[1]CONVERTING TURKEY OFFAL INTO BIO-DERIVED HYDROCARBON OIL WITH THE CWT THERMAL PROCESS

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The CWT Thermal Process (CWT-TP) converts organic materials into clean fuels, fertilizers, and specialty chemicals. Waste, by-products, or low-grade organic material go into the CWT-TP process and three or more separate streams come out: a clean fuel-gas, light organic liquid, and solid products that can be used as fuel, fertilizer, or adsorbent carbon. This paper will describe the CWT-TP process, compare it to pyrolysis and gasification, and present results from the 1st commercial CWT-TP plant located in Carthage, MO processing turkey offal and waste grease into a medium Btu fuel gas, oil, carbon and fertilizer. The plant is owned and operated by Renewable Environmental Solutions, LLC (RES), a joint venture between ConAgra Foods Inc. and Changing World Technologies, Inc. (CWT).

Initial CWT-TP process work was conducted in small batch reactors, scaled-up to a 1 t/d continuous unit, then a 7 t/d continuous pilot plant, and finally to a 200 t/d commercial unit. The CWT-TP process is designed to handle almost any imaginable waste, including turkey offal, tires, plastic bottles, harbor-dredged sediment, old computers, municipal sewage sludge, cornstalks, paper-pulp effluent, infectious medical waste, and oil-refinery residues (refs. 1-4). Development work for the agricultural and animal waste industry has progressed fastest (to commercial scale) because there was an end-user champion that decided to address its waste disposal issues in a proactive manner.

THE CWT-TP PROCESS

The CWT-TP process consists of three main steps: 1) pulping into a water slurry and heating of the feedstock under pressure to the 1st stage reaction temperature, 2) flashing the slurry to a lower pressure and separating the 1st stage oil from water, and 3) heating the 1st stage oil to higher temperature to crack the oil into light hydrocarbon leaving a solid product. The process temperatures for the initial slurry phase of processing are between about 200^{o}C to 300^{o}C (392^{o}F to 572^{o}F). For the second processing stage the temperatures are near 500^{o}C (932^{o}F).

The individual steps of the CWT-TP process have been well developed in other industries such as petroleum processing. The CWT-TP plant looks like a small refinery operation. Photographs of the 7 ton-per-day pilot plant unit located in Philadelphia are shown in Figures 1 and 2. The final scale-up data for the first commercial plant in Carthage, MO were obtained at this plant site. Ample quantities of product samples were generated from the plant that allowed product quality evaluations/experiments to be performed. Product evaluations were required to assign values to

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products for initial plant financial projections. Based on the favorable financial projections for the CWT-TP process, development has been proceeding at an accelerated pace.

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Figure 1. CWT-TP 7 t/d Pilot Plant

Figure 2. Pilot Plant Flash Vessels

There are no process discharges to the atmosphere from the CWT-TP plant. The only gaseous product is a medium to high Btu fuel-gas that is used for process heat for the plant, or as fuel for a boiler or turbine. Emissions from the turbine (in the case of the pilot plant) were independently verified to be in compliance with the Clean Air Act. The oil product is typically a light hydrocarbon similar to diesel fuel. It can be easily used for heating oil, or converted into higher value products. The solid products are a carbon and a fertilizer that is rich in micronutrients.

The products leave the CWT-TP unit at about 100°C (212^{o}F) after heat recovery. With full heat recovery, the overall energy efficiency can be above 85% based on the heating value of the products and the dry feedstock.

To understand the CWT-TP process it is necessary to remember that many of the materials in everyday life are polymers, i.e. are made up of many small molecules that have been strung together in a chain. The CWT-TP process breaks down these polymers nearly to their smallest unit.

On the molecular level the individual links in the polymer chain are held together with chemical bonds. The CWT-TP process breaks these bonds, and the two halves of the broken bond are either incorporated into the molecule or attach to hydrogen and hydroxide donated by the water slurry. After the flash step they separate from the water just like oil or charcoal would.

200 T/D COMMERCIAL PLANT IN CARTHAGE, MO

An operating plant based on the CWT-TP process has been constructed in Carthage, MO next to a turkey-processing slaughterhouse. The CWT-TP facility processes approximately 200 t/d of turkey offal and grease continuously, 7 days a week. Included in the feedstock are the offal, bones, heads, feet, blood and feathers from the turkeys. The plant produces about 500 bbl/d of

API 40+ oil together with about 7 t/d of carbon, 8 t/d of mineral fertilizer, 12 t/d of a nitrogen-rich fertilizer, and a medium Btu gas that is used internally.

