A NEW DEVELOPMENT IN RENEWABLE FUELS: GREEN DIESEL

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ABSTRACT

The production of renewable fuels is continuing to expand worldwide as a result of increasing petroleum prices, government regulations, and commitments to greenhouse gas reduction. There has been little integration of renewable fuels production within petroleum refineries to date, despite the rapidly increasing growth in renewable fuels demand. The segregated production of renewable fuel components increases cost, since the existing infrastructure for distribution and production of petroleum-based fuels is not utilized. Renewable fuels can have greater application in meeting the increasing demand for transportation fuels if economic opportunities for blending or co-processing them within traditional petroleum refineries can be developed. UOP LLC and Eni S.p.A. are jointly developing new technology to utilize renewable feedstocks derived from vegetable oils for the production of high quality diesel fuel.

This paper introduces the new UOP/Eni Green Diesel™ Process and discusses the advantages it has over other technologies to produce renewable diesel fuel, such as Fatty Acid Methyl Ester (FAME), also known as Biodiesel.

INTRODUCTION

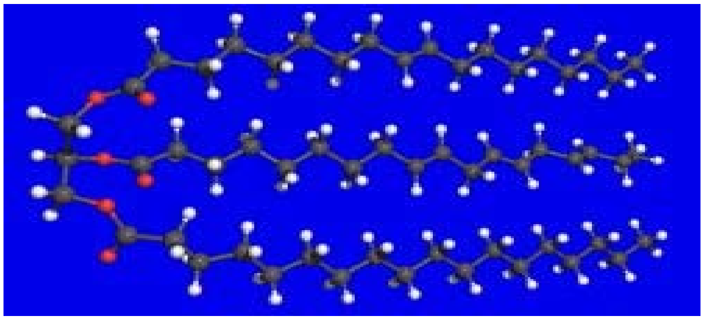
The production of biofuels is expanding at a rapid pace worldwide as a result of increasing petroleum prices, government regulations, and commitments to greenhouse gas reduction. Future widespread use of biofuels depends on developing new technology to produce high quality transportation fuels from highly oxygenated, biologically derived, feedstocks. These new biofuels also need to be compatible with the existing fuel transportation and infrastructure.

Existing technology for producing diesel fuel from vegetable oil has largely centered on production of FAME or biodiesel[1,2]. While FAME has many desirable qualities, such as high cetane, there are other issues associated with its use such as poor stability and high solvency leading to filter plugging problems. UOP and Eni, S.p.A. recognized the need for different processing route to convert vegetable oils into a high quality diesel fuel or diesel blend stock that is fully compatible with petroleum derived diesel fuel. The two companies started a collaborative research effort in 2005 to develop such a process based on conventional hydroprocessing technology that is already widely deployed in refineries and utilizes the existing refinery infrastructure and fuels distribution system. The result of this effort is the UOP/Eni Green Diesel Process. This new technology utilizes widely available vegetable oil feedstocks to produce a high cetane, low gravity, aromatics and sulfur free diesel fuel. The cold flow properties of the fuel can be adjusted over a range to meet various cloud point specifications in either the neat or blended fuel. The new process is targeted for commercialization in 2009 in an Eni refinery in Italy.

PROCESSING BIOLOGICALLY DERIVED FEEDSTOCKS

Processing of biologically derived feedstocks is complicated by the fact that these materials contain a significant amount of oxygen. The feedstocks of primary interest in the Green Diesel Process are primarily vegetable oils such as soybean, palm, jatropha, or rapeseed oils. Other products such as animal fats and greases can also be used as a feedstock. Plant oils mainly consist of triglycerides with typically 1-2% free fatty acid content. The chemical structure of a triglyceride molecule is shown in Figure 1 (red=oxygen, white=hydrogen, grey= carbon atoms).

Figure 1
Chemical Structure of Triglycerides



Triglycerides and free fatty acids both contain relatively long, linear aliphatic hydrocarbon chains. The aliphatic hydrocarbon always contains an even number of carbon atoms, is generally unsaturated, and also corresponds to the carbon number range typically found in diesel fuels. There is also a three carbon "backbone" in the triglyceride molecule. The properties of various vegetable oils are compared to petroleum derived diesel fuel in Table 1. The volume yield of diesel fuel potential from vegetable oils is nearly 100% where diesel represents only about 20% of the volume of crude oil when distilled.

