Green diesel production by hydrorefining renewable feedstocks

Life cycle analysis of green diesel produced from renewable feedstocks indicates relatively high energy efficiency and low greenhouse gas emissions

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Approximately 50% of globally produced crude petroleum is refined into transportation fuels, the fastest growing component of the energy sector. This sharply rising use of a non-renewable feedstock has a significant impact on greenhouse gas emissions. Biomass is the only renewable energy source that can be converted into liquid transportation fuels. Therefore, increasing biofuel usage in the transportation sector can significantly reduce greenhouse gas emissions as well as diversify energy sources, enhance energy security and stimulate the rural agricultural economy. Worldwide production of biofuels has experienced rapid growth and increased international market demand. Projected future shortages of crude oil coupled with the growing worldwide demand for transportation fuels has also raised interest in synthetic diesels (syndiesels) produced by Fischer-Tropsch (FT) synthesis of a syngas stream derived from coal (CTL), stranded natural gas (GTL) or biomass (BTL).

This article describes the UOP/Eni Ecofining process for green diesel production, and compares the energy efficiency and green house gas (GHG) emissions associated with green diesel to those of petroleum diesel, biodiesel and syndiesel derived from coal and natural gas.

Two-stage hydrorefining

The Ecofining process is an integrated two-stage hydrorefining process. A simplified block flow diagram of the process is shown in Figure 1. In the process, feedstock is pumped to process pressure, mixed with recycle hydrogen, then sent to a multi-stage adiabatic, catalytic hydrodeoxygenation reactor (R1), where the renewable oil is saturated and completely deoxygenated. Gas recycle to R1 is set to achieve a minimum hydrogen partial pressure at the reactor outlet. Conversion of feed is complete and the volumetric yield of deoxygenated hydrocarbon products is greater than 100%. Selectivity to diesel boiling-range paraffin is very high. The primary deoxygenation reaction by-products are propane, water and carbon dioxide. The effluent from R1 is immediately separated at reactor pressure to remove carbon dioxide, water and low molecular weight hydrocarbons. The resultant diesel is mixed with additional hydrogen gas and then routed to an integrated catalytic hydro-isomerisation reactor (R2), where a branched paraffin-rich diesel fuel is produced. In this manner, the cold flow properties of the diesel are adjusted to meet required specifications. The isomerisation reaction is also selective and, as a result, consumes very little hydrogen.

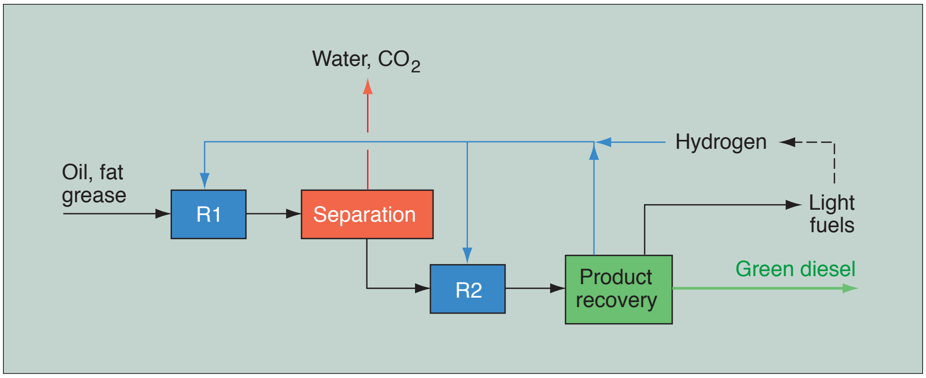

Figure 1 Simplified Ecofining process diagram

Isomerised product is separated from excess hydrogen in a conventional gas/liquid separator. After purification, the excess hydrogen is recycled back to R1 and R2 to maintain the minimum required hydrogen partial pressure. Make-up hydrogen is added to the process to balance both chemical consumption and solution losses. The liquid product is sent to the product recovery section of the process, where conventional distillation steps are employed to separate co-products such as propane and naphtha.

