Alternative Diesel from Catalytic Hydrotreating of Waste Cooking Oil

S. Bezergianni, A. Dimitriadis, L. Chrysikou*

Laboratory of Environmental Fuels and Hydrocarbons (LEFH), Chemical Processes and Energy Resources Institute (CPERI), Centre for Research and Technology Hellas (CERTH), Thessaloniki 54635, Greece. *sbezerg@cperi.certh.gr

ABSTRACT

A new alternative diesel fuel was developed in CPERI/CERTH based on catalytic hydrotreating of waste cooking oil (WCO). The main premise of this process is the conversion of WCO fatty acids into an oxygen free final product containing normal- and iso-paraffins, so called "white diesel", also promoting WCO recycling. The produced 2nd generation biofuel has been applied to a designated garbage truck of the municipality of Thessaloniki for demonstrating both the benefits of using this alternative fuel and of recycling WCO. Moreover, the environmental implications of white diesel production were addressed by performing Life Cycle Analysis (LCA) and quantifying its greenhouse gas (GHG) emissions. Finally, it should be noted that this new biodiesel production technology is extremely appealing as it employs existing refinery infrastructure and expertise, offers feedstock flexibility, leaves no by-products and above all is economically attractive. This study is part of the BIOFUELS-2G project which is co-funded by the European Program LIFE+.

INTRODUCTION

The advanced and developing economies are strongly dependent of fossil fuels for transportation. It is estimated that within the EU countries around 90% of the CO_2 emissions between 1990 and 2010 are attributed to the transportation sector (BIOFRAC, 2006). For this reason the European Union and other developing countries have established specific action plans for the promotion of biofuels in their markets, such as the 2003 EU directive (2003/30/EU) which suggested that all Member States should blend biofuels in conventional fuels at a 2% ratio in 2005, which will gradually rise up to 5.75% in 2010. In 2007 the EU Commission put forth the ambitious "20/20" energy-climate package for reducing the greenhouse gas (GHG) emissions by 20%, which included a 10% share of biofuels in the transportation sector by 2020 (COM, 2007).

The main type of first generation biofuels used commercially is FAME biodiesel (i.e. fatty acid methyl-esters) of which worldwide large quantities have been produced so far and for which the production process is considered 'established technology'. FAME is a substitute of diesel and is produced through transesterification of vegetable oils, and residual oils and fats, while it does not require major engine modifications. However its current production processes faces several considerations. One such concern is the association of FAME with the food vs. fuel debate, according to which the rising food prices are due to the increase of energy crops over food crops. Even though FAME biodiesel has shown a potential of reducing the net carbon dioxide emissions, its high production cost as compared to petroleum-based diesel limits its large scale commercialization. Studies show that most of its production cost (70-95%) arises from the cost of raw material; that is, the cultivation cost of energy crops. Moreover, FAME biodiesel has lower energy content over conventional diesel, causing power decrease and increased fuel consumption (Demirbas, 2009). A significant problem of FAME biodiesel is that its usage exhibits cold start problems (Demirbas, 2007) due to its long chains that increase cloud point, pour point, cold-flow plugging point (CFPP), etc. Finally the production of FAME leads to glycerin formation, which has problematic disposal.

Second generation biofuel technologies have been developed to overcome the limitations of first generation biofuels production. The goal of second generation biofuel processes is to extend biofuel production capacity by incorporating residual biomass of the non-food parts of food crops (such as stems, leaves and husks) as well as other non-food crops (such as switch grass, jatropha, miscanthus and cereals that bear little grain) and industrial and municipal organic waste such as skins and pulp from fruit pressing, waste cooking oil, animal fats etc.