Figure 3. Carthage Plant

Figure 4. Oil Storage Tanks at Carthage

Product Oil – API 40+

The product oil produced from the Carthage, MO plant is a high value crude oil that may be compared to diesel fuel. Both diesel fuel and TDP-40 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. TDP-40, and other bio-derived fuels such as bio-diesel, 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 will cause some differences in combustion characteristics that can translate into improvements (reductions) in combustion pollutant emissions.

Table 1. Distillation (D-86) of Product Oil

Recovery, Volume Percent	Temperature, ^{o}C (^{o}F)
I.B.P.	52 (125)
10	71 (160)
20	104 (220)
30	138 (280)
40	168 (335)
50	204 (400)
60	232 (450)
70	260 (500)
80	304 (580)
90	349 (660)
Total Recovery, Vol. Pct.	95%

A common method of classification for petroleum is the PONA system – PONA is an acronym for paraffins, olefins, naphthenes, and aromatics. Paraffins are straight-chain or branched hydrocarbons in which there are no double or triple bonds between carbon atoms. Olefins are similar to paraffins, but they contain at least one multiple bond in their chemical structure. Naphthenes are saturated hydrocarbons, just like paraffins, but they incorporate a ring of carbon atoms into their chemical structure. Aromatics contain a benzene ring in their structure. A PONA classification of the TDP 40 oil is shown below in Table 2.

Table 2. Classification of TDP-40 Oil by PONA

PONA, wt%	D-5443 method
Paraffins	22
Olefins	14
Naphthenes	3
Aromatics	6
C14/C14+	55
TOTAL	100

The oil classification is useful for predicting fuel performance when used in combustion, e.g. as a diesel fuel replacement. The classification is also a useful prediction for fuel refiners or blenders in determining product distribution in a refinery or specialty chemical plant.

The product oil classification distribution resembles a typical delayed coker output. The output contains light and heavy napthas, a kerosene, and a gas oil fraction. There are essentially no heavy fuel oils, tars, asphaltenes, or waxes present.

Solid Products, Carbon and Minerals

The fixed carbon solids produced by the CWT thermal process have multiple uses – as a filter, a fuel source and a fertilizer. The highest value for the carbon products would be as activated carbon to be used in wastewater cleanup as a filter medium. The lowest value use of the carbon product is as a fuel. With a heating value of approximately 27.9 MJ/kg (12,000 Btu/lb, pure carbon is 14,093 Btu/lb, ref. 5) the carbon product could be substituted for coal use. The fixed carbon production from the process will assist in sequestering CO_2, a global greenhouse gas that contributes to global warming.

The mineral/micronutrients that comprise the typical mineral mix from the Carthage, MO plant are shown in Table 3. Of major interest are the N, P, K elements that comprise the fertilizer. The calcium in the mix comes from the bones of the animals. The N, P, K, Ca components represent nearly 80% of the total fertilizer. The mineral product acts as a naturally self-limiting, slow release soil amendment that puts the essential nutrients back in the soil. The minerals will help to rebalance macronutrients and replace depleted essential micronutrients in the soil, encouraging healthy plant growth and development.

Table 3. Typical Mineral Mix From Plant

Mineral/Micronutrient	Concentration, kg/tonne (lbs/ton)
Nitrogen (N)	60 (120)
Phosphorus (P)	380 (760)
Potassium (K)	10 (20)
Calcium	340 (680)
Chloride	2 (4)
Copper	0.1 (0.2)
Iron	2 (4)
Magnesium	13 (26)
Manganese	0.2 (0.4)
Silicon	9 (18)
Sodium	9 (18)
Sulfur	6 (12)
Zinc	0.8 (1.6)
Fixed Carbon	20 (40)
Organic Matter	147.9 (295.8)
Total	1,000 (2,000)

CWT-TP COMPARED TO PYROLYSIS AND GASIFICATION

Pyrolysis and gasification are alternative ways that can, and have been used to convert organic wastes and by-products into fuels and chemicals. The basic principal of these, and of the CWT-TP process, is that polymeric materials break down at high temperatures. This is just an extension of the every day observation that meat becomes tender after cooking in a stew, or that wood logs in a fireplace burn to form a gaseous flame, some tar-like deposits in the flue, and a solid charcoal.

