institute of Technology**

# Abstract

Hydrothermal processes are possible attractive components for biorefineries, for converting different biomass streams into a range of products. This study investigates the environmental performance of a hydrothermal process plant in Carthage, Missouri under development by Changing World Technologies (CWT). The plant converts the refuse from Butterball Turkey production into diesel oil, fertilizer products and carbon. The CWT process is essentially a closed system with few emissions, avoiding odor problems from the handling and giving products free from pathogens. Life Cycle Assessment has been used to investigate the overall environmental performance of the process and the performance of this process is discussed in comparison to other process routes to give the same products.

**KEY WORDS**

biorefinery, hydrothermal processing, food industry, diesel oil, life cycle assessment.

# Introduction

Since the early 1980s biorefineries have been discussed as means to displace fossil hydrocarbon feedstocks and utilize renewable sources for energy, materials and chemicals [Ng et al, 1983, Kamm and Kamm, 2004]. The concept was first discussed mainly in terms of biotransformation of material, but has now developed to consider the use of many sorts of chemical process solutions, including hydrothermal conversion, to reach the desired goals. A similar enlargement of scope can also be seen regarding raw materials, from focusing on specific biomass for the purpose of use in a biorefinery into a broad range of biomass and increased interest in biowaste. It should be remembered that chemical processes and products will not fit the criteria of sustainability solely because they are based on biomass, or even biowaste. All proposed processes should be evaluated from an environmental systems perspective to establish their environmental performance as well as identify possible improvements to the processes.

Hydrothermal processes are possible attractive components for biorefinery application as they could be used to convert a variety of wet biomass streams into a range of products. An example of a wet biomass feedstock is food industry waste. Large flows of material processed by the food industry are not converted into marketable food products. The hydrothermal conversion process studied in this paper has been designed to overcome some problems connected to this kind of material flow: odor, the risk of spreading of pathogens and contaminants (concerns over the possible propagation of Mad Cow disease have emphasized this problem) and low market value of recovered products (often the case with compost products).

This study investigates the environmental performance of a hydrothermal process plant in Carthage, Missouri under development by Changing World Technologies (CWT). The plant converts the refuse from Butterball turkey production into diesel oil, fertilizer products and carbon. It is possible to incinerate this kind of organic waste, thereby eliminating the risk of spreading pathogens, but water content makes it a troublesome fuel.

The technology has been developed by CWT and tested in a pilot plant in Pennsylvania [CWT, 2004]. A full scale commercial plant has now been constructed to handle the turkey offal from a ConAgra Butterball turkey processing facility in Carthage, Missouri. The process is described by Roberts *et al* [2004] and Adams *et al* [2004]. This study gives a preliminary environmental system evaluation of the Carthage hydrothermal conversion process, based on this information. Processes to convert organic waste into liquid fuels have been studied earlier, see e.g. the review given by Zahang *et al* [1999], but have often been hampered by low grade of conversion into the desired product or low energy efficiency.

# Process Overview

The hydrothermal conversion process flow sheet is shown in Figure 1 (see Roberts *et al*, [2004] and Adams *et al* [2004] for further details). The process is divided into two main stages. In the first stage the feed is pulped into slurry, then pressurized to about 40 bar and heated to the reaction temperature (200-300°C). The solids are separated and the liquid is flashed to separate water. The non-aqueous phase is further processed by heat treatment in a second stage reactor (around 500°C). Recovered from the first stage are a solid phase (minerals) and liquid phase (containing nitrogen), both possible to use for fertilizing purposes. From the second stage fuel gas, carbon and diesel oil are recovered. The fuel gas is used for the internal heat needs. The minerals, the liquid containing nitrogen, the carbon and the diesel oil are all marketable products, but in this preliminary environmental evaluation only the oil has been considered. The oil is dominated by straight hydrocarbons with a chain length between 15 and 20, in the shorter range of conventional diesel oil [Roberts *et al*, 2004]

## Life Cycle Model of the Carthage Plant

Two benefits of using hydrothermal conversion of food industry waste can be identified immediately: fewer odors from open processing and transport of non-processed organic waste and sterilized process outputs minimizing risks for spreading of pathogens. Here, however, the focus is on the environmental systems performance in terms of impact on global warming, acidification and photo oxidant creation from the generation of synthetic diesel oil from a renewable feed stock.

In striving towards increased eco-efficiency in society, it is widely recognized that an activity must bear the burden not only of direct emissions from the activity but also from all directly and indirectly related activities brought on by its existence. This ‘life cycle thinking’ has stimulated the development of tools to study the total life cycle environmental impact of products or services. Life cycle assessment (LCA) is a structured way to calculate and evaluate, quantitatively, the environmental load caused by a product or a service during all phases of its life cycle; the environmental impact from “cradle to grave”. In an LCA, extraction and transports of raw materials, upgrading of raw materials, actual production and use of the product, necessary energy requirements and transformations, waste collection and treatment, etc., are studied in order to determine the total life cycle impact.

In this study, a life cycle approach has been used for a preliminary evaluation of the hydrothermal process in Carthage, Missouri as waste handling method for food industry organic wastes. An overview of the systems model is given in Figure 2. The activities are briefly described below.

The CWT TP Carthage box in Figure 2 describes the entire conversion plant and is modeled based on data from the process simulations use to design the plant, as given by Roberts *et al* [2004] and Adams *et al* [2004]. Feedstock inflows per day to the process are 191 metric tonnes of wet turkey offal, 3.0 tonnes of sulfuric acid and 91.2 MJ of grid electricity. Product outflows per day from the process are 2506 GJ diesel oil, 274 GJ fuel gas, 30.6 tonnes liquid nitrogen fertilizer, 7.5 tonnes mineral fertilizer, 6.1 tonnes carbon and 79.9 $m^3$ waste water. Of the outflows the use of the two fertilizer products and the carbon have not been followed downstream further than transport of the products from the plant.

Sulfuric acid is assumed to be produced from a mix of mined virgin sulfur (60%) and sulfur from desulphurization of oil at refineries (40%) [Greshick *et al*, 1998]. The latter form of sulfur has been considered a residual product, and no environmental impacts from the crude oil processing have been included. Sulfuric acid production is an exothermic process, creating surplus heat. No beneficial use of this heat has been included. The grid electricity from the local utility used by the Carthage plant are generated from coal and nuclear plants; around 96% from coal condensing power and around 4% from nuclear power [Adams, 2004]. The environmental impact has been described under the assumption of a 9% grid loss [Frees *et al*, 1998; Brännström-Norberg *et al*, 1996].

The fuel gas produced is a mixture of methane, carbon monoxide, carbon dioxide and low molecular-weight hydrocarbons. The fuel gas is used internally, covering the heat need of the hydrothermal process. The plant is predicted to generate a surplus of fuel gas, but here all gas is assumed to be used internally. Again this can be seen as a worst case scenario. The combustion of the fuel gas has been described by emission factors for combustion of LPG [Corinair, 1996], but the carbon dioxide produced is regarded as of biologic and not fossil origin.