(Bezergianni et al., 2010a). A new technology based on catalytic hydrotreating of Waste Cooking Oil (WCO), towards a new type of biodiesel production, has been developed in the CPERI/CERTH (Bezergianni et al., 2010a). The aim of the project was to produce two tonnes of this biofuel in order to be utilised in a demonstration garbage truck of the Municipality of Thessaloniki in Greece for three months. The project has lasted three years and now is on the final stage where the fuel is used in the garbage truck. Apart from the production of a new biodiesel from WCO, an integrated environmental assessment of the proposed process is also attempted via Life Cycle Analysis (LCA). Specifically, LCA evaluates the environmental impacts of the proposed technology, by quantifying the associated greenhouse gas (GHG) emissions. So far, LCA has been applied for evaluating the sustainability of conventional diesel and FAME biodiesel. Based on literature data the production of conventional diesel has variant GHG emissions depending on the refinery configuration and energy integration and ranges from 0.447 kg CO_2 eq-/kg diesel up to 3.738 kg CO_2-eq/kg diesel (ECOFYS, 2009; Kochaphum et al. 2012; Sunde et al. 2011). Regarding FAME production the GHG emissions also present high degree of variability, based on the feedstock (i.e. energy crops) used and range from 0.444 kg CO_2 eq-/kg FAME to 5.5 kg CO_2 eq-/kg FAME (Reijnders et al., 2008; Fontaras et al., 2012). Furthermore, FAME from residual feedstocks such as WCO are associated with lower GHG emissions compared to FAME produced from energy crops and vary from 0.3 kg CO_2 eq-/kg FAME (Peiró et al., 2010) to 2.323 kg CO_2 eq-/kg FAME (des Pontes Souza et al., 2012), based on the boundaries and inputs of the LCA.

METHODOLOGY

The basis of the BIOFUELS-2G project is the new 2nd generation biofuels production technology based on catalytic hydrotreatment of WCO. The technology was developed by the Hydroprocessing Group of the Laboratory of Environmental Fuels and Hydrocarbons (LEFH) of Center of Research and Technology Hellas (CERTH) (Bezergianni et al., 2010b). The sustainability of the proposed technology was further enhanced by incorporating solar hydrogen based on a system designed and constructed by Laboratory of Process Systems Design and Implementation (PSDI) of CERTH (Ziogou et al., 2012). The technology was scaled up aiming for the production of 2 tons of 2nd generation biodiesel, named “white” diesel. For this reason an existing large hydroprocessing pilot-plant was upgraded and integrated with a newly constructed batch distillation unit. The production of 2 tons of the white diesel lasted approximately 8 months and offered a large yield of ~92% v/v.

Instrumental for demonstration was the collection of over 3 tons of WCO managed by the Municipality of Thessaloniki from 23 local participating restaurants designated by the Association of Restaurants and Cafes of Thessaloniki. The new fuel was evaluated in engines and passenger cars by the laboratory of Applied Thermodynamics (LAT) of Aristotle University of Thessaloniki (AUTh). The white diesel was tested in terms of pollutant emissions (regulated and non-regulated), fuel combustion characteristics, fuel consumption and engine operation and durability (Kousoulidou et al., 2012; Fontaras et al., 2009). The last and most significant part of the project was the demonstration of the new biodiesel-2G in a garbage truck operated by the Municipality of Thessaloniki, which started on September 10, 2012. The overall process of the whole project is shown in the simplified process diagram in Figure 1.