Pyrolysis is the process of heating the feedstock in the absence of air. A hot fuel-gas and a char are produced. Part of the fuel-gas can usually be condensed into oil. Gasification involves the use of a fraction of the air or oxygen that would be required to completely burn the feedstock. A hot, voluminous fuel-gas is produced. Both processes break down the polymer chains just as the CWT-TP does, with high temperatures.

The difference between the CWT-TP and the other two processes is the ability of the CWT-TP to work well with wet feedstocks, the ease of separating the products, and the low temperature of the gaseous product.

Processing the feedstock in water slurry during the 1st stage is central to the CWT-TP process for ease of handling, for uniform heating of the slurry, and to make water available to depolymerize the organics to prepare them for chemical reforming. This is the key to making valuable products and ones that can be easily separated from water.

The low temperature of the gaseous products makes handling easy and avoids the energy loss often experienced for gas cleanup prior to use as gas turbine fuel. As well, the fuel gas does not contain alkali metals such as sodium and potassium that are very detrimental to gas turbines.

FUEL-GAS CHARACTERISTICS

Many years of work on gasification, pyrolysis, and the CWT-TP processes show that the fuel-gases produced by heating organic material consist of decomposition products such as CO_2, CO, H_2O, H_2, together with light hydrocarbons and organics such as methane and methanol (ref. 6). The amount of oxygenated gases depends on the oxygen content of the feedstock. The value of the gas phase as a fuel-gas for gas turbines or other combustion equipment depends on several characteristics including: 1) the heating value of the gases, 2) the temperature of the gases, 3) the alkali metal content in the gases, and 4) the extent of contamination of the gases with nitrogen and sulfur compounds.

FUEL-GAS HEATING VALUE

The heating value of the fuel-gases for most reported gasification processes ranges from about 3.7 MJ/m^3 to 19 MJ/m^3 (100 Btu/ft^3 to 500 Btu/ft^3). For reference, pipeline-grade natural gas is about 37 MJ/m^3 (1000 Btu/ft^3). Published work shows that fuel-gases with more than 3.7 MJ/m^3 (100 Btu/ft^3) can be successfully burned in gas turbines, boilers, and kilns. The heating value is given here in terms of energy per unit volume. This is for the very practical reason that the fuel-gases must be transported to the combustion equipment, and transportation of voluminous quantities of low calorific value gases can be very expensive and inefficient.

The factor that has the biggest impact in determining the heating value of the fuel-gas from most gasifiers is the concentration of nitrogen in the gas. Nitrogen is blown into a gasification unit together with oxygen (generally as air) to partially burn the feedstock and raise its temperature. Air-blown gasifiers produce low heating value fuel-gases, while oxygen-blown gasifiers and pyrolysis units produce medium heating value fuel-gases.

The CWT-TP process does not use air or oxygen to provide the heat to drive the process, so the heating value of the CWT-TP fuel-gases is quite high. CWT-TP fuel-gases typically have measured heating values between 13.3 and 28.5 MJ/m^3 (350 and 750 Btu/ft^3). For feedstocks low in bound oxygen content, such as crude petroleum oil, heating values are near the upper range. For feedstocks with significant oxygen content, such as cellulose, the generated fuel gases are near the lower range of medium-heating-value fuels.

FUEL-GAS TEMPERATURE

The temperature of the fuel-gases is also important both because it strongly affects the volume of the gas, and because it represents a portion of the total energy in the fuel-gas. A fuel-gas produced at relatively low temperature (below about 100°C or 212°F), characteristic of the CWT-TP process, has only about half the volume of one produced at 450°C (842°F), which is typical of gasifiers.

For the low temperature CWT-TP fuel-gas, nearly 100% of the energy in the gas is in a chemical form (i.e. it is a fuel) instead of in a thermal form (i.e. it is a hot gas). For high temperature fuel-gas, a substantial portion of its total energy is lost if it must be cooled to prepare it for gas cleanup.

FUEL-GAS ALKALI METAL CONTAMINATION

Alkali metal compounds containing potassium and sodium (K and Na) can cause corrosive deposits (refs. 7 and 8) on turbine blades, so must be removed efficiently from most fuel-gases. Removal of alkali metal compounds from fuel-gases is a difficult process due to the small size of the alkali particles, which are typically sub-micron. With hot fuel-gases, removal is difficult, but the alternative of cooling the gas for easier removal represents a significant efficiency loss. This is not a problem for the CWT-TP fuel-gas because it is cool and contains no alkali metals.