In more conventional turkey processing waste treatment, the turkey offal is subjected to dehydration and fat removal to transform it into meat and bone meal, which is then used as animal feed. This process is known as rendering. Our study has been expanded to take into account this process that now is avoided by instead using CWT hydrothermal conversion. The model system is also expanded to include the animal feed production that is necessary to make up for the meat and bone meal that no longer is produced. The avoided rendering process is described according to UNEP [2000] and Nielsen [2003]. The animal feed that now is necessary to produce by other means is assumed to be based on soybeans, which gives a similar protein contents in the feed. The feed production process is described according to Hospido *et al* [2003] and Nielsen [2003b]. For the agricultural production of the necessary soybeans, average data for fertilizer and fuel use in seven states in the US have been used [Kim and Dale, 2004]. It could be argued that there should not be any system expansion for animal feed production, e.g. if meat food processing waste by reasons of food safety precautions should be phased out anyway, but in this study we have chosen to include these activities.

The outflows of fertilizers and carbon represent useful and marketable products. However, no system expansion has been made to take into account the benefits from these products. Transport of these products to use has been included as a 250 km transport with a light truck (tailpipe emissions [NTM, 1998] and environmental impacts from diesel oil production [Frischkknecht *et al*, 1994] have been included).

The waste water is sent to a municipal waste water treatment plant. The environmental impacts from the waste water treatment have in this screening evaluation been described with an approximate electricity use for waste water treatment, based on Dennison *et al* [1998]. No other impacts from waste water treatment have been accounted for.

The thermal conversion diesel oil acts as a drop-in substitute for conventional diesel oil. In the model this flow is used to generate the avoided emissions from production of an equivalent amount of conventional diesel oil production based on energy content as well as the carbon dioxide emissions that are avoided when diesel derived from a renewable source is used compared to fossil diesel [Frischkknecht *et al*, 1994]. This serves to give an understanding of the magnitude of the environmental impacts caused by hydrothermal conversion of the turkey wastes. Furthermore, the diesel oil produced from the hydrothermal conversion process has a composition that might give a cleaner combustion compared to conventional diesel oil, since the slightly shorter chain length of the hydrocarbons can be assumed to give less particle formation, but no such beneficial effects have been included in the present study.

## Results and Discussion

The summarized emissions from the activities described in the environmental systems model have been characterized into global warming potential, acidification potential and photo oxidant creation potential [Hauschild and Wenzel, 1998].

In Figure 3 the modeled impact on global warming from processing of one wet tonne of turkey offal is given in kg of carbon dioxide equivalents. The production of the electricity used in the process is clearly of importance, and it would be beneficial to investigate if it is possible to further optimize the process to lower the electricity use. The second largest impact occurs from the agricultural production of soybeans as alternative to the animal feed no longer produced from the turkey offal. The global warming impact from the model of the agricultural production of soybeans originates to a large extent from the production and use of nitrogen fertilizer. In Figure 3 the impact from each activity is divided into the species of emissions generating the global warming potential. The main species contributing to global warming are carbon dioxide and, for the soybean production, nitrous oxide. The nitrous oxide is generated partly in the production of the nitrogen fertilizer and partly from soil microbial transformation of added fertilizer nitrogen (1.5% of added nitrogen is transformed into nitrous oxide [Kim and Dale, 2004]). The result indicates that if crops are grown specifically for use in biorefineries it will be important to optimize the environmental performance of the feed generation; it is not enough to rely on a renewable feedstock, renewable resources must also be managed in a sustainable manner.

Figure 4 gives the results for global warming impact when also taking into account the avoided conventional diesel production and the fossil carbon dioxide emissions which are avoided by displacing conventional diesel with non-fossil diesel. The avoided impacts from these processes are clearly dominating the picture.

In Figure 5 the acidification potential for the investigated system is shown, and the outcome is similar to that of the global warming characterization.

In Figure 6 the photo oxidant creation potential for the investigated system is shown. The outcome is totally dominated by the emissions of volatile organic compounds avoided from conventional diesel production (extraction and refining). The animal feed production gives an impact, mainly connected to diesel use in agricultural production of soybeans.

The outflows from the hydrothermal process are sterile. The process conditions are such that even relatively heat-stabile infectious materials like prions can be expected to be destroyed [Casolari, 1998]. This is a beneficial outcome that is not covered by characterizations into global warming, acidification and photo oxidant creation potentials. The production of other useful materials, fertilizers and carbon, can be compared in terms of global warming and acidification potentials but this part of the system has not yet been studied.

The environmental impacts from generating the turkey offal have not been included in the study, but allocated to the production of turkey food items. Thus, the results from this study does not implicate that increased poultry production is a good way to generate all diesel needed in society, but that hydrothermal conversion as a way to handle waste from food processing industry comes out positively in this screening life cycle assessment.

The environmental systems performance of hydrothermal conversion of organic waste should be studied further to describe the system in detail, to refine the description of animal feed production and to include the fertilizer and carbon by-products in the investigated system. In future work more environmental impact categories should be investigated to get a more detailed understanding of benefits and drawbacks of the process.

## CONCLUSIONS

The importance of evaluating environmental performance for new and proposed processes from a systems perspective has been emphasized. This is particularly relevant to processes that have significant feedstock and energy requirements where large impacts may occur from processes outside the boundaries of the chemical process plant itself. The use of combinations of hydrothermal processes seems to have a role in future biorefineries. In this screening life cycle assessment study hydrothermal conversion of turkey offal into diesel oil comes out beneficial regarding global warming potential, acidification potential and photo oxidant creation potential. When considering biomass as a renewable feedstock for a more sustainable chemical industry it is important to also environmentally optimize biomass production and agricultural processes. For a total evaluation of the CWT hydrothermal system further refinements are needed to describe the utilization of all products.