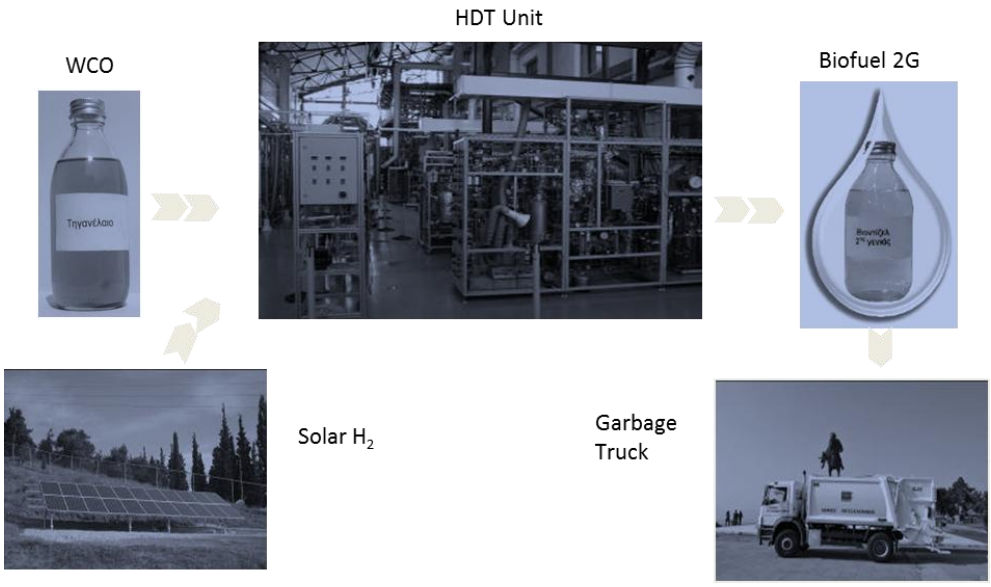

Figure 1: BIOFUELS-2G project in a nutshell

For this study a large-scale hydroprocessing pilot plant (HDT) of CPERI/CERTH was utilized. The HDT unit is a continuous-flow pilot plant, which mainly consists of a liquid feed system, a hydrogen feed system, a reactor system and a product separation system, as schematically depicted in Figure 2. It can be used for both hydrotreating and hydrockracking reaction at high pressures and temperatures. The feedstock employed was 100% WCO.

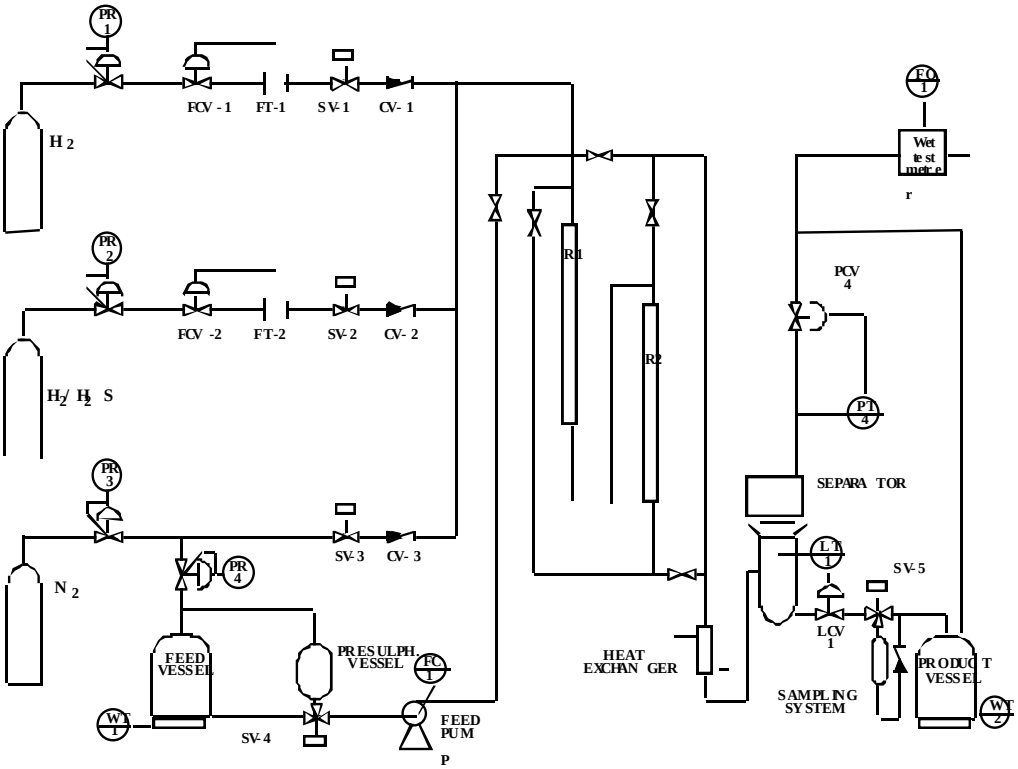

Figure 2: Simplified diagram of the large-scale hydroprocessing pilot plant HDT of CPERI/CERTH

The catalyst used in this study is pre-sulfided according to the catalyst provider´s recommended procedure. The product is separated among the gas and total liquid product. The gas product contains the excess H_2, the decarbonylation and decarboxylation by products CO and CO_2, as well as light hydrocrarbons (C1-C6). It should be noted that in an industrial-scale application,

the gas product, after cleaning is compressed and then recycled as a main source of H_2. The total liquid product contains the useful diesel molecules, which are mainly paraffins and isoparaffins (Bezergianni et al., 2010b), as well as the resulting water from the decarbonylation and deoxygenation reactions. The water is then separated as a different phase in a precipitation vessel. The water-free product finally undergoes fractionation in a batch distillation unit (HYDIS) shown in Figure 3, in order to isolate the useful diesel molecules from the unconverted heavy molecules. The capacity of the HYDIS unit is 40L. The overall process of converting WCO to "White" diesel is shown in the simplified process diagram in Figure 4.