FUEL-GAS SULFUR AND NITROGEN

The two main classes of contaminant species that can be found in all fuel-gases are the nitrogen gases and the sulfur gases. For most industrial combustion equipment, diatomic nitrogen (N_2) is not a problem. Diatomic nitrogen constitutes 79% of the air we breathe, so a little diatomic nitrogen in the fuel-gas does not constitute a detrimental emission potential. However, ammonia (NH_3) and other nitrogen-containing compounds in the fuel-gas can lead to the emission of the oxides of nitrogen (NOx) in the combustion product gases.

Ammonia is a potential product in all gasification, pyrolysis, and CWT-TP fuel-gases whenever protein materials are being processed. Proteins are collections of amino acids that contain small quantities of the amine group (NH_2) attached to a carbon atom. The nitrogen in amino acids would be the “fuel-nitrogen” for protein material if it were used directly as combustion fuel. A portion of these amine groups will become ammonia during the CWT-TP process, so can be released into the fuel-gas. The most common way to treat the fuel-gas to remove ammonia is to scrub it with water at modest temperature conditions (ref. 9). This can be done with the CWT-TP fuel-gas without loss of energy efficiency because of the relatively low temperature of the CWT-TP fuel-gases. Scrubbing the higher temperature fuel-gases from gasification processes significantly reduces energy efficiency.

There can also be sulfur in the feedstock to the CWT-TP. In the normal range of temperatures for the CWT-TP only a portion of the sulfur is released into the fuel-gas. Most of this sulfur is in the form of hydrogen sulfide (H_2S) that can be removed by an alkaline scrubbing of the fuel-gases. For feedstocks with a substantial component of organically-bound sulfur, such as Kraft black liquor from wood pulping for paper manufacture, a fuel-gas clean up similar to that for sour natural gas would be needed. Either approach to sulfur removal from the fuel-gases requires that the gas be at modest temperature, which is the case for the fuel-gas from the CWT-TP process, but not for pyrolysis and gasification processes.

ENERGY EFFICIENCY

Energy efficiency is one important measure of the performance of any process that converts waste materials into energy products. The CWT-TP is designed to do just this for many different kinds of feedstocks, including agricultural wastes, scrap tires, and waste plastics. The diagrams in Figures 5 and 6 show the material and energy balances for a CWT-TP plant designed to operate with a combination of turkey offal and grease as a feedstock.

The energy efficiency of the plant can be calculated in several ways depending on what aspect of performance is of interest. The energy efficiency that is probably of most interest is the energy

