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CETC CANMET ENERGY TECHNOLOGY CENTRE

INDUSTRIAL INNOVATION

THE CETC SUPERCETANE™ TECHNOLOGY

CLEAN ENERGY TECHNOLOGIES

The production of diesel fuel from renewable sources is being pursued because of climate change, a desire to develop new markets for agricultural products and increasing petroleum prices. The production of biodiesel from vegetable oils and yellow grease via esterification processes has generated the most interest and business development. However, other technologies are nearing commercialization that can convert vegetable oils, waste greases, animal tallow and other feedstocks containing triglycerides and fatty acids to value added energy and chemical products. The CANMET Energy Technology Centre (CETC), Natural Resources Canada, has developed a novel technology that can convert these materials into a high cetane diesel fuel blending stock referred to as SUPERCETANE™.

Advantages of the CETC SUPERCETANE™ Technology

- Ability to process a wide variety of feedstocks, including high free fatty acid (FFA) materials.
- Production of high yields of CETC SUPERCETANE™ with a high cetane number (~ 100) and low sulphur content (less than 10 ppm S).
- The SUPERCETANE™ product is very stable. No storage stability problem.
- The SUPERCETANE™ product is fully compatible with petroleum-derived diesel fuels at all concentrations. No blending problem.
- Produces higher cetane diesel fuel than from esterification processes.
- Reductions in diesel exhaust emissions of NO_x, particulates, hydrocarbons and CO due to higher cetane value and higher hydrogen/carbon fuel ratio.
- Production of useable hydrocarbon co-products that are suited to petroleum refinery streams.

Process

The CETC process adapts a hydrotreating process using conventional petroleum refinery hardware and under proprietary operating conditions generates its cetane-enhancing product. See process schematic in Figure 1.

Several reactions occur in the process including hydrocracking (breaking apart of large molecules), hydrotreating (removal of oxygen), and hydrogenation (saturation of double bonds). The process employs a commercial refinery hydrotreating catalyst and hydrogen. The CETC technology has been used to successfully process a number of feedstocks including canola oil, soya oil, mustard seed oil, different grades of yellow greases and animal fats from the rendering industry, and tall oil (a by-product of the kraft pulping process). Yields of 85 – 93% (by volume) of SUPERCETANE™ were achieved. Table 1 gives the main characteristics of SUPERCETANE™ products obtained from several triglyceride-containing feedstocks. In addition, CETC has investigated feedstock pretreatment in order to process lower quality feedstocks such as restaurant trap grease (RTG). Properties of RTG-derived SUPERCETANE™ are given in Table 1.

CETC has recently constructed a 0.2-barrel/day process development unit (PDU) in order to produce large volumes of SUPERCETANE™ for engine and exhaust emission tests. The PDU complements a semi-pilot plant unit (700 mL tubular reactor) also located at CETC. Both units are used to continue process optimization. The SUPERCETANE™ process has also been successfully tested in a one-barrel/day hydrotreating pilot reactor at the CETC research facilities using depitched tall oil (DPTO) as feedstock. Approximately 3800 litres of SUPERCETANE™ was produced from DPTO for emission testing at Environment Canada in Ottawa, Ontario and for road tests with Canada Post in Vancouver, BC.