The process for producing green diesel operates in mild conditions and integrates well within existing petroleum refineries. If required, a portion of the light fuel co-product can be steam reformed to generate all of the hydrogen consumed in the process.

Feedstocks

Feedstocks that are suitable for the process include plant-derived oils such as soybean, rapeseed and palm. However, in the future, non-edible oils such as jatropha and algal oils will become increasingly important sources of Ecofining feedstock. Unlike base-catalysed transesterification, the Ecofining process is robust to high concentrations of free fatty acids, enabling other, lower-cost materials such as tallow oil and waste greases to be used as feedstocks. Feedstocks rich in saturated fats, such as palm and tallow oils, require substantially less hydrogen than feedstocks with a higher olefin content, such as soybean and rapeseed oils. However, depending on the concentration of specific contaminants, a pretreatment of these materials to remove solids and salts may be required.

Product range

While the primary product of the Ecofining process is green diesel, smaller amounts of other renewable fuels are also produced. Table 1 contrasts Ecofining inputs and

Comparison of process feeds and main products

	Ecofining green diesel			Biodiesel	
Feeds	**Weight, %**	**Volume, %**	**Feeds**	**Weight, %**	**Volume, %**
Vegetable oil	100	100	Vegetable oil	100	100
Hydrogen	1.5–3.8	–	Methanol	10	11
			Chemicals	4	–
Products	**Weight, %**	**Volume, %**	**Products**	**Weight, %**	**Volume, %**
Propane	5	9	FAME	96	100
Butane	0–2	0-3	Glycerol	10	7
Naphtha	<1–7	1–10			
Green diesel	75–85	88–99			

Table 1

Comparison of diesel fuel quality

	Diesel (ULSD)	Biodiesel (FAME)	Green diesel	FT diesel
Oxygen, %	0	11	0	0
Specific gravity	0.84	0.88	0.78	0.77
Sulphur, ppm	<10	<1	<1	<1
Heating value, MJ/kg	43	38	44	44
Cloud point, °C	-5	-5 to +15	-20 to +20	Not available
Cetane	40	50–65	70–90	>75
Stability	Good	Marginal	Good	Good

Table 2

Green diesel blending benefits[1,6]

	Base case	W/green diesel
Refinery capacity, kBPD	150	150
% green diesel in diesel pool	0	5.75
Yield of Euro IV diesel + jet fuel	Base	+30%
Refinery margin, $/bbl crude	Base	+0.6

Table 3

outputs to those of conventional biodiesel production. Feeds containing fewer unsaturates require less hydrogen input (for instance, palm oil compared with rapeseed oil). Higher processing severity results in a lower diesel cloud point at the expense of a yield shift from diesel to lower molecular weight fuels. The process is flexible. Operating conditions can be adjusted and optimised to accommodate changes in feedstock and seasonal variations in diesel cloud point specification.

Green diesel is of a higher quality than biodiesel and is similar in both composition and combustion properties to syndiesel. A comparison of these fuels with petroleum diesel fuels is shown in Table 2.[1, 2] In contrast to fatty acid methyl esters, whose fuel properties depend on feed origin, green diesel product is independent of feed origin and cold flow properties can be controlled by adjusting hydroisomerisation reactor severity, making the process more flexible than biodiesel production with respect to feedstock selection and plant location.

Diesel blending qualities

From a petroleum refiner's perspective, green diesel is a premium diesel-blending component. The boiling range is comparable to conventional diesel products, and green diesel has substantially higher cetane content and lower density. These properties enable refiners to optimise the amount of lower-value refinery streams that can be blended into the refinery diesel pool, while still meeting all required diesel specifications.

For this reason, a refinery optimisation or linear programming (LP) study was performed to determine the impact of green diesel (or syndiesel) blending in a typical EU petroleum diesel pool.[3] A hydrotreater revamp was also employed to desulphurise the low cetane diesel range product produced in the refinery's fluid catalytic cracking (FCC) unit.