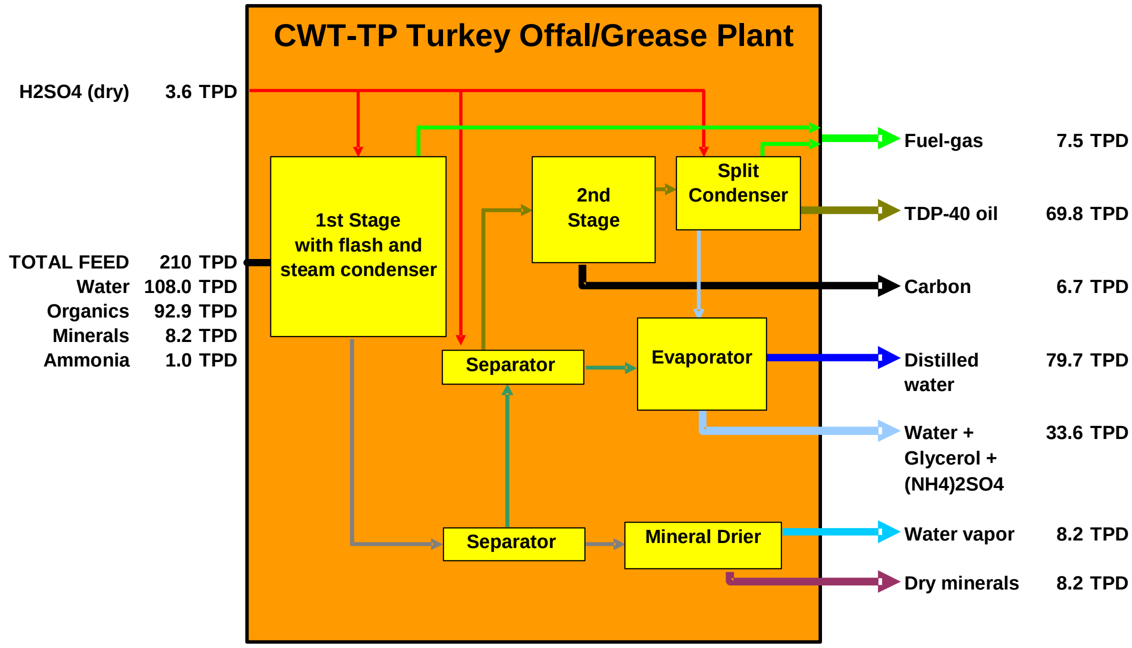

Figure 5. Material Balance Illustration

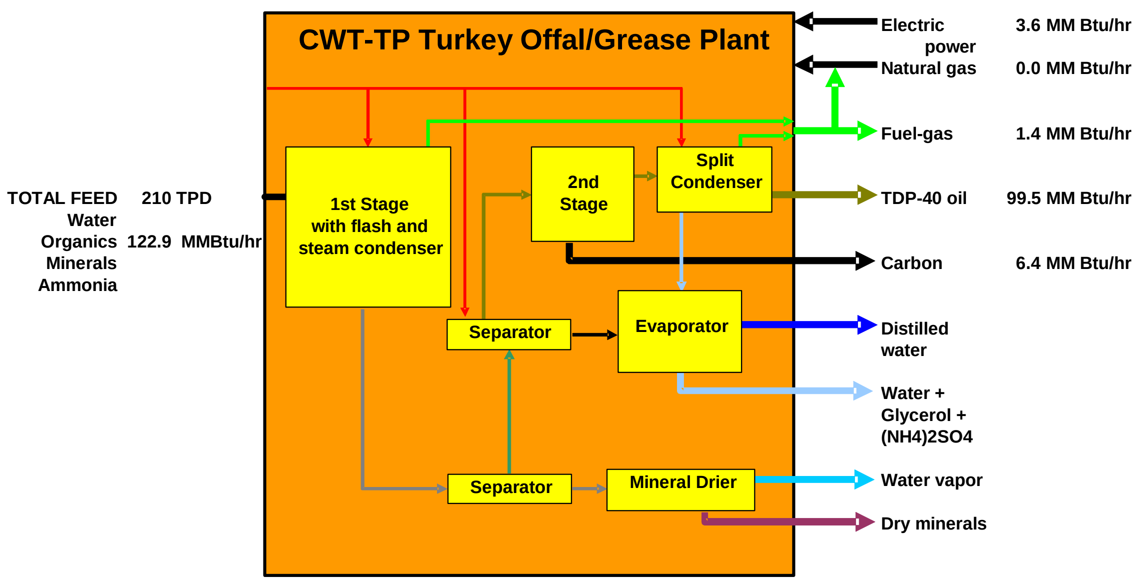

Figure 6. Energy Balance Illustration

in the combustible products that leave the plant divided by the total energy input. The energy input includes the energy in the dry feed, the electric power used, and any purchased natural gas that must be fired.

Energy efficiency for this design of the CWT-TP process is about 85%. Some of the CWT-TP fuel-gas must be used to operate the plant and, of course, pumps, motors, and some heaters require electric power.

The energy efficiency of the CWT-TP process is generally fairly high because most of the water that enters the plant leaves as a liquid rather than as water vapor. This is because the CWT-TP process is designed to use the steam that is generated internally to heat the incoming feedstock.

Energy efficiency is only one measure of the performance of the plant. For the CWT-TP plant shown in Figure 6, "economic" efficiency is more important. To achieve this, additional equipment is incorporated in the design to produce a saleable dry mineral product and a glycerol plus $(NH_4)_2SO_4$ product. A plant designed for a different feedstock, such as tires or plastics, would have less equipment, and even higher energy efficiency.

SUMMARY

The CWT-TP process treats a wide range of organic waste and by-product materials as well as coal and difficult crude oils to produce cleaner, higher value products. Using water as a medium improves both the process (including heat transfer, transport, and chemistry) and the selection of available industrial equipment. Water is also the key to the chemical reforming process because it produces in each product stream a range of products that readily separate from water. The process conditions are modest by industrial standards and the process is environmentally clean. Valuable fuels and specialty chemicals can be produced from low-grade feedstocks in an energy efficient way for on-site use or sale. The CWT-TP treats a wide range of organic waste and by-product materials to produce low temperature, alkali-free medium-heating-value fuel-gas. The nitrogen and sulfur compounds that can contaminate all fuel-gases can be efficiently removed from CWT-TP fuel-gases due to their inherent low temperature.

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