Table 1

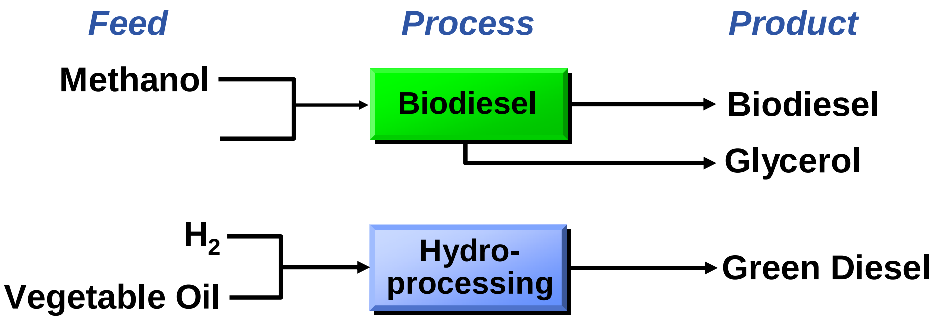
Comparison of Vegetable Oil Feedstocks[3,4,5]

Bio Feedstock	*Price ($/bbl)*	*Diesel Yield, v%*	*Carbon Number*	*Olefins, mol-%*
WTI/Brent Crude	**68**	**20**	**11-22**	**0**
Rapeseed oil	**89**	**99**	**16-22**	**94**
Soy oil	**75**	**99**	**16-18**	**84**
Palm oil	**62**	**99**	**16-18**	**58**
Jatropha oil	**44**	**99**	**16-18**	**77**

There are two processing routes for converting vegetable oil to diesel fuel as shown in Figure 2. The conventional processing route for diesel fuel production is via esterification with methanol in the presence of caustic to produce FAME with glycerol as a by-product. The glycerol is produced from the three carbon "backbone" and has a limited market, particularly in an unrefined form.

The hydroprocessing route uses hydrogen to remove the oxygen from the triglyceride molecules. This is the route used in the Green Diesel Process. The oxygen is easily removed via two competing reactions: decarboxylation and hydrodeoxygenation. The extent of each reaction depends on the catalyst and process conditions used for the process. The three carbon "backbone" in the Green Diesel Process yields propane and can be recovered easily in when the process is integrated into a refinery. The oxygen contained in the feed is rejected either as CO/CO_2 or water. In addition, all olefinic bonds are saturated, resulting in a product consisting of only paraffins.

Figure 2
Vegetable Oil Processing Routes



The chemistry used in the biodiesel or FAME route is problematic from a processing viewpoint. The stoichiometry of the reaction is as follows:

Triglycerides	+	Methanol	====>	FAME	+	Glycerol
100 bbl		13 bbl	NaOH	99 bbl		8 bbl

About 8% of the product volume is glycerol, which is a low value product in unrefined form and has a limited market when refined. Methanol is required as a co-feed and feedstocks containing high concentrations of free fatty acids can cause operational problems due to saponification reactions with the caustic present as a catalyst.

As noted previously, the Green Diesel Process removed the oxygen by reaction with hydrogen producing a pure paraffinic product. The volume yield is 99% and the primary co-product is propane and the by-products are water and carbon oxides. Feedstocks containing free fatty acids can be processed in the Green Diesel process without the problems caused in FAME production.

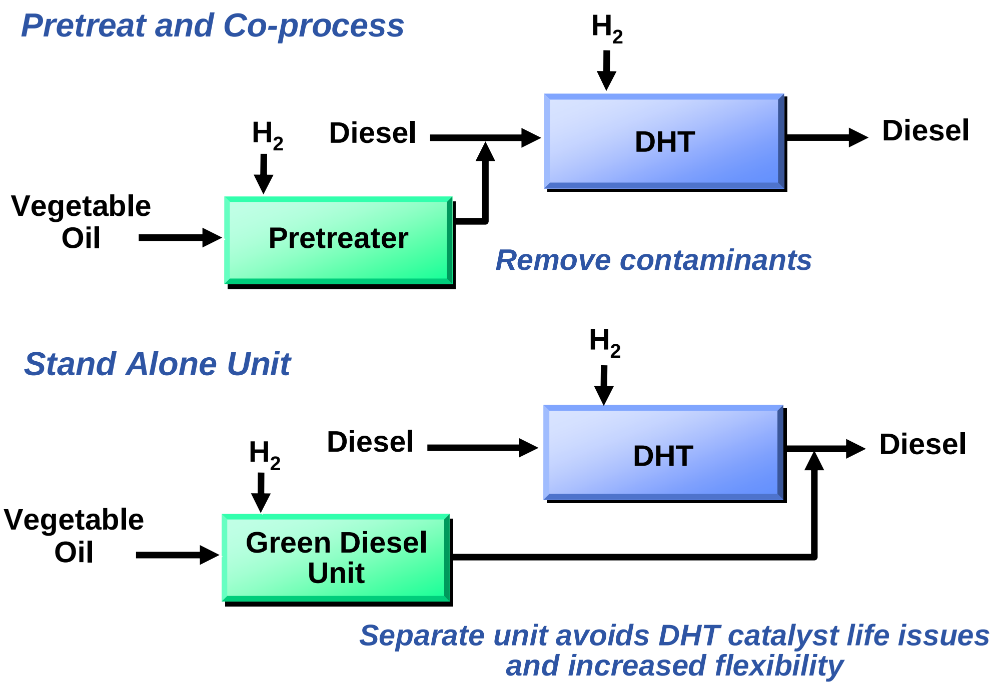
Triglycerides	+	H_2	====>	Green Diesel	+	H_2O/CO_2	+	Propane
. 100 bbl			Catalyst	99 bbl				9 bbl

