Production of renewable liquid fuels through hydrotreatment and transesterification: LCA comparison and sustainability aspects

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Abstract There is a common worldwide call for sustainable energy solutions where biomass is seen to have a great potential, yet this development must be sustainable. Hydrotreatment of vegetable oils produce renewable fuels with promising characteristics; in this field ECOPETROL S.A. has developed a patent on hydrotreatment of palm oil to produce renewable diesel fuel Biocetano®, at the same time that methyl ester biodiesel could also be produce from the same feedstock. LCA is used to analyze carbon intensity, cumulative energy demand and energy ratios for both fuels considering palm as feedstock; results show that both renewable fuels present similar energy indicators per functional, however better climate change performance and renewability is found for hydrotreated fuels. From a technical perspective, trade-off between fuel chemical and physical characteristics suggest that these two renewable fuels could deliver jointly fine performance properties.

1 Introduction

Sustainable energy development is currently a crucial matter in both developing and industrialized countries. Energy independence, fossil resources depletion and climate change issues are the main driving forces. Moreover, different countries have established ambitious renewable quotas within their energy mix. For liquid transportation fuels this may vary from 2-10% for biodiesel and up to 85% for ethanol.

Biomass is seen as a large potential source for biofuels and current technologies produce biodiesel and ethanol at commercial scale, first generation biofuels represent about 1.5% in total transport fuels equivalent to 35Mtoe. This biofuel
participation is predicted to grow to 25% of the total transport fuel share for 2050, including second-generation biofuels [1]. Nevertheless, many different sustainability issues have arisen from biomass to energy solutions. Both production and conversion need to be sustainable and issues such as food, fodder, greenhouse gas balance, energy efficiency, land use changes, labor, water requirements and economics, need to be accurately addressed.

Ethanol and biodiesel are currently the largest and commercially available liquid transportation renewable fuels, both produced from biomass and known as first generation biofuels. Hydrotreatment for bioenergy is a novel technology which produces a diesel-like fuel from renewable oils and animal fats; this renewable fuel is known as renewable diesel and presents technical advantages over traditional FAME biofuels. ECOPETROL S.A. has developed a patent on hydrotreatment of palm oil to produce renewable fuel Biocetano®.

One of the main purposes of this study is to compare FAME and renewable diesel through LCA and highlight benefits as they both potentially involve the same feedstock and may be seen as competitors. Nevertheless, they may complement each other in diesel fuel blending, which is a discussion topic in this document. An issue to be considered will be sustainability analysis through life cycle assessment focused on climate change as main indicator as well as emphasize on sustainability research challenges.

For bioenergy and biomass to energy solutions is common to see a general use of the term sustainability and authors often present different approaches to define it; before discussing LCA for biofuels is worth attempting to place a sustainability concept; however, is known that no single generally agreed-upon definition of the term is available ([2] Tabak, 2009). Patzek T. and Pimentel D. [3] present a definition deduced from thermodynamics, “a cyclic process is sustainable if – and only if— i. It is capable of being maintained indefinitely without interruption, weakening, or loss of quality and ii. The environment on which the process depends and into which the process expels any waste material is itself equally renewable and maintainable” ([4] Mousdale D. M., 2008). The reason for this misunderstanding of the term sustainability is due to lack of a common definition or at least parameters that describe its assessment as a multidimensional yet manageable and measurable task ([5] Markevicic A. et al., 2010)

During this research work Life Cycle Assessment was used to determine sustainability climate change indicators such as carbon intensity as well as fossil energy demand and renewable energy ratios for renewable diesel and fatty acid
methyl ester from the same vegetable oil source: palm oil. Simapro 7.2.2 was used. Additionally chemical and physical properties of the fuels are discussed.


2 **LCA and Sustainability Assessment**

Is necessary to recognize that LCA by itself is not a complete enabling tool for a comprehensive sustainability assessment. LCA only addresses– according to its methodology– environmental issues and does not consider economic performance. Life Cycle Costing (LCC) is a procedure for cost analysis which starts from the proposition that the initial or acquisition cost of any investment must be compared with all the running cost or the operating and maintenance cost of the investment over its entire lifetime, in order to make accurate judgement of its cost effectiveness ([6] Belding, 1978). Environmental accounting, integrating LCA and LCC, is a technical approach to internalize environmental externalities of bioenergy projects, yet social issues need to be integrated. Valuing and costing hidden impacts in environmental issues is a technical and research challenge, especially in traditional neoclassical economic models where only items with a market value are taken into account, failing the environment to comply with this condition as most cases is not particularly owned nor has an agreed value ([7] Gluch P. et al, 2004).

In spite of the previous remarks during this research work greenhouse gas balance and energy intensity was only considered to study FAME and renewable diesel from palm oil; yet the author recognizes that future bioenergy studies must integrate environment, economic and social performance.