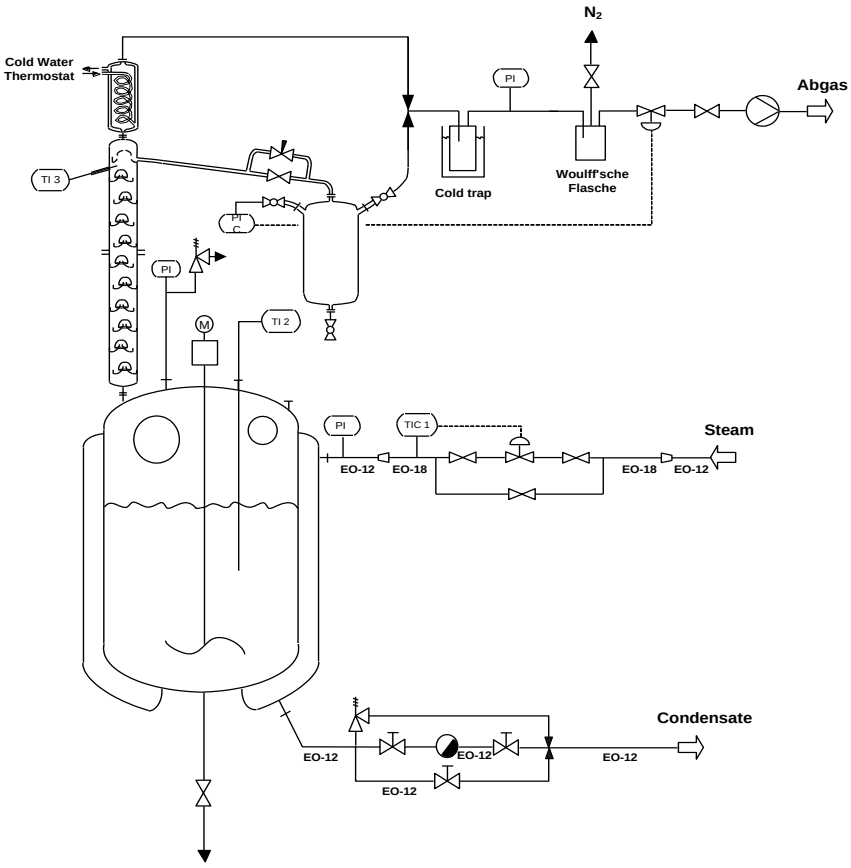

Figure 3: Simplified diagram of the HYDIS unit

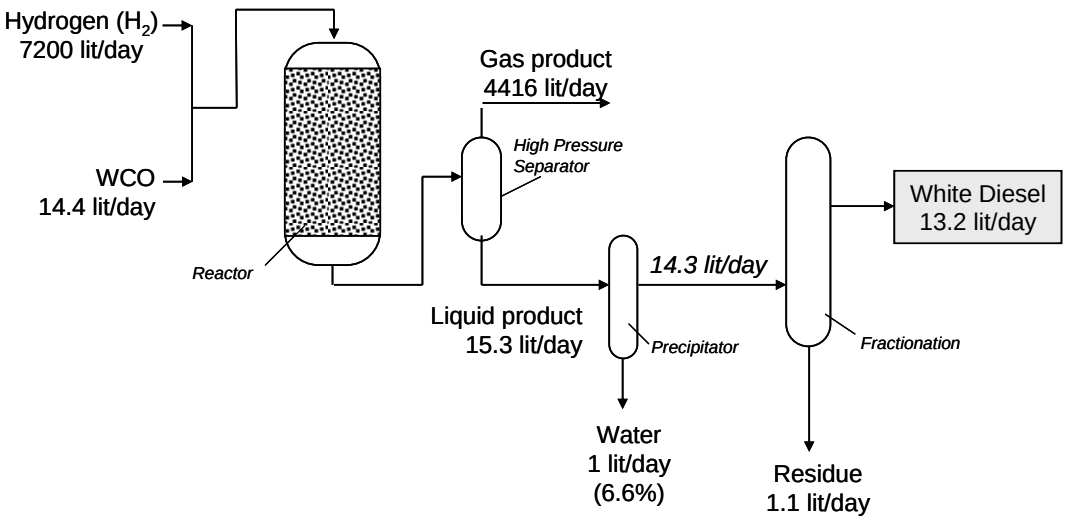

Figure 4: Overall pilot plant process for WCO conversion to White Diesel

The project also aims to perform an environmental evaluation of the "white diesel" production from WCO for a simulated refinery unit with production capacity of 30000 tonnes per year for "white diesel", which equals to 4.21 m^3/h. The refinery unit was simulated using the process simulator ASPEN Plus Version 10.2, designed to operate in a continuous mode. The GHG emissions of the simulated production process were evaluated using the GEMIS software (Edition 4.7, available from Öko-Institut, Darmstadt, Germany). The functional unit selected for the LCA study is the production of 1 kg of "white diesel".

RESULTS AND DISCUSSION

As it was mentioned above, the main premise of this research was to study the overall process of converting WCO to "White" diesel, which is shown in the simplified process diagram in Figure 4. According to the HDT daily capacity, 14.4L of WCO are processed daily, the properties of which are given in Table 1. According to the aforementioned liquid federate, the daily needs of hydrogen are 7200L. As it was observed, hydrotreating reactions cause an increase in volume and thus a total of 15,3L/d were produced daily. The water is then separated from the total liquid production in a precipitation vessel (total water 1L/d). Finally the water-free hydrotreating product underwent fractionation in the distillation unit, and 13.2L of "white" diesel were produced daily. The conversion of WCO to "white" diesel is estimated 91.6% (v/v). This result is very important because most of the WCO is converted to biodiesel.

Apparently, the catalytic hydrotreating process favours the conversion of heavy molecules in to lighter molecules (Figure 5). As it is observed, WCO consists of heavy molecules with very high boiling point while the hydrotreating product consists of lighter molecules within the diesel boiling point range. This is due to the fact that catalytic hydrotreating reactions favour cracking and therefore the production of lighter molecules.