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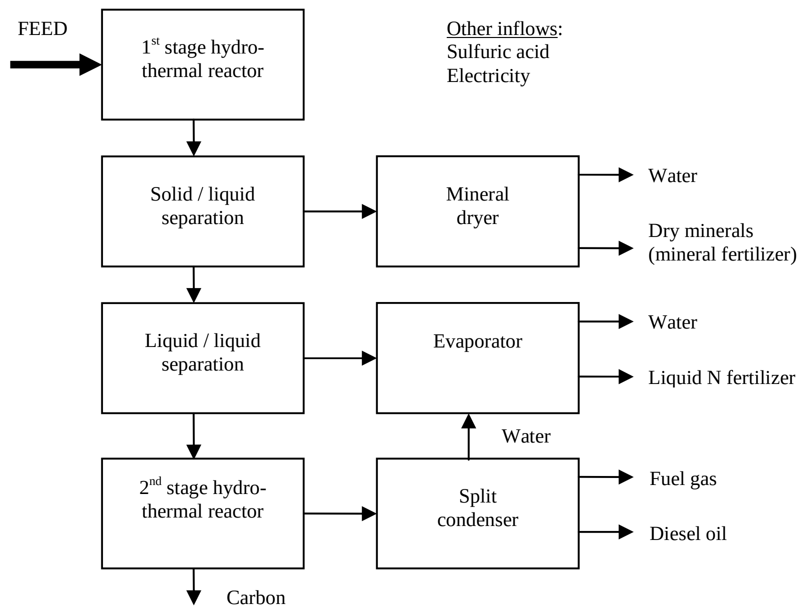
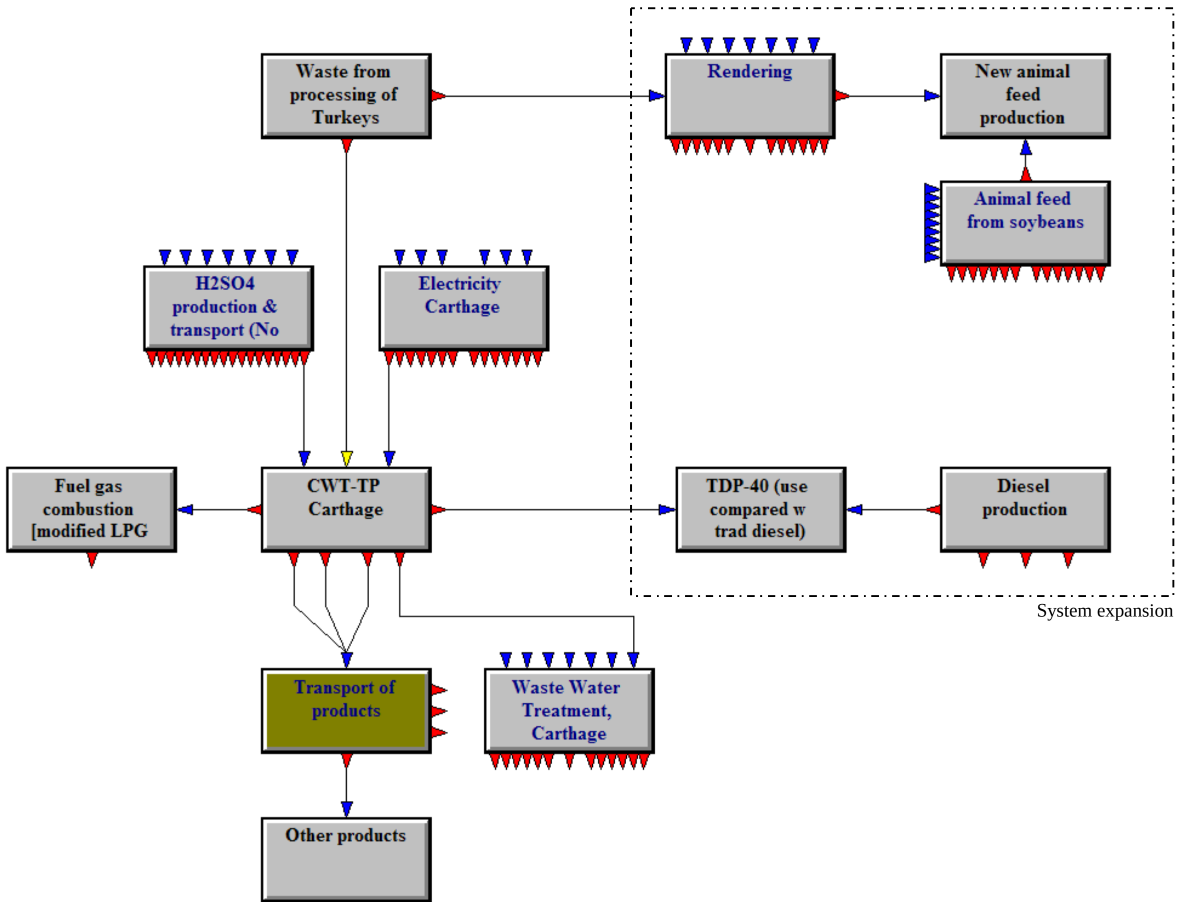
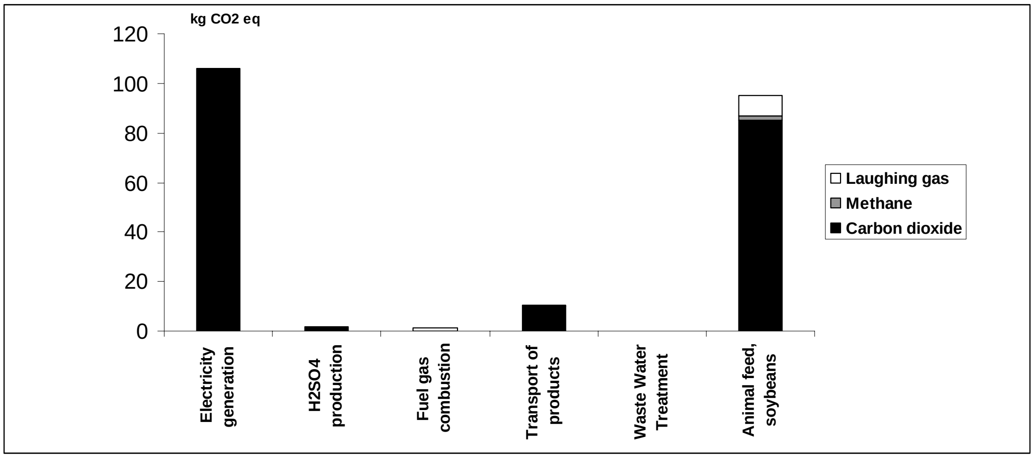
# FIGURES



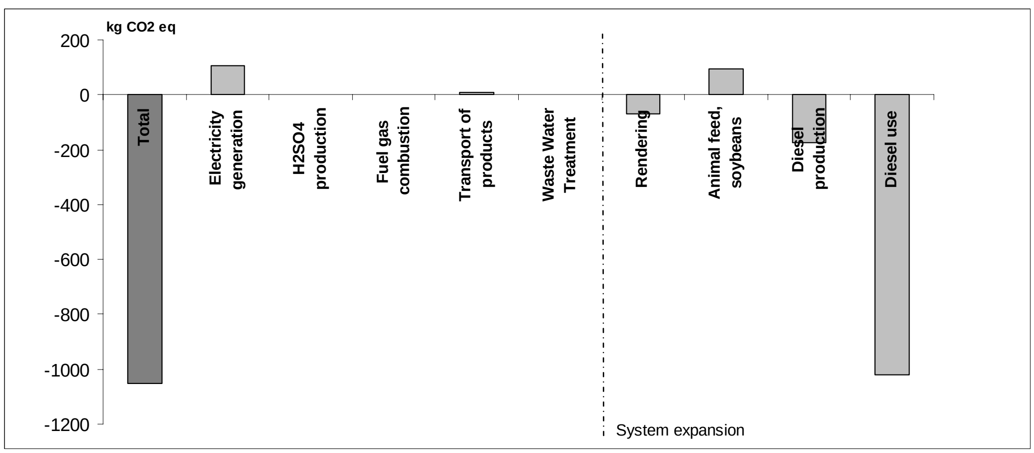

- FIGURE 1 – OUTLINE OF THE HYDROTHERMAL CONVERSION PROCESSING OF TURKEY OFFAL INTO DIESEL OIL, ADAPTED FROM ROBERTS *ET AL* [2004].