3 **Biofuels considered: First generation biofuel from palm oil - background**

For this study renewable diesel is produced from palm oil hence the biofuel is considered to be a first generation type. However, the naming of a biofuel relies on the feedstock and hydrotreatment novel processes could produce second/third generation biofuels when using feedstock such as jatropha oil, algae oil or bio-oil
from thermo-chemical processes. Therefore renewable diesel could be considered a first generation as well as a second-generation biofuel depending on the feedstock.

FAME biodiesel is used worldwide and its environmental benefits also bring with different quality conditions. Due to its oxygen content –coming from the carboxylic group within the fatty acid molecule- the FAME is a polar molecule and has chemical affinity to water which represents an issue in terms of quality and regular diesel blending. In addition, cold flow properties of FAME biodiesel present particular conditions due to the formation of solid particles, which affect cold weather engine performance; these conditions depending on the fatty acid profile source. These undesired characteristics have impeded biodiesel blends to be representative and specially to use extensively existing fossil pipeline infrastructure to transport FAME. Separator condensation decantation

Notwithstanding renewable diesel represents a novel biofuel produced from triglycerides through hydrogenation processes. More specifically renewable diesel is produced via hydrodeoxygenation, decarboxilation and hydroisomerization. The fuel is a mixture of paraffinic hydrocarbons similar to a diesel fuel with negligible sulfur and aromatics, their chemical structure is represented as CnH_{2n+2} ([8] Kalnes T. et al, 2007). The main reagent is hydrogen which saturates and deoxygenates the fatty acids to produce renewable diesel (paraffinic molecules from the triglyceride), propane, naphtha, water and carbon dioxide. A simplified diagram of the hydrotreatment of renewable loads is shown in figure 2.
Hydrotreated vegetable oils (HVO) fuels present promising characteristics over current FAME fuels. Firstly, HVO fuels have superior cetane number (CN) which is a measurement of the ignition quality of the fuel; CN for Palm renewable diesel is found to be up to 95CN whereas FAME presents 58CN and diesel fuel 50CN. In addition, considering its paraffinic characteristic and lack of oxygen, HVO fuels are suitable to be transported using existing pipelines without compromising other fuels integrity which from a logistic and economical point of view is a desirable characteristic. However, due to hydrogenation reactions cloud and pour point for HVO fuels may need adjustments.

Considering that both renewable fuels, PME and renewable diesel, present different chemical and phisical properties and could be produced from the same feedstock, LCA is used to address whether these fuels compete or complement each other; well to wheels LCA is conducted using carbon intensity and energy indicators.

4 LCA comparison

Purpose The purpose of the study is to have a better understanding of the environmental benefits of two different renewable fuels: palm oil methyl ester (PME) and hydrotreated palm oil. Carbon intensity and climate change are the main issues herein considered.
**Scope** The diesel fuel considered, which is the baseline for the comparison, was modeled based on a detailed study from the Colombian Petroleum Institute on fossil production, including oil production, transport to a complex refinery, refining, transport to its point of use and use. Production of PME considers agricultural production, transportation to hub plants, oil extraction and transportation to a biodiesel plant purposely located at same refinery considered for diesel production. FAME process studied is transesterification of palm oil with methanol. Hydrotreated renewable diesel –Biocetane- is produced from palm oil at a hydrogenation facility within the boundaries of the refinery considered. The consumption of all fuels is assumed to be at 100 km from the refining/tranesterification plant. Low-Sulfur fossil diesel and renewable diesel are transported through pipeline –energy and emission inventory using local data- and PME uses trucks as means of transportation. Total carbon dioxide emissions from the usage of both low-Sulfur fossil diesel and Biocetane are considered to be equal as renewable diesel has paraffinic non-oxigenated molecules similar to a diesel fuel; this consideration is also established by Rantanen et al. (9, 2005) as one conclusion of a Neste oil’s study on NExtBTL fuel –renewable fuel produced from the hydrotreatment of vegetable oils and animal fats- proving that this hydrotreated fuel does not affect fuel consumption nor CO2 at different blends when compared to EN590 or EC1 fuels. CO2 Emissions from the consumption of PME are considered neutral as they come from a biogenic source. Carbon stock depletion and land use changes are not considered.

**Systems and Functional Unit:**
The functional unit is the amount of fuel equivalent to 1 MJ of energy. The fuels considered are: (i) Diesel baseline (B0-RD0), (ii) PME baseline (B100), (iii) Palm renewable diesel (Palm RD) and (iv) a blend of diesel fuel, PRD 10% and PME 2%.

**Inventory Fossil diesel baseline:** As previously stated, low-sulfur diesel fuel LCI was modeled from local information on both up and downstreaming processes at one local refinery. **Palm oil production:** LCI information on palm agricultural stages for the Colombian scenario is not considered due to availability; international data is consulted instead. See table 1.