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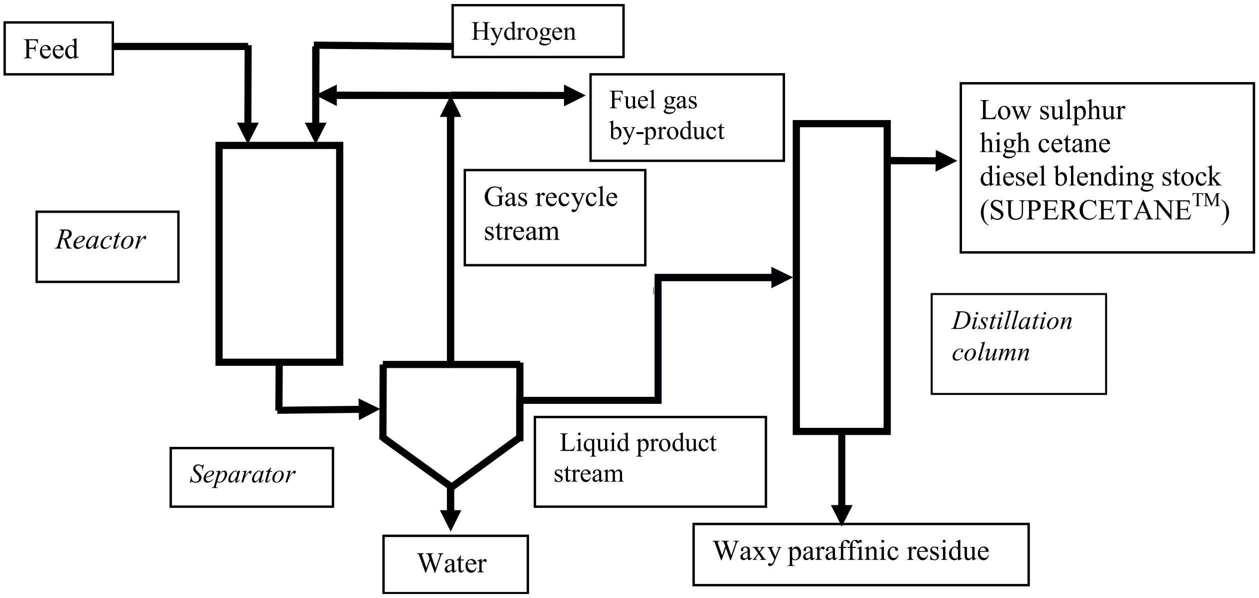

Product

The CETC process generates a hydrocarbon liquid with co-products being burner gas and water. No glycerol is formed in this process.

The hydrocarbon liquid can be distilled into three fractions: naphtha, middle distillate (CETC SUPERCETANE™) and waxy residues. When yellow grease, animal tallow and vegetable oils are used as feedstocks, negligible amounts of naphtha and small volumes of waxy residues are produced. Since the naphtha fraction is so small it is usually not necessary to remove it from the SUPERCETANE™. The waxy residue is paraffin-rich and can be used as refinery feedstock or power boiler fuel. The distillation cut points can be adjusted in order to modify the ratio of liquids to waxy residue.

The middle distillate (SUPERCETANE™) is the primary liquid product and yields of 70-80% (by weight) and 85-93% (by volume) were achieved for yellow grease and tallow. It consists mainly of straight chain hydrocarbons in the diesel fuel boiling range with a cetane number of up to 100 depending on feedstock (cetane number is a measure of ignition quality).

A high cetane diesel fuel is generally recognized as a means of reducing emissions of engine pollutants and improving fuel economy. A higher cetane number is normally achieved by using commercial nitrate based cetane additives and/or by more intensive refining of petroleum in the production of diesel fuel. The CETC SUPERCETANE™ provides a new and renewable alternative. It resembles conventional diesel fuel when analyzed by GC/MS and is miscible in all proportions with diesel fuel. Its sulphur content is less than 10 ppm thus it meets the 2006 diesel fuel specifications.

Commercial alkyl nitrate cetane improvers have a non-linear impact on cetane numbers (leveling off after a limited cetane number increase). In contrast, the CETC SUPERCETANE™ has a linear impact on the cetane value of diesel fuel, directly proportional to its concentration in the blend. The CETC studies have indicated that when SUPERCETANE™ is blended with conventional cetane improvers (nitrates), the cetane value of the final blend improves synergistically, i.e., the increase in cetane number due to nitrates is more significant as more SUPERCETANE™ is added.

The CETC SUPERCETANE™ specific gravity is similar to that of regular diesel while its viscosity is similar to that of biodiesel. Biodegradability of SUPERCETANE™ was tested at the University of Sherbrooke using CEC Respirometry Test Method L-33-T-82. An esterified biodiesel soya oil sample and hydrotreated soya oil sample were tested. Both samples were 97% biodegradable compared with 45% for regular diesel.