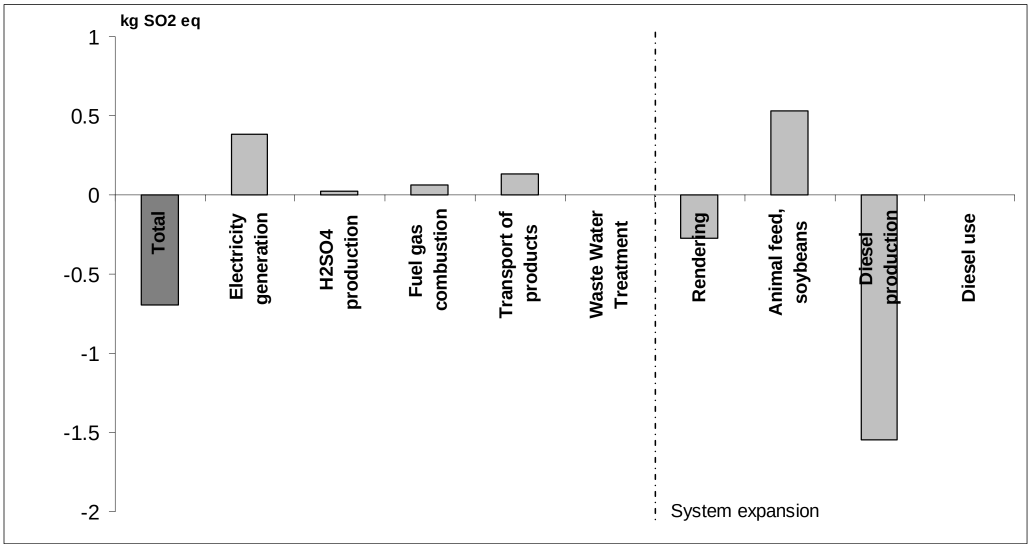
- **FIGURE 2 – ACTIVITIES IN THE ENVIRONMENTAL SYSTEMS STUDY OF THE HYDROTHERMAL PROCESSING OF TURKEY OFFAL INTO DIESEL OIL (SEE TEXT FOR DETAILS)**



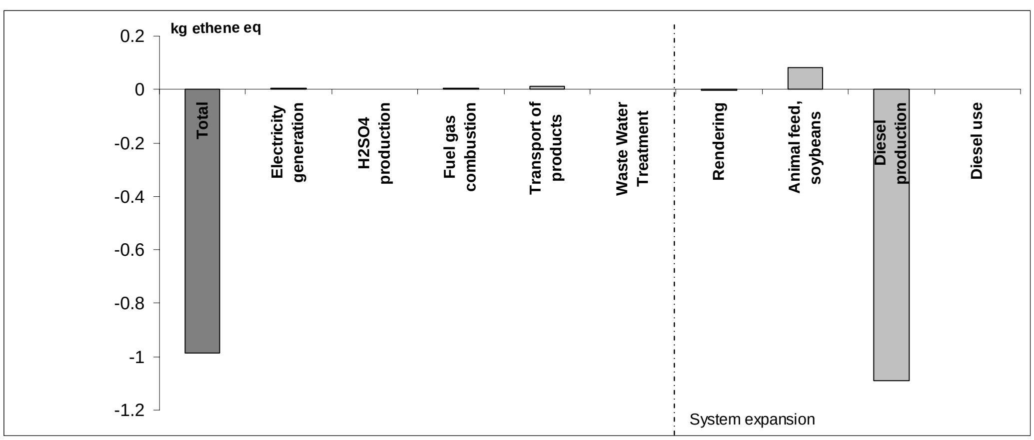

- FIGURE 3 – GLOBAL WARMING POTENTIAL FOR ACTIVITIES CAUSED BY THE TURKEY WASTE PROCESSING. THE INDIRECTLY CAUSED AGRICULTURAL PRODUCTION OF SOYBEAN ANIMAL FEED HAS A LARGE IMPACT, MAINLY CONNECTED TO THE PRODUCTION AND USE OF NITROGEN ARTIFICIAL FERTILIZER. [KG CARBON DIOXIDE EQUIVALENTS PER WET OF TURKEY WASTE]




- FIGURE 4 – GLOBAL WARMING POTENTIAL FOR ACTIVITIES IN THE SYSTEM INCLUDING AVOIDED RENDERING AND AVOIDED PRODUCTION AND USE OF CONVENTIONAL DIESEL TO AN EQVIVALENT AMOUNT. PROCESSES THAT ARE AVOIDED GENERATE NEGATIVE BARS.
- [KG CARBON DIOXIDE EQUIVALENTS PER WET OF TURKEY WASTE].




- FIGURE 5 – ACIDIFICATION POTENTIAL FOR ACTIVITIES IN THE SYSTEM INCLUDING AVOIDED PRODUCTION OF CONVENTIONAL DIESEL TO AN EQVIVALENT AMOUNT (NEGATIVE BAR). THERE IS NO PREDICTED CHANGE IN ACIDIFYING EMISSIONS FROM USE OF THE DIESEL, AND THUS NO BAR SHOWS.
- [KG SULFUR DIOXIDE EQUIVALENTS PER WET TON OF TURKEY WASTE]




- FIGURE 6 – PHOTOOXIDANT CREATION POTENTIAL FOR ACTIVITIES IN THE SYSTEM INCLUDING AVOIDED PRODUCTION OF CONVENTIONAL DIESEL TO AN EQVIVALENT AMOUNT (NEGATIVE BAR). THERE IS NO PREDICTED CHANGE IN EMISSIONS CONTRIBUTING TO PHOTOOXIDANT CREATION POTENTIAL FROM USE OF THE DIESEL, AND THUS NO BAR SHOWS.
- [KG ETHENE EQUIVALENTS PER WET TON OF TURKEY WASTE]

# TURKEY PROCESSING WASTES TO DIESEL OIL –

# INVESTIGATING THE ENVIRONMENTAL PERFORMANCE OF A HYDROTHERMAL PROCESS FOR TRANSFERRING FOOD INDUSTRY WASTE INTO USEFUL PRODUCTS

**Morgan Fröling [1,2] Andrew Peterson[2] and Jefferson W Tester [1,2]**

**[1] Laboratory for Energy and the Environment, Massachusetts Institute of Technology,**

**[2] Department of Chemical Engineering, Massachusetts Institute of Technology**

## Abstract

Large flows of material processed by food industry are not converted into marketable food products. These materials, a biological feedstock recourse, are today in many cases considered waste to be land filled or reused in lower grade rendering applications. Even if utilized, processes used are often troubled by odor and there is a market resistance to some of the conversion products caused by risks for spreading of pathogens and contaminants. In Carthage, Missouri, a plant has been built by Changing World Technologies (CWT) to convert the turkey offal waste refuse produced by a large food processing plant into diesel oil, gaseous fuels, low-grade thermal energy and fertilizer products. The CWT hydrothermal process operates as an essentially closed system with minimal emissions avoiding odor problems from handling and gives products free from pathogens. The oil itself is at the same time free from fossil carbon and relatively clean burning in engines. In this study, Life Cycle Assessment has been used to investigate the overall environmental performance of the process. The environmental performance of this route for production of diesel oil is compared to the traditional diesel oil refining process.

## KEY WORDS

Food industry, Diesel oil, Hydrothermal processing, Life cycle assessment.

# Introduction

Large flows of material processed by food industry are not converted into marketable food products. These materials, a biological feedstock recourse, are today in many cases considered waste to be land filled or reused in lower grade rendering applications. Even if utilized, handling and processing of this kind of materials are often troubled by odor. There can be market resistance to some of the conversion products, caused by perceived risks for spreading of pathogens and contaminants; the discussion on the Mad Cow diseases has emphasized this problem. Recovered products are sometimes of low market value (as is often the case with compost products).

It is possible to incinerate this kind of organic wastes, thereby eliminate the risk of spreading pathogens, but water content makes it a troublesome fuel. Processes to convert organic waste into liquid fuels have been studied earlier, see e.g. the review given in [1], but often hampered by low converting grade or low energy efficiency.