The basis of the study was as follows:

- Northern European location
- 150 000 barrels per day (bpd) capacity
- Crude mix: 50% Brent/44% Arab Light/6% Arab Heavy
- Crude price: $491/MT Brent, $458/MT Arab Light, $423/MT Arab Heavy
- Refinery product slate: LPG, gasoline, jet A-1, Euro IV diesel and fuel oil
- Diesel cloud point -7°C winter, +2°C summer

The results of the study (see Table 3) show that the introduction of green diesel (or syndiesel) into the existing refinery diesel pool enables the refiner to blend low cetane, desulphurised light cycle oil (LCO) into the transportation diesel pool, thus improving overall refinery yields and the operating margin. The improved margin helps justify the investment in the green diesel unit and distillate hydrotreater revamp.

Similar blending studies were performed assuming FAME was used to meet the EU's 5.75% renewable fuel target. In this case, the specific gravity of FAME (0.88) did not allow for the addition of any desulphurised LCO to the diesel pool. The refinery margin actually decreased slightly with FAME due to a required movement of jet fuel to the diesel pool to meet both density and winter cloud point specifications.

Based on the results of this study,[3] it was estimated that green diesel could attract a premium price of up to $35 per barrel compared to FAME due to its superior properties of low density, high cetane and controlled cloud point.[3]

Diesel life cycle analysis

Bio-based diesel fuel substitutes have the potential to reduce GHG emissions by replacing conventional, petroleum-based diesel fuel. The magnitude of this reduction can best be determined by life cycle analysis (LCA). In an earlier publication,[4] the authors reported the Ecofining process to be very promising with respect to GHG reduction. GHG emissions from green diesel were more than 80% lower than from petroleum diesel and about 40% less than from biodiesel.[4]

Following this, several LCA studies were performed to determine the impacts of biofuel feedstock, allocation method and other study assumptions on biofuel production. Study assumptions from several literature sources were evaluated. These included the effects of feedstocks of rapeseed oil, palm oil and inedible tallow. Four inventory data sources were included in the scope of the expanded study, with the aim of adding confidence to the study's conclusions. The study's major assumptions and references are shown in Table 4. Even though the LCAs reported in the sources in Table 4 used different allocation methods, their inventory data enabled us to calculate and apply energy allocation factors to the LCAs reported here based on product and co-product lower heating values. These studies highlight important differences in LCA input data for many raw material choices. Other important study assumptions for green diesel and biodiesel are the inclusion of N_2O emissions, which contribute significantly to the greenhouse gas inventories of biofuels from agricultural activities, and the effects of land use. Although N_2O emissions are included in this study, the effects of N_2O variation are not. This factor and land use change, although important, are not within the scope of this study, but will be included in future work.

The system boundaries include the following life cycle stages: raw material extraction, raw material transportation, raw material processing to final product, product transportation and end use (combustion in a direct injection-internal combustion engine). For end use, biodiesel is often mixed with petroleum diesel at a concentration of 20% (B20). Green diesel can be used as a straight diesel substitute. However, this study only accounts for the combustion of petroleum diesel, syndiesel and biofuels.

The functional unit for this LCA is one megajoule (MJ) of petroleum fuel, FT syndiesel, biodiesel or green diesel. Inventories of inputs of materials and energy over the life cycle for each fuel product were accumulated based on this functional unit. The software used for this LCA was SimaPro 7.0, and for processes not already in the SimaPro library (such as biodiesel and green diesel conversion process steps) the data were obtained either from the sources cited in Table 1 or supplied by UOP for certain processes such as green diesel production via the Ecofining process.