The burner gas co-product consists mostly of hydrogen with low levels of methane, ethane, propane, carbon monoxide and carbon dioxide.

Combustion and Emissions Tests

Single and multi cylinder engine combustion and emission tests were performed on the CETC SUPERCETANE™ by ORTECH (Toronto, Canada), the Environmental Technology Centre (ETC), Environment Canada (Ottawa, Canada), the National Research Council of Canada (Ottawa, Canada) and

Advanced Engine Technology Ltd. (Ottawa, Canada). In general, the CETC product showed gaseous emission reductions of total hydrocarbons (THC and NMHC), NO_x, particulates (PM) and carbon monoxide. These emission reductions were found to be due in large part to improved combustion characteristics. As expected, the higher emission reductions occurred when the CETC SUPERCETANE™ was added to lower grade diesel fuel (cetane numbers below 40). As such, CETC SUPERCETANE™ may prove most valuable as a blending stock for lower quality middle distillates.

CETC completed a project with Ottawa-based Advanced Engine Technology Ltd. (AET) to determine whether the addition of small amounts of SUPERCETANE™ and biodiesel to oil sands derived diesel fuel can improve the quality and exhaust emissions of the fuel. Results indicated that blending these renewable fuels with low cetane diesel fuels reduced exhaust emissions of particulate matter and oxides of nitrogen. Unburned hydrocarbons increased slightly but this effect could be reduced or eliminated with the use of oxidative catalytic converters. It was observed that as the concentration of SUPERCETANE™ increased a corresponding emission reduction for particulates and oxides of nitrogen.

CETC also participated in a study performed by the National Research Council of Canada looking at various alternatives for increasing the cetane number of oils sands derived diesel fuels and its impact on diesel exhaust emissions. Results indicated that the use of SUPERCETANE™ had a positive impact on cetane number and led to lower emissions of particulate matters and oxides of nitrogen.

The SUPERCETANE™ product was also evaluated at the National Research Center for Alternative Fuels, Engines and Emissions, West Virginia University (WVU), as part of the Texas Low Emission Diesel (TxLED) program of the Texas Commission on Environmental Quality (TCEQ). WVU observed reductions in emissions of total hydrocarbons (THC and NMHC), carbon monoxide (CO), particulates (PM), and NOx using blends of SUPERCETANE™ (6 and 12 vol%) with EPA diesel fuel or B20 (20% methyl esters and 80% EPA diesel fuel).

Fuel economy savings using the CETC SUPERCETANE™ are another benefit – in a six-month test program using a fleet of Canada Post delivery vans operating in Vancouver, Canada, fuel economy savings of 8% was achieved.

Economic feasibility study

Under a contract from CETC, Calgary-based C.J. Wheeler Process Consultant Inc. completed in 2006 a second engineering and economic feasibility study (business confidential) for the construction and operation of a commercial plant to convert biomass-derived oils (including vegetable oils and yellow grease) to a cetane enhancer and a highly paraffinic lubricant basestock (wax). Two plant sizes were considered: 400 and 800 barrels/day. The study included the preparation of a process flow diagram, the computer simulation of a commercial scale plant to establish mass and energy balances, the sizing and costing of all major pieces of equipment and the estimation of capital investment, operating costs and payout time. The plant location was set in Edmonton, Alberta, Canada. The capital cost to build an 800 barrels/day plant would be about US$12.7 million (2005). The payout time would be about 2.4 years based on a price of hydrogen of US$2.96/kg, a feedstock price of US$0.33/kg and a SUPERCETANE™ selling price of US$0.69/kg. The payout time corresponds to the capital cost divided by the net income. Plant location, hydrogen cost, and feedstock availability and cost are key factors in the economic viability of a plant. Tax incentives were not taken into account in this economic feasibility study.