The hydrothermal conversion process studied in this paper has been designed to overcome some of these problems. The technology has been developed by Changing World Technology [2] and tested in a pilot plant in Pennsylvania. A full scale commercial plan has now been constructed to handle the turkey offal from a Con Agra plant in Carthage, Missouri. The process is described in [3], [4] and a popular overview is given in [5]. This study gives a preliminary environmental system evaluation of the Carthage hydrothermal conversion process, based on the information given in [3] and [4].

# The Hydrothermal Processing Plant in Carthage

The hydrothermal conversion process is briefly outlined in Figure 1. Please, refer to [3], [4] and [5] for further details. The process is divided into two steps. In the first stage the feed is pulped into slurry and pumped and heated to the reaction temperature (200-300 C). The solids are separated and the liquid flashed to separate water. The non aqueous phase is further processed by pumping and heat treatment in a second stage reactor (around 500 C). From the first stage are recovered a solid (minerals) and liquid phase, both containing nitrogen and possible to use for fertilizing purposes. From the second stage fuel gas, carbon and diesel oil are recovered. There are no direct emissions to the atmosphere from the hydrothermal process itself. The fuel gas is used for the internal heat needs. The minerals, the liquid containing nitrogen, the carbon and the diesel oil are all marketable products, but in this preliminary environmental evaluation only the oil has been considered. The oil is dominated by straight hydrocarbons with a chain length between 15 and 20, in the shorter range of conventional diesel oil [3]

# Environmental Systems Model

Two benefits of using hydrothermal conversion of food industry waste can be identified immediately: fewer odors from open processing and transport of non-processed organic waste and sterilized process outputs minimizing risks for spreading of pathogens.

In striving towards increased eco-efficiency in society, today it is widely recognized that an activity must bear the burden not only of direct emissions from the activity but also from all directly and indirectly related activities brought on by its existence. This 'life cycle thinking' has stimulated the development of tools to study the total life cycle environmental impact of products or services. Life cycle assessment (LCA) is a structured way to calculate and evaluate, quantitatively, the environmental load caused by a product or a service during all phases of its life cycle; the environmental impact from "cradle to grave". In an LCA, extraction and transports of raw materials, upgrading of raw materials, actual production and use of the product, necessary energy transformations, waste collection and treatment, etc., are studied in order to determine the total life cycle impact.

In this study, a life cycle approach has been used for a preliminary evaluation of the hydrothermal process in Carthage as waste handling method for food industry organic wastes. An overview of the systems model is given in Figure 2. The activities are briefly described below.

The CWT TP Carthage box describes the plant in Carthage using data from the process simulation use to design the plant, given in [3], [4]. Inflows per day to the process are 191 metric tonnes of wet turkey offal, 3.0 tonnes of sulfuric acid and 91.2 MJ of grid electricity. Outflows per day from the process are 2506 GJ diesel oil, 274 GJ fuel gas, 30.6 tonnes liquid nitrogen fertilizer, 7.5 tonnes mineral fertilizer, 6.1 tonnes carbon and

79.9 $m^3$ waste water. Of the outflows the use of the two fertilizer products and the carbon has not been followed downstream further than transports of the products from the plant.

Sulfuric acid is assumed to be produced from a mix of mined virgin sulfur (60%) and sulfur from desulphurization of oil at refineries (40%) [6]. The later form of sulfur has been considered a residual product, and no environmental impacts from the crude oil processing have been included. Sulfuric acid production is an exothermic process, creating a large amount of surplus heat. No beneficial use of this heat has been included. The grid electricity is described as coal condensing power [7] with a grid loss of 9%. This does not describe the actual grid electricity in Carthage, Missouri, but can be seen as a worst case scenario.

The fuel gas produced is a mixture of methane, carbon monoxide, carbon dioxide and low molecular-weight hydrocarbons. The fuel gas is used internally, covering the heat need of the hydrothermal process. The plant is predicted to generate a surplus of fuel gas, but here all gas is assumed to be used internally. Again this can be seen as a worst case scenario. The combustion of the fuel gas has been described by emission factors for combustion of LPG [8], but the carbon dioxide has been regarded as of biologic and not fossil origin.

The outflows of fertilizers and carbon represent useful and marketable products. However, no system expansion has been made to take into account the benefits from these products. Transport of these products to use has been included as a 250 km transport with a light truck (tailpipe emissions [9] and environmental impacts from diesel oil production [10] have been included). The waste water is sent to a municipal waste water treatment plant. The environmental impacts from the waste water treatment have not been included in this preliminary evaluation.

The thermal conversion diesel oil acts as a drop in substitute for conventional diesel oil. In the model this flow is used to generate the avoided emissions from production of an equivalent amount of conventional diesel oil production based on energy content [10]. This serves to give an understanding of the magnitude of the environmental impacts caused by hydrothermal conversion of the turkey wastes. The diesel oil from the hydrothermal conversion process has a composition that will probably give a cleaner combustion compared to conventional diesel oil, and its use will not generate fossil carbon dioxide. Neither of these benefits has been included in the present study.

## Results and Discussion

The summarized emissions from the activities described in the environmental systems model have been characterized into global warming potential and acidification potential [12]. To better understand magnitudes, the characterized impacts of the hydrothermal conversion process have been compared to the impacts from conventional diesel oil production (shown as bars in negative direction)..

In Figure 3 the global warming potential for the different activates involved are shown. The electricity production is clearly dominating the impact. An efficient design of the process to minimize electricity use is thus important. Note that the global warming potential from electricity is a worst case scenario; all electricity used is modeled as coal condensing power.

Even with this worst case scenario the total global warming potential for the hydrothermal conversion processing is smaller when compared to the impacts created by conventional production of the equivalent amount of diesel oil (based on energy contents). The hydrothermal conversion process thus comes out beneficial regarding global warming in a systems perspective.

In Figure 4 the acidification potential are shown, and the outcome is similar to that of the global warming characterization, but the transport of products from the hydrothermal process have an increased relative impact. The use of these products (nitrogen fertilizers, coal powder) has not been studied further, but the result emphasis that use for these products should preferably be found locally, to minimize transports.

The outflows from the hydrothermal process are sterile. The process conditions are such that even infectious materials like prions can be expected to be destroyed.

It should be noted that the environmental impacts from generating the turkey offal has not been included in the study, but allocated to the production of turkey food items. The results from this study does not implicate that poultry is a better way to produce diesel, it only discusses hydrothermal conversion as a way to handle waste from food processing industry.

The environmental systems performance of hydrothermal conversion of organic waste should be studied further to describe the energy system in detail and to include the fertilizer and carbon products in the investigated system.

## CONCLUSIONS

1. Hydrothermal processing of turkey offal into diesel oil comes out beneficial in a preliminary environmental evaluation.

2. Two issues important for the environmental performance of the process are to use electricity in an efficient manner within the process and to find use for products as locally as possible.

3. For a total evaluation it is important to further investigate the use of all products from the process and to refine the environmental model of the energy supply to the process.