Even though sulphur is artificially added to the feedstock in significant amount to regulate catalyst activity, the produced "white" diesel contains only traces of sulphur. This is due to the fact that hydrotreating reactions include heteroatom removal (mainly sulphur, nitrogen and oxygen), the extent of which is an important measure of the overall hydrotreatment effectiveness, as heteroatoms are not desired in the final product. The absolute values of concentrations of sulphur, nitrogen and oxygen of the hydrotreatment feed and product are given in Table 1. The extent of heteroatom removal is expressed as the percentage of the sulphur, nitrogen and oxygen contained in the feed, which has been removed during hydrotreatment reactions. In particular oxygen from 14.57% in WCO is lowered to 0.38% in the hydrotreated WCO. As it was mentioned above, the main premise of this research was to study

the overall process of converting WCO to “White” diesel. The conversion of WCO to “white” diesel is estimated 91.6% (v/v). The fuel properties of “white” diesel are given in Table 1.

Table 1: Properties of “White” Diesel

Property	Units	Value
Density (at 60°C)	g/ml	0.7532
Sulfur	mg/kg	1.54
Nitrogen	mg/kg	1.37
Cetane index		77.23
Flash point	°C	116
Water	mg/kg	0
Viscosity (at 40°C)	cSt	3.54
Total acid number (TAN)	mg KOH/gr	0
Copper strip corrosion (3 h in 50°C)		1b
Induction time/Oxidation stability (at 110°C)	h	>22
Distillation of 90%	°C	302.6
Net heating value	MJ/kg	49
Cold Filter Plugging Point (CFPP)	°C	20
Pour point	°C	23

This new biodiesel shows remarkable properties. It is a light diesel with no impurities (S, N, O, H_2O). It has an impressive cetane index which exceeds 77 (compared to fossil diesel with values ~50) and a net heating value of 49 MJ/kg (compared to conventional fossil diesel with 42-43 MJ/kg). Furthermore, even though “white” diesel is a bio-based fuel, it shows high oxidation stability (>22h while the EN standard is 6hr) and also negligible acidity (TAN). As “white” diesel is highly paraffinic(Bezergianni et al., 2010b), it exhibits problems regarding its cold flow properties, which can be addressed downstream via additives. As far as the emissions during its combustion are concerned, the use of white diesel on diesel car engines has shown a reduction on CO, CO_2 and PM emissions.The produced 2nd generation biofuels “white diesel” at this momentis employed by a designated garbage truck of the municipality of Thessaloniki for demonstrating both the benefits of using biofuels for transportation and of recycling used cooking oil.