The Green Diesel Process has several basic advantages over FAME production in a refinery setting. Hydrogen required for the reaction is readily available and the products are all ones that are already normal refinery products and do not require any special handling. The products can all be easily blended with conventional refinery products.

THE GREEN DIESEL PROCESS

While hydroprocessing was clearly the chemistry preferred for refinery applications, how to implement it in a process design was not obvious. There are two options that can be considered: co-processing in an existing distillate hydroprocessing unit or building a stand alone unit as shown in Figure 3.

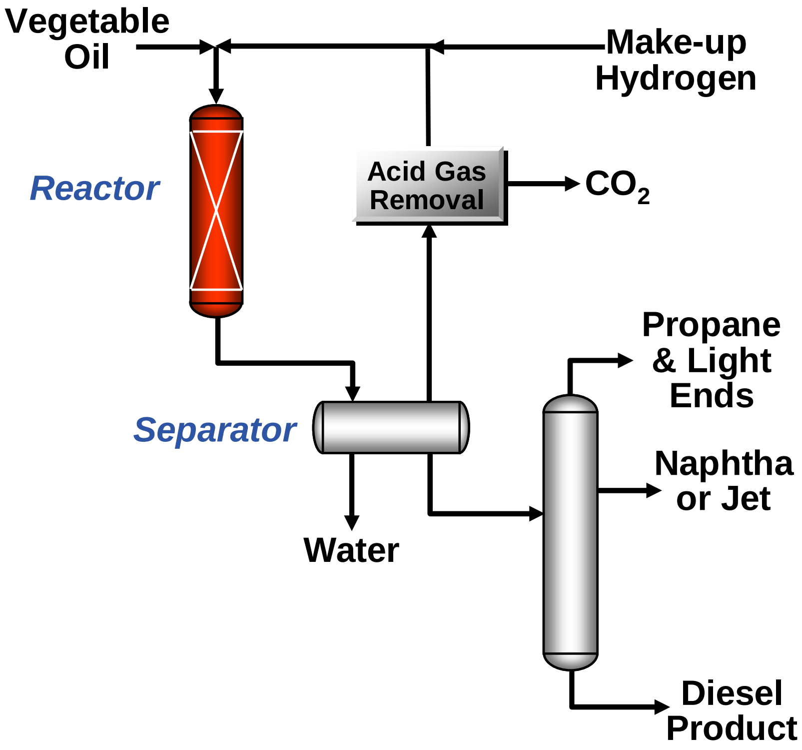
Figure 3
Vegetable Oil Hydroprocessing Alternatives



The co-processing route was initially evaluated as an attractive option, since existing equipment could be used, resulting in a lower cost implementation. Co-processing was found to be problematic after some initial evaluations were completed. Vegetable oils contain trace metal contaminants such as phosphorous, sodium, potassium, and calcium. These require addition of a pre-treating reactor for removal as the existing reactor will generally not have sufficient catalyst volume for the treating catalyst. The reactions involved in processing vegetable oil are fairly exothermic, and may require quench capabilities that may not necessarily be available in a given unit. The deoxygenation products (H_2O, CO, CO_2) will require revamping of the recycle gas system for removal, or use a substantial purge stream. The cold flow properties of the combined diesel product may limit the quantity of vegetable oil that can be processed, as normal paraffins are the primary product from hydrotreating vegetable oil and will impact the cloud point.