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# FIGURES

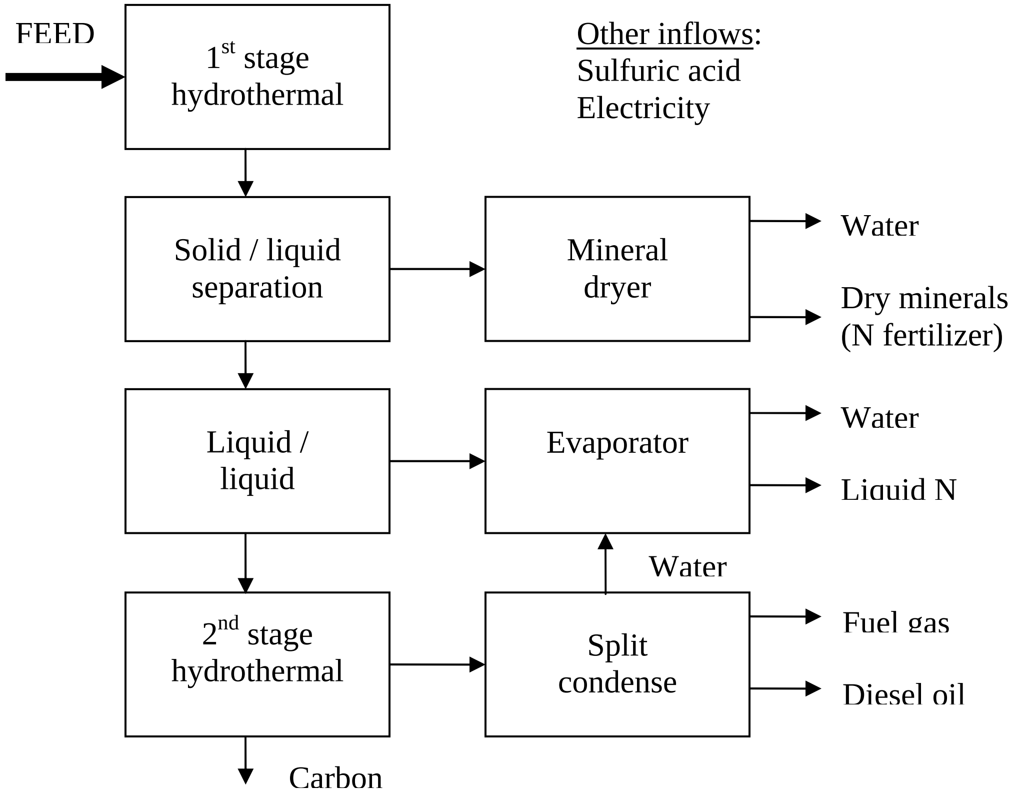


**FIGURE 1 – OUTLINE OF THE HYDROTHERMAL CONVERSION PROCESSING OF TURKEY OFFAL INTO DIESEL OIL, ADAPTED FROM [3],[4]**

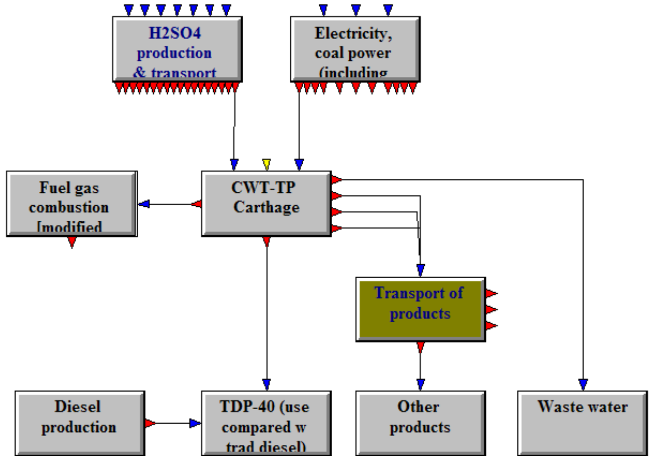

Figure 2 – activiteis in the study of the hydrothermal processing of turkey offal into diesel oil (see text for details)

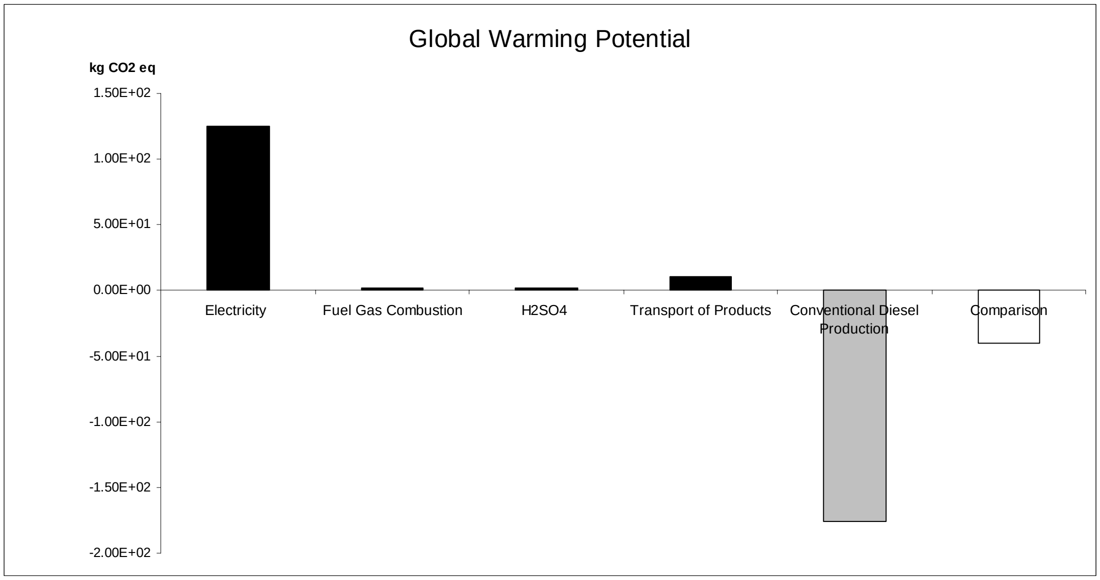


**FIGURE 3 – GLOBAL WARMING POTENTIAL CREATED BY THE ACTIVITEIS IN THE PROCESS TREE [KG CARBON DIOXIDE EQUIVALENTS PER DRY WET OF TURKEY WASTE]**

**THE GLOBAL WARMING POTENTIAL GENERATED BY USING THE HYDROTHERMAL PROCESSING IS SHOWN AS BARS WITH POSITIVE SIGN. THE GLOBAL WARMING POTENTIAL OF CONVENTIONAL PRODUCTION OF THE EQUIVALENT AMOUNT OF DIESEL OIL IS SHOWN AS A BAR WITH NEGATIVE SIGN FOR THE SAKE OF COMPARISON. THE TOTAL OF ALL BARS IS SHOWN AS THE BAR WITH THE DENOTAITION 'COMPARISON'. THIS VALUE IS NEGATIVE, SHOWING THAT THE GLOBAL WARMING POTENTIAL CREATED BY CONVENTIONAL DIESEL OIL PROCUTIONS IS LAGER COMPARED TO WHAT IS CREATED BY THE HYDROTHERMAL PROCESS**