For this study, the impact assessment methods used in SimaPro were Cumulative Energy Demand (CED) and total GHGs from Eco-indicator 95. The Cumulative Energy Demand is all of the energy that is consumed throughout the entire life cycle, including the energy that is contained within the product of interest, as well as primary forms of that energy (fossil, biomass and so on). Of further interest is the Fossil Energy Demand (FED), which accounts for all of the fossil energy sources used throughout the life cycle, including the fossil energy contained in the fuel. This is particularly important, because biofuels often require larger amounts of biomass-derived energy, which is a renewable source of energy. Greenhouse gas emissions were calculated using the Eco-indicator 95 method in units of CO_2 equivalents for all GHGs. Primary GHGs of concern were CO_2, N_2O and CH_4 (IPCC, 2007). GHG emissions were derived from all combustion processes consuming fuels containing fossil carbon (diesel for transportation, electricity consumption and so on). The combustion of bio-based fuels in vehicle engines was not included in the GHG assessment. For example, green diesel contains carbon derived only from renewable oils, and therefore CO_2 emissions following combustion do not count towards GHG totals. For biodiesel, only methanol-derived CO_2 (assumed to be of fossil origin) was included in GHG totals from combustion emissions.

Comparisons of diesel life cycles

LCA inputs for low sulphur petroleum diesel were taken from the ecoinvent database in SimaPro 7.0, assuming average European technology. Biodiesel and green diesel inventory data were input into SimaPro 7.0 using values from the studies cited in Table 4. Inputs for biofuel production include the farming of an energy crop, in this case rapeseed or palm oil, or the production of tallow. Energy crop production requires four major inputs: seeds, fertilisers, chemicals such as pesticides, and fuel used for harvesting and sowing, among other farm uses. After harvesting, the seeds are transported to a processing facility, where they are crushed to extract oil. The conversion of plant oil to biodiesel was modelled using data from a 2003 Nexant report,[1] and conversion to green diesel was modelled using data from UOP and Eni. Tallow, unlike energy crops, is considered a waste from the meat processing industry, and thus carries no environmental burdens. However, tallow must still be transported and rendered to become a usable feedstock. Once tallow has been rendered, it can be processed into biofuel in accordance with input data supplied by a 2002 literature source,[5] or converted into green diesel in accordance with data supplied by UOP.

Unlike the cases based on rapeseed and tallow oils, the palm oil case can vary greatly, depending on the process.[7] As standard practice, palm meal from the oil extraction step is burned on-site for power generation, so displacing fossil fuels. Palm oil mill effluent (POME), a nutrient-rich liquid, is anaerobically digested on-site to produce a solid that can be used as fertiliser on the palm plantation, a measure that displaces imported fertiliser. A methane-rich biogas is produced as a digestion by-product. This is a factor in establishing GHG emissions, because the biogas can contain as much as 70% methane by mass. For this study, the composition is assumed to be 70% methane, 20% carbon dioxide, 7% nitrogen, 1% hydrogen and 2% hydrogen sulphide. This biogas is often simply vented to the atmosphere, but can be captured and burned on-site for energy production.[8] Thus, there are two likely scenarios: one in which the biogas is vented, and another in which the biogas is combusted to produce electricity for the oil extraction/biofuel processing stage.

Study assumptions and sources

Diesel source	Transportation	Study allocation method	Data source
Coal gasification FT synthesis Wax refining	Estimated	Energy	Marano, 2001[6]
NG gasification FT synthesis Wax refining	Estimated	Energy	Marano, 2001[6]
Rapeseed	Not included	Displacement	Concawe, 2006
Palm oil	Estimated	Not allocated	Yusoff, 2007[7]
Tallow	Estimated	Energy/economic	Judd, 2002[5]