After considering all of the potential issues, UOP and Eni decided that it was much more cost effective to build a larger sized, dedicated unit that was optimized for vegetable oil processing due to the unique nature of these feedstocks. A simplified flowscheme showing the principles of the process is shown in Figure 4.

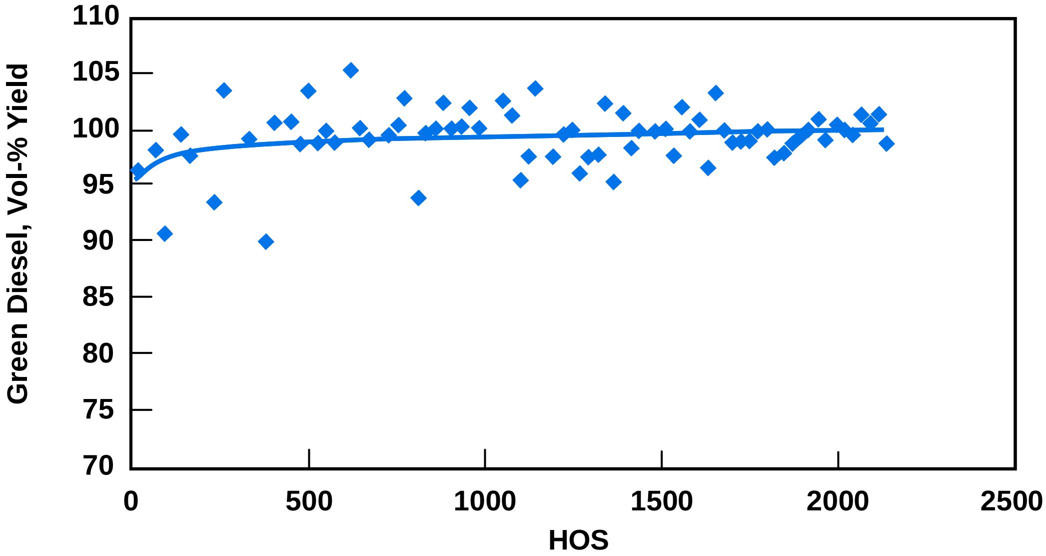
Figure 4
Simplified Green Diesel Flowscheme



In the process shown in Figure 4, vegetable oil is combined with hydrogen, brought to reaction temperature, and is then sent to the reactor where the vegetable oil is converted to the Green Diesel product. The product is separated from the recycle gas in the separator and the liquid product sent to a fractionation section. The design of the fractionation section can vary from a one column system producing on-specification diesel and unstabilized naphtha to a three column system producing propane, naphtha, and diesel products. It is envisaged that most installations will be a single column and the lighter products will be recovered in other existing refinery process units. The recycle gas is treated in an amine system to remove CO_2.

UOP and Eni have done extensive process performance testing to determine optimum process conditions, catalyst stability, and product properties. A range of vegetable oil feedstocks have been processed in pilot plants at both UOP and Eni facilities including soybean, rapeseed, and palm oil. An extensive program is underway to evaluate other potential feedstocks including tallow and greases derived from animals. We have done considerable testing to confirm stability of catalyst system employed and data from an on-going stability test evaluating rapeseed oil is shown in Figure 5. There is no measurable deactivation after over 2000 hours on stream.

Figure 5
Catalyst Stability Testing



Product properties are similar for all the vegetable oils processed. Typical product yields are shown in Table 2. Cold flow properties can be controlled by the severity used in the process, so the diesel yield will vary from 99 vol-% to about 88 vol-% that is required to achieve a -10°C cloud point. The diesel yield loss is to kerosene and naphtha. In all cases, the product has a very high cetane number (>80) and contains no sulfur or aromatics. The range of hydrogen consumption shown in Table 2 is what is required for different feedstocks. Palm oil requires substantially less hydrogen than rapeseed oil due to the lower olefin content of that feedstock.