Potential commercial applications

- The SUPERCETANE™ product can be blended with off-spec middle distillates in order to increase their cetane number, improve their combustion in diesel engines and reduce their exhaust emissions. There is no miscibility or stability problems since the SUPERCETANE™ components are essentially hydrocarbons already present in petroleum middle distillates.

- A major problem with B20 biodiesel blends (20% methyl esters, 80% diesel fuel) is that the NO_x emissions are similar to and sometimes higher than those for regular diesel. The addition of CETC SUPERCETANE™ to biodiesel blends has been shown to reduce NO_x emissions.

- Certain diesel stocks do not respond well when traditional nitrate based cetane enhancers are added. The CETC SUPERCETANE™ can increase the responsiveness of these diesel fuels. The CETC SUPERCETANE™ has been shown to have a synergistic effect on commercial cetane improvers (nitrates), enhancing their performance as more SUPERCETANE™ is added to the diesel fuel.

- The CETC SUPERCETANE™ and the heavier waxy fraction (residue) can be sources of renewable n-paraffins for refinery and petrochemical applications.

Patents

1. Craig, W.K. and Soveran, D.W. “Production of hydrocarbons with a relatively high cetane rating”, US Patent No. 4,992,605 (February 12, 1991).

2. Craig, W.K. and Soveran, D.W. “Production of hydrocarbons with a relatively high cetane rating”, Canadian Patent No. 1,313,200 (January 26, 1993).

3. Monnier, J., Tourigny, G., Soveran, D.W., Wong, A., Hogan, E.N. and Stumborg, M. “Conversion of biomass feedstock”, US Patent No. 5,705,722 (January 6, 1998).

4. Monnier, J., Tourigny, G., Soveran, D.W. “Conversion of depitched tall oil to diesel fuel additive”, Canadian Patent No. 2,149,685 (September 14, 1999).

Patent applications

5. Monnier, J., Ikura, M. and Tourigny, G., “Production of high-cetane diesel fuel from low- quality biomass-derived feedstocks”, U.S. Patent Application No. 2007/0068848 (March 29, 2007).

6. Monnier, J., Ikura, M. and Tourigny, G., “Production of high-cetane diesel fuel from low-quality biomass-derived feedstocks”, International Patent Application (PCT) No. WO 2007/033460 (March 29, 2007).

Table 1 - Characteristics of SUPERCETANE™ produced from vegetable oils, animal fats and waste restaurant grease

Feed		YG / tallow blend	Crude Brown Grease	Soya oil	Restaurant trap grease (Note 1)
Density at 25°C, kg/m^3	ASTM D4052	775.4	785.8	776.7	783.2
API gravity API, °API	ASTM D1250	49.07	46.79	n.d.	n.d.
Elemental analysis					
C, wt%	ASTM D5291 (method B)	85.2	85.2	85.1	85.9
H, wt%	ASTM D5291 (method B)	15.0	14.7	14.6	14.1
N, ppm	ASTM D4629	<0.3	<0.3	<5	8
S, ppm	ASTM D2622	<10	10	<5	<10
O, wt%	NAA	n.d.	n.d.	<0.01	0.05
Kinematic viscosity @ 40°C, cSt	ASTM D445	3.17	3.16	3.54	2.079
Flash point, °C	ASTM D93 / D6450	112	108.5	138.2	73.0
Cloud point, °C	ASTM D5773	18.4	14.9	21.8	-2.5
Total acid number, mg KOH/g	ASTM D664	<0.05	<0.05	0.042	0.013
Cetane number	ASTM D6890	106.3	87	109	75.4
Lubricity test, micron	BOTD Wear Scar Diam.	571	617	n.d.	n.d.
Simulated distillation, °C	ASTM D2887				
IBP		169.2	171.7	194.1	137.8
10		273.6	252.6	290.9	195.6
50		313.4	303.5	331.8	273.6
90		333.8	317.9	326.0	302.4
FBP		359.6	377.4	332.5	317.4

Note 1: Characteristics of products from modified process

Appendix – Characteristics of SUPERCETANE™ Products

SUPERCETANE is a trademark of Her Majesty the Queen in Right of Canada

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