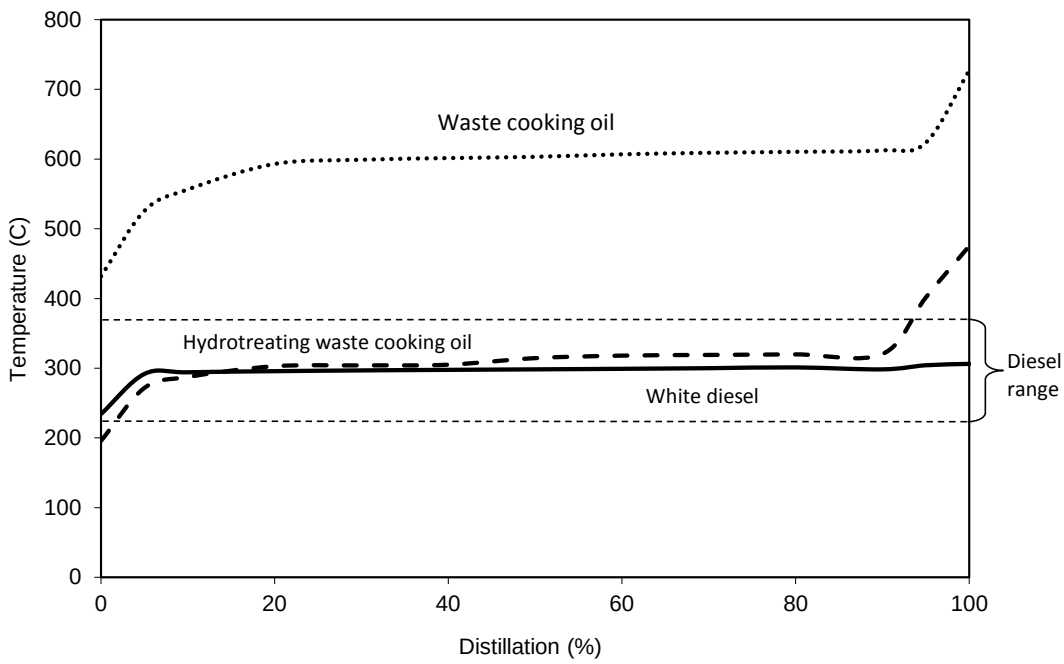

Figure 5: Comparision of distillation curves (recovery %) of WCO, hydrotreated WCO and white diesel

Finally, in the examined process (see Figure 4) the GHG emissions were estimated as 0.149 kg CO_2 eq-/ kg “white diesel” based on energy and hydrogen consumption data, rendering “white diesel” the most sustainable fuel as compared to fossil diesel and FAME biodiesel from WCO. The highest contribution to GHG emissions is attributed to the hydrogen production required in the catalytic hydrotreatment process, which depends on steam reforming of natural gas (93.95%). Furtheremore, the LCA of the proposed technology was extended to a process that incorporates solar hydrogen which offers a total reduction of 71 % on GHG emissions, improving even more the “white diesel” sustainability.

CONCLUSIONS

In this paper, the large-scale pilot plant demo-application of catalytic hydrotreating of Waste Cooking Oil (WCO) is presented. In particular, the new technology that was recently developed is currently applied in large-scale pilot hydroprocessing and distillation units in order to produce 2 tonnes of a new biodiesel to be called “white” diesel. The overall process exhibits an impressive 91.7%v/v yield from WCO to “white” diesel. Furthermore, the new “white” diesel has superior qualities over conventional fossil diesel as well as conventional biodiesel (FAME). In particular, “white” diesel has higher cetane number and heating value, increased oxidation stability as well as no water and no acidity. The only drawback of “white” diesel is associated with its cold flow properties, which can be addressed downstream incorporating an additional upgrading step (i.e. hydrocracking) or by simply mixing it with conventional diesel. Furthermore, the proposed technology was simulated on Aspen Plus in order to address its environmental impacts, in terms of the GHG emissions by performing LCA. According to the LCA results the sustainability of “white” diesel is higher than of fossil diesel, and FAME biodiesel produced from WOC. However, this sustainability can be further improved by incorporating solar hydrogen which can decrease the GHG emissions by about 71%, rendering the proposed technology extremely appealing also from an environmental perspective.

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