FT = Fischer-Tropsch, NG = Natural gas

Table 4

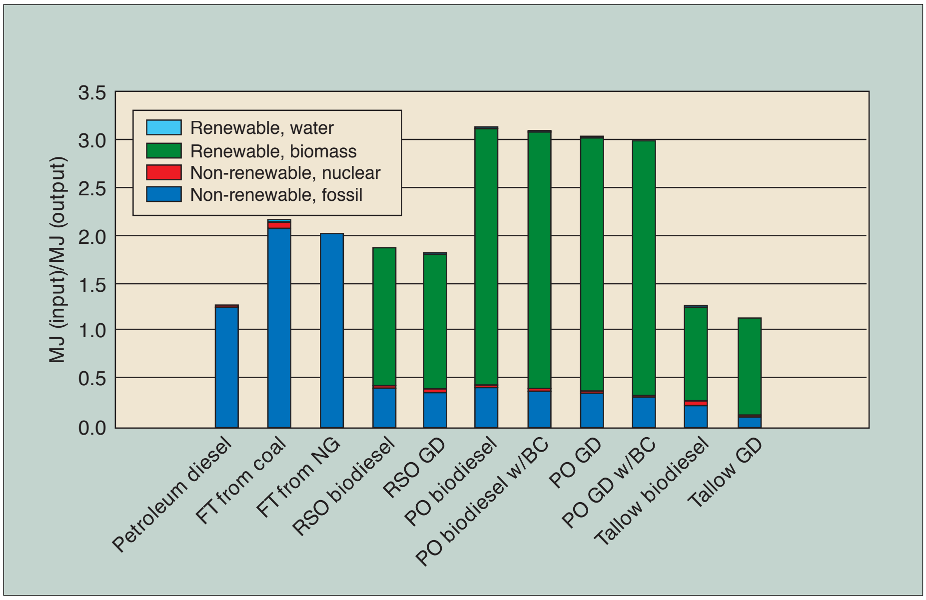

Figure 2 Cumulative energy demand for petroleum diesel, FT syndiesel, biodiesel and green diesel

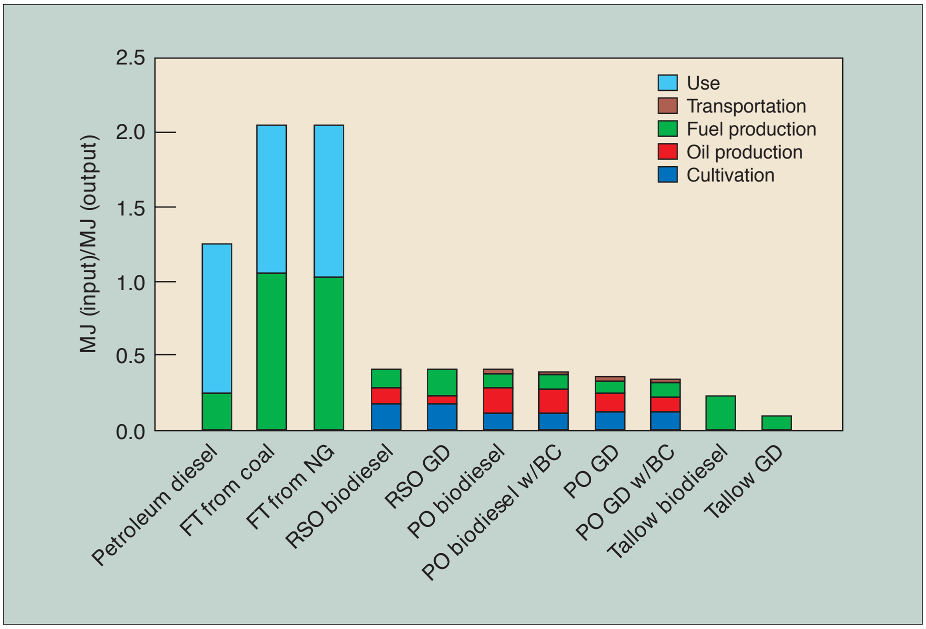

Figure 3 Fossil energy demand for petroleum diesel, FT syndiesel, biodiesel and green diesel

The production of FT syndiesel varies slightly from biofuel production. The coal pathway includes inventory data for the current European Union (EU) hard coal mix, as well as gasification using steam reforming and partial oxidation followed by FT synthesis. The life cycle for the conversion of natural gas to syndiesel is assumed to represent average conditions in Europe, which includes long-distance transport from Russia and the Middle East. As with the coal pathway, steam reforming of natural gas followed by FT synthesis is included. For the syndiesel life cycles, inventory data was input into SimaPro 7.0 from data supplied by a 2001 study for the US Department of Energy.[6] The impact of carbon sequestration technologies was not included in this study.