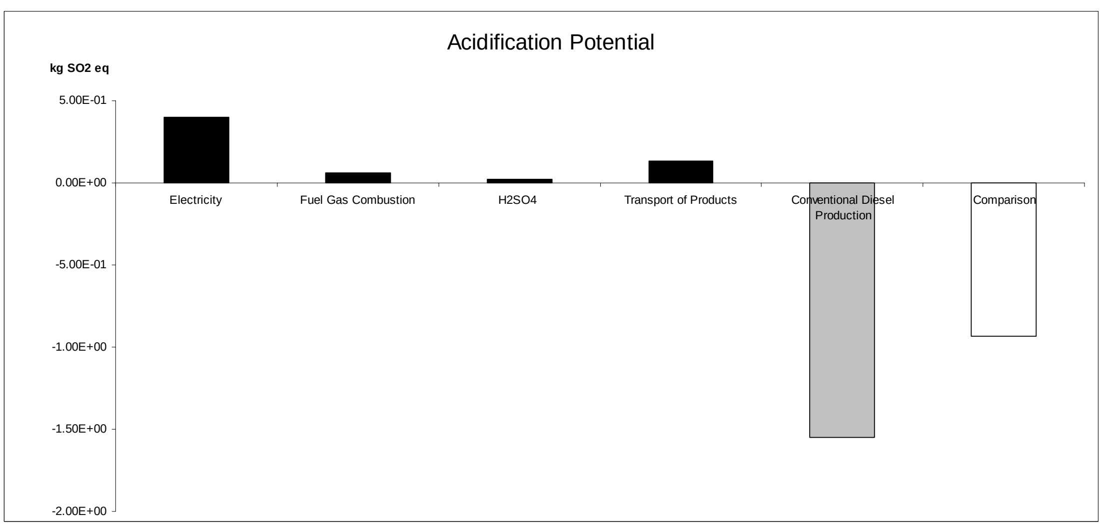


**FIGURE 4 – ACIDIFICATION POTENTIAL CREATED BY THE ACTIVITEIS IN THE PROCESS TREE [KG SULFUR DIOXIDE EQUIVALENTS PER WET TON OF TURKEY WASTE]**

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**COMPARISON. THE TOTAL OF ALL BARS IS SHOWN AS THE BAR WITH THE DENOTAITION 'COMPARISON'. THIS VALUE IS NEGATIVE, SHOWING THAT THE ACIDIFICATION POTENTIAL CREATED BY CONVENTIONAL DIESEL OIL PROCUTIONS IS LAGER COMPARED TO WHAT IS CREATED BY THE HYDROTHERMAL PROCESS**

# Appendix 3- CWT Capital and Operating Expenses

OPERATING EXPENDITURES:

**Variable Expenses**: Plant Water and Electricity Consumables
- Bottled Gases
- Bulk Nitrogen
- Plant Utility Gas

**Fixed Expenses**: Plant Payroll (Hourly)
Plant Salaries (Salary)
Plant Burden
- Workers Comp
- Benefits
- Unemployment (State & Federal)
- Social Security
- Medicare

Taxes and Licenses
Transportation
O&M Contractor Services & Materials
Rentals (Lifts, Trailers, Land, etc.)
Insurance
Chemicals
Commissioning
License Fees
Employee Expenses (Shoes, travel, entertainment, training, etc.)

**Raw Materials**: Waste By-Product Feedstock (incl. diversions and transportation)

CAPITAL EXPENDITURES:

Grant funding provided through the grant was applied to support the following capital expenditure categories during plant optimization.

| **Capital Items** | **Description** |
|---|---|
| Fatty Acids | Split fatty acids for a higher revenue stream |
| Coker | Modification to improve Coker efficiencies and operations |
| Steam Clean Up/Odor Control | Modifications to capture VOCs in flash steam and control emissions from various processes thru-to TOX |
| Material Separation | Plant modification and installation of larger Centrifuges for better yields and material separation |
| Trailers | Secure additional trailers to transport material from the Butterball plant to the TCP facility. |
| Steam Capacity | Install larger boiler and related piping needed due to additional heat requirements because of modifications. |

| | |
|---|---|
| Grease Tank | Additional storage capacity to increase ability to receive more grease |
| Vacom | Modifications to Water Clean-up System |
| pH Adjustment | Replacement of carbon steel piping with stainless steel due to acid addition to facilitate material separation |
| Reactor and Vessel Replacement Strategy | Replacement of carbon vessels to stainless due to corrosion |
| Redundancy | Purchase and install redundant equipment to improve efficiencies and up time |
| Receiver Area Modifications | Modifications and equipment added to increase variety of materials received and improvement of pulping and grading process |
| Miscellaneous | Various small plant modifications and projects to improve plant operations, products, and thru-puts |

## CAPEX ITEMS

| PROJ # | **Project Description** |
|---|---|
| **A** | **Fatty Acids** |
| A1 | Distillation Column |
| **B** | **Coker** |
| B1A | R-460 to R-470 piping and control valve |
| B1B | Additional Coker Modifications due to first test run |
| B1C | Additional Coker Modifications due to second test run |
| B2 | TI & sample point on R-470 discharge |
| B3 | R-470 heater control logic |
| B4 | A-476 condensate recovery |
| B5 | V-600 water take-off mods |
| B6 | V-600 water discharge destination |
| B7 | Modifications to Coker System to Increase Temperature & Pressure |
| B8 | At P-605, at E-620, Modify Piping to LV-2131 |
| **C** | **Steam Clean-up/Odor Control** |
| C1 | Sparge to V-140 |

C2 E-535 cut and cap and re-slope line to V-260
C3 V-260 let down line and valve to LP steam header
C4 V-260 line and valve, clean steam make-up
C5 Condensate pot, pumping trap to T-550 and T-570. V-800 TO T-840 PIPING.
C6 E-530 level control to LP condensate
C7 E-990 trim condenser system
C8 Recycle and produced water header interconnect.
C9 Nalco chemical inject point.
C10 Odor control / biofilter ducting for original centrifuges
C11 Odor control / biofilter ducting for new centrifuges
C12 Bypass Around Flame Arrester to Odor Incinerator
C13 Modifications to Odor Control Header. Relocating T-430, 710A/B, 860 to suction of blower
C14 Install Knock Out Drum at Incinerator
C15 Additional Modifications to Incinerator
C16 Additional Modifications to V-800 Steam Condenser
C17 Additional Modifications to Odor Control System
C18 At T-570, Install pH Control System
C19 Installation of Scrubber for Process Building
C20 Install Upgrade E-535, High Pressure Process Steam Boiler
C21 At V-1000, Connect Vent Scrubber
C22 At C-280, C-285, and Sweco, Connect Vent Line to Scrubber
C23 At PV-3040B, Install Steam Trap Station
C24 Connect Receiving Area Ventilation System to Scrubber
C25 At Odor Control Skid, Modify Piping per Instructions
C26 At E-530, Add Check Valves for Steam Clean-up
C27 Install Tarp on Dump Trailers per DNR
C28 At Process Building Scrubber, Add Vapor
C29 Upgrade Thermal Oxidizer per DNR
C30 At T-860, at E-850, Upgrade Heat Exchanger
C31 Increase Odor Control Blower Capacity and Modify Piping
C32 Add Ozone System to Process Building Scrubber
C33 Containment System for Mineral Tote Handling
C34 Restore Bio-Filter to Specifications
C35 At Receiving Area Scrubber, Repair and Modify per Instructions
C36 At T-120A, Contain Thief Hatches and Route to Odor Control Skid
C37 At Tank Farm, Modify Piping and Add B-1040E/F
C38 At Scrubber, Install 90' Stack