**Tab.1: Summary of GHG emissions for palm agricultural stages**

<table>
<thead>
<tr>
<th>Source</th>
<th>gCO2/MJ Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>RED (2008)</td>
<td>18</td>
</tr>
<tr>
<td>Ecoinvent LCI (2007)</td>
<td>26.4</td>
</tr>
<tr>
<td>RFTO (2008)</td>
<td>25</td>
</tr>
<tr>
<td>Nikander (2008)</td>
<td>Allocated</td>
</tr>
<tr>
<td></td>
<td>Cultivation: 6.54 (fossil)</td>
</tr>
<tr>
<td></td>
<td>Processing: 19.77 (fossil) and 19.70 (biogenic)</td>
</tr>
<tr>
<td></td>
<td>Non-allocated</td>
</tr>
</tbody>
</table>
Cultivation: 8.72 (fossil)  
Processing:  
26.36 (fossil) and 26.27 (biogenic)


[12] RFTO (UK Renewable Fuel Transport Obligation, 2008) – Palm to ME Biodiesel Fuel Chain Summary, considering crop production, feedstock transport, palm oil extraction and transport and its conversion to refined oil. Indonesian average is 25 gCO2/MJ and Malaysian 25.1 gCO2/MJ.


For this study inventory for oil palm production will be taken from Ecoinvent database which is Malaysian and Indonesian average inventory data. Means of transport and distances are adjusted. It shall be noted that yields and material inflows for the Colombian scenario may vary. According to the mass balance presented by Ecoinvent, 1 ton of palm fruit bunches produces 215.8 kg of palm oil, 26.6 kg of palm kernel oil and 31.7 kg of palm kernel meal (Life Cycle Inventories of Bioenergy, 2007). Allocation between products is made based on economic values: palm oil 81.3%, palm kernel oil 17.3% and 1.4% palm kernel meal. Liquid effluents are treated in local wastewater treatment plants through open ponds.

**Fuel processing - palm oil Hydrotreatment.** Palm oil is hydrotreated at a hydrogenation within the studied refinery. Hydrogen is produced at a reforming plant from natural gas which is modeled upon local inventory data, as well as all other refining services. For palm oil hydrotreatment, although different simultaneous reactions take place during hydrotreatment of vegetable oils ([14] Guzman A. et al, 2010), mass balances are made under a assumption where each molecule of triglyceride produces three molecules of hydrogenated paraffin –of the size of the original fatty acid-, one molecule of propane, CO2 and water. Conversion of palm oil to renewable diesel is considered to be 80% and 7% to light fuels. CPO it assumed to be 45% Palmitic acid, 40% Oleic acid and 15% linoleic. Under this consideration hydrogen consumption is 2.4% of the CPO feed. Kalnes et al. (2007) uses 1.5-3.8% for vegetable oil hydrotreatment. Energy intensity and emissions for hydrogen production, and hydrogen recycling operations, are taken from local refinery GHG and criteria pollutant inventory. For the CPO hydrotreatment, main co-products naphta and propane are allocated on a mass basis, 5.77% and 1.88% respectively. **Fuel processing - PME:** The transesterification plant is considered to be located at the same geographical zone...
as the refinery. The process to produce PME considered is transesterification of palm oil with ethanol, information on transesterification of palm oil is used for energy and inflows to the process. Palm oil is assumed to be transported 20 km to the processing plant. Allocation between PME and glycerol is 87.1% and 12.9% respectively on an economic value basis; assignment values taken from Ecoinvent (Life Cycle Inventories of Bioenergy, 2007).

**Fuel distribution and usage.** All fuels are considered to be used at 100 km from the manufacturing plants. Low-sulfur diesel fuel and renewable diesel are transported through pipeline and PME through trucks. Tailpipe emissions for the combustion of diesel baseline and PME B100 are 142.32 g/km and 142.38 g/km respectively ([15] CIEMAT, 2006). It should be noticed that emission calculation for pure biodiesel are made upon a mixture that contains 45% palm oil and other different pure oils including sunflower and rape. In the other hand, considering that hydrotreated vegetable oils have similar molecular characteristics to those of a diesel fuel, CO2 emissions and fuel consumption is assumed to remain invariable.

5 LCA results

LCA is performed using SIMAPRO 7.2. One indicator considered is carbon intensity per functional unit, which in this case is the amount of CO2eq per MJ of fuel. The method used for this characterization is IPCC 2007 GWP 100 with climate change factors within a timeframe of 100 years.