Summary of LCA results

Figure 2 indicates Cumulative Energy Demand (CED) for petroleum diesel, FT syndiesel, biodiesel and green diesel derived from various feedstocks. Table 5 contains a legend for the abbreviations used in Figure 2. Petroleum diesel, which is used as the baseline for comparison, requires 1.27 MJ of input energy to yield 1 MJ of diesel fuel. FT syndiesel requires higher energy inputs throughout the life cycle, regardless of feedstock, although natural gas FT syndiesel requires slightly lower energy inputs compared to those for coal syndiesel. Rapeseed oil biodiesel and green diesel both have a slightly lower CED than FT syndiesel, with green diesel requiring slightly lower inputs than biodiesel. When palm oil is used as a feedstock, the CED is substantially higher than for petroleum diesel. This reflects the reuse of biomass waste from palm oil production as a fertiliser or a thermal energy source.

Since all of the by-products of palm oil production are used in the oil extraction process, the biomass energy inputs are higher. Furthermore, all of the environmental burdens are carried by the oil because no by-products leave the process. Rapeseed as feedstock, for example, shares 39% of the burdens with rapeseed cake. So although the inputs for palm oil are much lower, the lack of an allocation somewhat distorts the results. As with rapeseed oil, green diesel from palm oil shows slight benefits over palm oil biodiesel. And for the palm oil case, fewer energy inputs are needed when biogas is used as a fuel.

Tallow looks promising as a feedstock. Tallow biodiesel has a slightly higher CED than petroleum diesel, while tallow-derived green diesel is the only fuel to have a lower CED than petroleum diesel.

Fossil Energy Demand (FED) values are shown in Figure 3. The FED of petroleum diesel is very close to the CED value, at 1.25 MJ per MJ of fuel. Coal and natural gas syndiesel have significantly higher FED values compared with petroleum diesel, requiring about 60% more fossil energy for the same energy content of fuel. All of the biofuels have very similar FED values. For all feedstocks, green diesel has a slightly lower energy requirement than biodiesel (with a more significant reduction for tallow), and palm oil has a slightly lower FED than rapeseed oil. In palm oil production, the FED is reduced when biogas is combusted. An assessment of the processes that contribute to the FED shows that fuel use (the embodied energy of the fuel itself) is a major contributor for FT syndiesel and petroleum diesel, but has a negligible effect for biofuels. For rapeseed oil, cultivation is the largest contributor, with oil processing taking about as much energy as fuel production. The cultivation of oil palms requires less energy compared with the cultivation of rapeseed, as well as fewer oil processing requirements, but more energy is used for processing the fuel. Almost all of tallow's energy demands are from fuel production.