**D Material Separation - Throughput/Capacity**

D1 Liquid/Solid centrifuge purchase.
D2 Liquid/Liquid purchase.
D3A&B Installation for Liquid/Solid
D4A Liquid/Liquid installation.
D4B Structural Installation for Liquid/Liquid.
D5 Processing Building Modification [structural / civil / mechanical]

D6 A-315 modification.
D7 Dryer removal.
D8A Slop Tank purchase
D8B Piping/Instrumentation/Insulation/Pad for slop tank
D9 Sump pump upgrade & tie-in to slop tank
D10 Increase MCC Capacity due to additional centrifuge.
D11 Replace E-210/220/221
D12 Install Sweco Separator
D13 Steam Sparge to R-250
D14 Purchase and Installation of Second Liquid/Solid Centrifuge
D15 Reutilization of V-265 for Bone Removal
D16 Relocate Centrifuge Control Panel Outside of Explosion Proof Area
D17 Upgrade P-400 Pumps
D18 Add Multi-port Valve at Discharge of P-200
D19 At P-125, Install Flow Meter
D20 At V-265, at LV-2063, Install Y Strainer for Rubber Removal
D21 At P-200, Upgrade Knife Gate Valves
D22 At P-275 and P-200, Run Produced Water for Clean-out Purposes
D23 At E-390A/B, Upgrade Steam Traps
D24 At E-210, Modify Piping for Co-current Flow
D25 At Liquid/ Liquid Centrifuges, Modify Piping for Water Polishing
D26 At E-390A/B, Modify Piping for Series Flow
D27 At P-125, Install Flow Meter
D28 At P-200, Install Hydracell Pump for Testing

**E Trailers – Capacity**
E1 Additional trailers with drains
E2 Tankers Blood/DAF
E3 Flatbed (MDM)
E4 Additional trailers Phase 2

**F Steam Capacity**
F1 Utility boiler upgrade
F2 Additional Steam tracing and insulation

**G Grease Tank**
G1 Blood / Water Tank [T-027]
G1A Grease tank becomes blood tank, tie blood line to Grease Tank D-158. Relocate grease pump
G1B Possible second storage tank or purchase another blood/DAF tanker.
G1C Install flow meter to control rate to pulpers
G2 New Grease Tank
G2A Include flow metering to pulper.

**H Vacom**
H1 Check Vacom & Brass compatibility for 6 S.U. pH acid.

| | |
|---|---|
| H2 | Vacom modifications for efficiency and capacity |
| H3 | P-106 Upgrade (Evaporator Effluent Sump Pump) |
| H4 | Installation of cooling water to effluent cooler (E-101). |
| H5 | Installation of Caustic Tower |
| H6 | Upgrade B-101, Vacom Blower |
| H7 | Add Desuperheater to Vacom System |
| H8 | Upgrade P-102, Vacom Recirculation Pump |
| H9 | Additional Piping Changes on Vacom |
| H10 | At E-102, Add Air Vents |
| H11 | At Vacom, at P-111, Add Metering Pump and relocate pH Probe |
| **I** | **pH Adjustment** |
| I1 | 1. pH probe and I.O. control at pulpers |
| I2 | 2. Two (2) pH probes and I.O. control at V-140 |
| I3 | 3. pH probe (relocation from V-805) and control at Vacom |
| I4 | 4. New acid pumps and housing for V-140 |
| I5 | 5. V-140 to E-210 piping |
| I6 | 6. P-200 A/B stainless steel upgrades |
| I7 | 7. P-200 Elastomer Selection |
| I8 | New high pressure acid pump for R-250 |
| I9 | At P-200 discharge, install acid injection point and increase tubing size to 1" |
| I10 | At V-140, modify pH Probe Location |
| I11 | Set-up for Phosphoric Acid Trial |
| **J** | **Reactor and Vessel Replacement Strategy** |
| J1-ST | R-250 residence time (inlet pipe & mixer) |
| J2-ST | V-265 bypass for liquor |
| J3-ST | Replacement of R-250 steady bearing |
| J1-LT | Replacement of R-250, V-260, V-265 and V-270 pressure vessels |
| **K** | **Redundancy** |
| K1 | P-275 B purchase and installation |
| **L** | **Receiver Area Modifications** |
| L1 | Pre-breaker/Installation |
| L2 | Feathers Pretreatment |
| L3A | Fine Grinder Bypass Piping |
| L3B | Purchase/Installation of Large Fine Grinder and Modification of Small Fine Grinders |
| L4 | Install Claflin or Other grinder assembly |
| L5 | Addition of Access Platforms in Receiving |
| L6 | Rebuilt Rotors and Stators for Pulpers |
| L7 | Upgrade Mixer on T-120A |
| L8 | Additional Crusher and Associated Equipment |
| L9 | Relocate Blood Unloading Station |
| L10 | In Receiving Area, Install Sump Pump |

L11 At Additional Crusher Equipment, Temporary Manpower for Operations
L12 At Receiving Area, Install Trailer and Area Washdown Stations
L13 At T-027, Upgrade Transfer Pump and Route to V-140
L14 At T-120A, Install Heat Exchanger Inside Tank

**M Miscellaneous**

M1 Yield measurement [additional meters?]
M2 DCS upgrade / mods
M3 HAZOP schedule / planning
M4 Handle rail spur deliveries and shipping deliveries.
M5 P-125 to V-140 (P-125 to T-120A - Recirc) piping **
M6 Suction strainers in V-140 for P-200 A/B **
M7 Suction strainer in T-350 for P-360 A/B **
M8 Suction modifications in T-710A/B
M9 Butterball modification - Belt conveyor for mixing
M10 Installation of magnet in receiving
M11 Recirculation line between pulper tanks
M12 Piping and Installation of P-125C (Recirculation Pump from T-120A to Pulper)
M13 Conversion of E-135 from 300# to 50# Waste Steam
M14 Various Modifications and Changes
M15 V-260 to V-265 Let Down Valve
M16 KPS Support for Engineering Design and Operations
M17 Pulper Rotor and Stator Upgrade
M18 Modify Steam Piping on V-381
M19 R-250 Let Down Valve
M20 Auto Samplers
M21 Additional Modifications at Pulpers
M22 Additional Piping Modification at T-120A
M23 Upgrade P-125C Pump
M24 Installation of Drains and Trenchers for Containment Purposes
M25 Redesign R-250 discharge to decrease velocity in piping
M26 Additional Building Heaters
M27 Install Fiber Optic Line
M28 Remove and Reutilize MT-100A/B
M29 Install Change Trailer per Kim Anderson
M30 Modify Piping at V-381 for Moisture Control
M31 At Receiving Dock, Install Containments to Collect Blood From Trailers
M32 Relocate East Fence and Add Parking Area
M33 At R-250, Upgrade Let Down Valve
M34 At P-400, Add Piping to T-120C, T860
M35 At V-260, Replace Piping with Lined Pipe
M36 At V-140, Route LP Steam form R-250 to V-140
M37 Building and Grounds, Repair Pavement
M38 At R-250, Upgrade Let Down Valve W/CCI Valve
M39 At V-800, Modify Recirculation Loop for Additional Cooling
M40 At P-705 and P-715, Tie Suctions Together

M41 At Tank Farm, Add First Flush System