![Graph showing CO2 emissions per MJ for different fuels: Palm RD, PME, PRD 10% - PME 2%, PRD 10%, DIESEL BASELINE. The graph includes a 35% carbon reduction threshold.](image)

<table>
<thead>
<tr>
<th>gCO2/MJ</th>
<th>Palm RD</th>
<th>PME</th>
<th>PRD 10% - PME 2%</th>
<th>PRD 10%</th>
<th>DIESEL BASELINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>gCO2/MJ</td>
<td>44.29</td>
<td>46.81</td>
<td>82.94</td>
<td>83.59</td>
<td>88.18</td>
</tr>
</tbody>
</table>

35% Carbon reduction threshold
Palm hydrotreated fuel (biocetano) presents the lowest carbon footprint of all fuels. Two thresholds are presented in figure 2, one according to the calculated diesel baseline (88.18 gCO2/MJ) and the other with the European default value (83.8 gCO2/MJ), however both use a 35% minimum sustainability value, as suggested by European directive (2009/28/CE) (thinner dotted line for the European hurdle and thicker dotted line for a 35% minimum on the local baseline) For palm oil hydrotreated fuels, the European directive (2009/28/CE) proposes a range between 26-40% of emission reduction; results show that hydrotreated CPO at studied conditions presents 49.7% CO2 reduction. If co-products such naphtha and propane are used to produce hydrogen, the overall carbon intensity can be reduced up to a 3%. PME is found to be also within sustainability values; yet values proposed by the European directive are between 36% and 19%. Co-processed hydrotreatment of diesel fuel with 10% of palm oil produces a 5.2% reduction in carbon intensity. Energy intensity of the systems is studied through Cumulative Energy Demand indicator. See figure 4.

As expected the lowest overall energy demand is presented by the diesel baseline with 1.22 MJ of energy required to produce 1MJ of available energy whereas both PME and Palm RD present the same value of 1.92MJ per available energy, superior to the fossil reference. However it shall be noticed that over 80% of the required energy comes from a renewable source, biomass in this case. In order to have a better understanding of the environmental benefits and renewability of the
systems, the energy ratio output/input (available energy per non-renewable energy required for fuel production) is calculated. See figure 5.

An energy sustainability concept could be established as the ratio between produced and input energy, which for a renewable fuel shall be superior to one. Failing any fossil fuels to comply with this characteristic, 0.82 ratio was found for the diesel considered; Palm RD was found to have the higher renewability ratio as requires the lesser amount of fossil energy; each unit of fossil energy represents 4.84 units of available energy. PME presented a renewability ratio of 4.17.

6 Conclusions

There are certain characteristics for both FAME and renewable diesel in terms of chemical and physical properties that should be considered in the discussion between these two liquid biofuels. Renewable diesel, a paraffinic fuel, has a higher cetane number compared to FAME and regular diesel which is due to a higher chain length and saturation degree, both ignition improvers. It is known that paraffinic –non branched- fuels have higher cetane numbers (CN) and higher melting points, therefore poorer cold flow properties (CFP), meaning that hydrotreated fuels will have better CN yet CFP to be improved. This also supports an additional isomerization process in HDT fuels in order to improve their CFP. In
conclusion there is a trade-off for higher ignition properties and poorer cold flow properties for renewable diesel. FAME biodiesel has polyunsaturated fatty esters which lead to oxidative instability whereas saturated fatty esters provide poorer cold flow properties. FAME’s also present contamination impurities such triglycerides, glycerol and residual alcohols. In addition, poor storage and hazing which is a solid formation because of phosphorous-related compounds. On the other hand, due to hydrotreatment processes in order to reduce sulfur and aromatics, lubricity properties have been affected for diesel fuel. Lack of lubricity causes equipment wear and breakdowns, however FAME addition is proven to enhance lubricity properties in ultra low sulfur diesel (ULSD). This trade-off in diesel properties for blends with FAME and renewable diesel may be an indicative that both fuels could be used simultaneously and complement each other in diesel fuel blends. In addition, integration of liquid renewable fuels to existing refining facilities and transportation pipelines, as mentioned before, is a leading condition in the economy and impact of biofuels – carbon footprint in terms of energy consumption. Moreover, HDT produces as by products propane, light ends and naphtha which could be converted to hydrogen avoiding an additional fossil input into the process, therefore improving its environmental performance.

Considering that both transesterification and hydrotreatment rely on the same feedstock, at least in the case to produce them from palm oil, a sustainability assessment seems to be a comprehensive tool to analyze and compare both options. Hydrotreated renewable fuels were found to have better performance on climate change mitigation, energy intensity and renewability. Furthermore, most of the work done in LCA to biofuels seems to be focused on climate and energy indicators, which is only one part of the environmental load of biomass to energy projects. In example, issues such waste management, land use change, carbon storage, biotic depletion, eco-toxicity and water management shall be considered in future studies where case specific present research opportunities.

7 References


Notes
† Special acknowledgement to the engineers Jaime Augusto Torres and Aldemar Martinez, Dr. Julia Acero and the biofuel research team at the Colombian Petroleum Institute of Ecopetrol for their comments, remarks and support.