Table 2
Green Diesel Product Yields

Feed	
% Vegetable Oil	**100**
% H_2	**1.5-3.8**
Products	
Vol. % Naphtha	**1-10**
Vol. % Diesel	**88-98+**
Cetane Number	**> 80**
ppm S	**< 1**

The Green Diesel product has excellent diesel fuel properties, and is very similar to diesel product that is produced via Fischer-Tropsch processes. The Green Diesel product properties are compared to mineral (petroleum) diesel and biodiesel in Table 3. The diesel fuel properties for FAME are not ideal for diesel blending. The gravity is high, which can limit blending of lower value products like hydrotreated LCO into a refinery diesel pool. It also has a narrow boiling range and can have issues in meeting stability specifications. The heating value is about 12% lower than typical mineral diesel, which will reduce the fuel economy of FAME/diesel blends relative to mineral diesel or Green Diesel/mineral diesel blends.

Table 3
Green Diesel Fuel Properties[5]

	Mineral ULSD	*Biodiesel (FAME)*	*Renewable Diesel*
%O	**0**	**11**	**0**
Specific Gravity	**0.84**	**0.88**	**0.78**
Sulfur content, ppm	**<10**	**<1**	**<1**
Heating Value MJ/kg	**43**	**38**	**44**
Cloud Point C	**-5**	**-5 to +15**	**-10 to +20**
Distillation	**200-350**	**340-355**	**265-320**
Cetane	**40**	**50-65**	**70-90**
Stability	**Good**	**Marginal**	**Good**

Green Diesel, however, is a premium diesel blending component. The boiling range is comparable to typical diesel products, with substantially higher cetane and lower density. These are very valuable properties as it allows blending low value hydrotreated LCO into a typical refinery diesel pool and still meet EU diesel specifications. An example is shown in Table 4, where a straight-run diesel and kerosene blend can be produced to meet a 50 cetane ULSD product specification. No LCO can be blended without the use of cetane enhancing additives. If Green Diesel is added to the pool, the high cetane value and low density allow for blending a nearly equivalent volume of hydrotreated LCO into the ULSD product. Assuming a typical discount of $4.60/bbl for fuel oil relative to ULSD, this translates to a benefit of $9200 per day or over $3 MM per year that could be realized through Green Diesel blending.

Table 4
Green Diesel Blending Benefits

Diesel Pool Components	*Barrels in Pool*	*Cetane Index*
Kerosene	500	41
Hydrotreated Straight Run Diesel	7500	52
Hydrotreated LCO	2000	20
Green Diesel	2346	74
Blended Product Cetane		50

GREEN DIESEL PROCESS ECONOMICS

UOP and Eni both conduct techno-economic feasibility studies as part of the development process to ensure that the technologies in development are competitive with alternatives that are available to refiners. As in all refinery processes, the primary factor in the Green Diesel Process economics is the cost of the feedstock. The capital and variable operating costs for two feedstocks are summarized in Table 5. The variable cost in this table includes utilities, hydrogen, catalyst, and chemicals costs. Hydrogen was valued at $3.00/MSCF in this evaluation.

Table 5
Economic Study Costs

	Palm Oil	*Soybean Oil*
ISBL Cost, $MM	33.9	33.9
OSBL Cost, $MM	6.8	6.8
Variable Cost, $/bbl	5.40	6.94

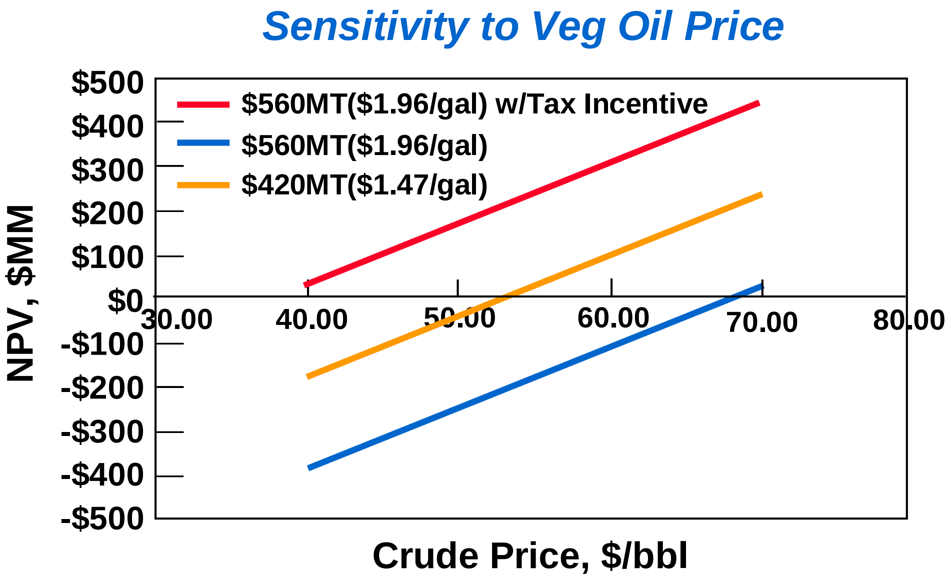
Since vegetable oil pricing is decoupled from crude oil pricing, a sensitivity analysis was conducted to determine the crude oil price required for the Green Diesel Process to be profitable.