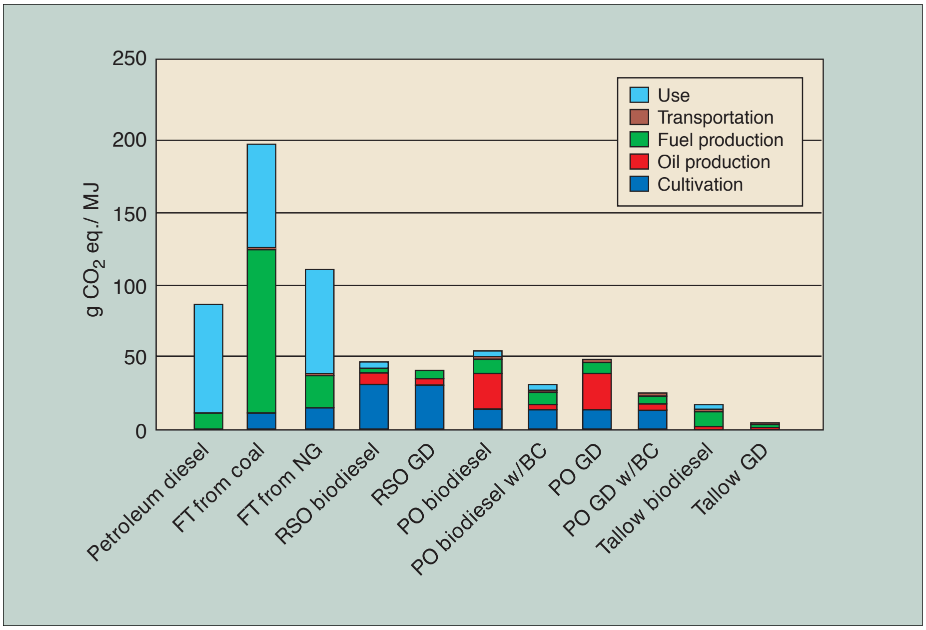

Figure 4 Greenhouse gas emissions for petroleum diesel, FT syndiesel, biodiesel and green diesel

GHG emissions associated with fuel life cycles are shown in Figure 4. FT syndiesel produced from a feedstock of coal produces more than twice as much greenhouse gas (in CO_2 equivalents) over its life cycle compared with petroleum diesel. Syndiesel from natural gas generates fewer emissions than syndiesel from coal, but still produces higher emissions than petroleum diesel. Neither of the syndiesel cases considered the potential impact of emerging carbon sequestration technologies to capture process emissions.

All of the biofuels considered produce lower GHG emissions than petroleum diesel. Overall, green diesel emits less GHG than biodiesel for all feedstocks. For rapeseed oil-based biofuels, cultivation accounts for a significant portion of life cycle GHG, due in part to emissions of N_2O from the field. Oil palms are responsible for fewer emissions in cultivation compared with rapeseed. However, depending on whether or not biogas is burned, palm oil processing can have a significant effect on GHG production. If biogas is burned, emissions are low and life cycle GHG emissions are very low. Inedible tallow, because it carries no environmental burdens, has very low GHG emissions. Processing tallow for biodiesel adds a small amount of GHGs.[9] Green diesel produced from tallow has emissions that are greatly reduced, with life cycle GHG emissions as low as 2% of petroleum diesel's emissions.

Summary

Growing worldwide demand for diesel fuel, coupled with concerns over global warming, has sparked interest in renewable alternatives that show the potential for reduced GHG emissions at a reasonable cost of production. LCA studies indicate that green diesel produced via the UOP/Eni Ecofining process can be an attractive supplement to petroleum diesel, biodiesel and syndiesel. However, the amount of green diesel that can be produced will be limited ultimately by feedstock availability and price.

Green diesel has quality attributes comparable with those of syndiesel, including complete compatibility with petroleum diesel, high energy density (44 MJ/kg), low specific gravity (0.78), excellent storage stability and very low combustion emissions. Furthermore, the cold flow properties of green diesel can be adjusted within the Ecofining process, enabling the producer to adapt to varying feedstock sources and seasonal product specifications.

As determined by LCA studies, green diesel produced via the Ecofining process has environmental benefits over petroleum diesel, biodiesel and fossil-derived syndiesel (without carbon sequestration). Although green diesel consumes more total energy to produce than petroleum-derived diesel, the majority of this energy is renewable. Compared to biodiesel, green diesel shows higher savings in fossil energy per tonne of biofuel, regardless of the source of input data or differences in study assumptions.

Overall, green diesel can contribute to the world's growing need for clean diesel fuel. Its environmental benefits alone are substantial, but when its fuel properties compared to those of biodiesel are taken into account it is clear that green diesel technology merits further investigation towards large-scale industrial production.

Ecofining is a mark of UOP LLC and Eni SpA.

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List of abbreviations used

Acronym	Meaning
FT	Fischer-Tropsch
NG	Natural gas
GD	Green diesel
RSO	Rapeseed oil
PO	Palm oil
BC	Biogas combustion

Table 5

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