Three cases were evaluated:

- Palm oil at $420/MT ($61/bbl)
- Soybean oil at $560/MT ($82/bbl)
- Soybean oil with $1/gal subsidy

Results of the evaluation are shown in Figure 6. Palm oil is profitable without any subsidy at a crude oil price of $52/bbl, while soybean oil is only profitable at a crude oil price of $67/bbl and will require a subsidy to be viable with currently published crude oil price forecasts. If the current subsidy of $1/gallon for FAME is assumed to be extended to Green Diesel, then the process is viable at a crude oil price of $38/bbl and has a payback of less than 1 year at a crude oil price of $60/bbl.

Figure 6
Green Diesel Economics

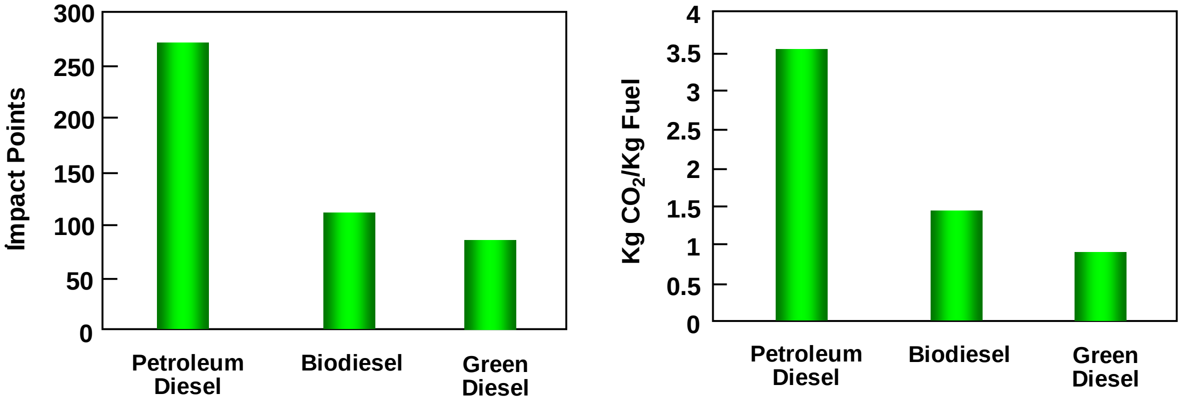


GREEN DIESEL: A MORE SUSTAINABLE PRODUCT

A Life-Cycle Analysis (LCA) of different diesel production routes was conducted using the Simapro™ LCA program. LCA is a method to determine and compare the environmental impact of alternative products or processes, including impacts of initial resource extraction to disposal of waste products. In this study, the scope of the analysis was from extraction of the crude oil through combustion of the refined diesel fuel in a vehicle. It was assumed that all fuels had the same performance in the vehicle for the purposes of this study. The primary focus of the analysis was on fossil energy use and emissions of greenhouse gases, although other impact categories are included.

The results of the analysis are shown in Figure 7. Both the FAME and Green Diesel products have a much lower total environmental impact scores than mineral diesel primarily because both have significantly lower production of climate-active CO_2. However, Green Diesel has both a lower environmental impact and lower climate active CO_2 production than FAME. The environmental impact of FAME production is higher due to the methanol feedstock requirement, which is produced from natural gas through a very energy-intensive process that has a high environmental burden.

Figure 7
Life Cycle Analysis Results
Impact Score and Climate Active CO_2 Production



SUMMARY

Refiners are well positioned to play a major role in renewable fuel production in the future. UOP and Eni have developed the Green Diesel Process, a new, sustainable, route for converting vegetable oil into premium quality diesel fuel as a first step in providing technology to enable refiners to participate in renewable fuels. The Green Diesel product is a superior alternative to FAME, with significantly better diesel product properties and is fully compatible with conventional mineral diesel products.

The UOP/Eni Green Diesel Process is fully developed and available for licensing from UOP. Eni is preceding with commercialization of the first unit in 2009 at one of the Eni refineries in Europe. UOP is currently working on developing projects with several other clients in North America and Asia.

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