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Resource Planning for Sustainable Production of Tailor-Made Green Diesel

Nurul Hanim Razak^{a,b}, Nor Alafiza Yunus^{*,b,c}, Haslenda Hashim^{b,c,} Nur Naha Abu Mansor^d

^aCentre of Advanced Research on Energy (CARe), Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

^bProcess Systems Engineering Centre (PROSPECT), Research Institute for Sustainable Environment, Universiti Teknologi Malaysia (UTM), 81310 Johor Bahru, Johor, Malaysia.

^cFaculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM), 81310 Johor Bahru, Johor, Malaysia. ^dDepartment of Management, Faculty of Management and Human Resource Development, Universiti Teknologi Malaysia (UTM), 81310 Johor Bahru, Johor, Malaysia.

alafiza@cheme.utm.my

Producing energy from biomass and other organic waste residues is essential for sustainable development. Like biodiesel, green diesel is a next generation biofuels emerging due to the need for a renewable replacement of petrodiesel. Green diesel is a mixture of carbon chains which are derived from lignocellulosic biomass and the fuel properties are naturally similar to the petrodiesel. This paper discussed an integrated green diesel production route from non-food biomass resources. A systematic literature for lignocellulosic biomass resources has been developed. The systematic literature focuses on hydrodeoxygenation or catalytic hydrothermal liquefaction.

1. Introduction

In the last few decades, global warming, which is the rise in average temperature of the earth and climate change coupled with the threat to energy security are undeniably predominant among the most important issues in the world. Escalating the percentage of CO_2 in the atmosphere, rising of global temperature and diminishing fossil energy resources has generated a great interest in renewable biofuels. Due to the scarcity of fossil fuels and to population increases, there is an urgent need for renewable energy sources that can replace petrodiesel. Biomass is one of the key renewable energy sources available for the replacement of traditional fossil fuels, and consequently the reduction of CO_2 emissions (Klemes et al., 2010).

Although there are sufficient researches showing that using biofuels can efficiently mitigate the air pollution issue, there are several factors hindering biofuels from replacing petrodiesel. The main constraints are always related to the inconsistent feed stock supply, economic factors such as production and industrial evolution cost, and the efficiency of biofuels in the existing diesel engine. In order to make it more practical and user friendly, the global fuel market is more interested to blend biofuels or biochemical with petrodiesel.

Biofuels as defined by Yogesh and Veena (2017) is a generic name for liquid or gaseous fuels that are derived totally from renewable biological sources or contains a proportion of non-fossil fuels. Various conversion routes can be used to produce liquid biofuel such as green diesel from biomass resources that contains lipid and cellulosic materials. Bioalcohols, biodiesel, bio-oils, bio-ethers, bio-esters, and synthetic hydrocarbons make up basic building blocks for liquid biofuels. Among these, biodiesel and bioalcohols are widely commercialized with bio-esters appearing as attractive new biofuels blend option. This paper discussed several routes to produce biofuels specifically green diesel from biomass resources.

1.1 Green Diesel

Green diesel also known as renewable diesel. The new term applied for green diesel is a second generation diesel that refers to petrodiesel derived from catalytic hydroprocessing of bio-based renewable feedstock.

Please cite this article as: Razak N.H., Yunus N.A., Hashim H., Mansor N.N.A., 2017, Resource planning for sustainable production of tailormade green diesel, Chemical Engineering Transactions, 56, 727-732 DOI:10.3303/CET1756122 Renewable diesel is composed primarily of long-chain alkanes and short- and branched-chain alkane and eligible aromatics. The cetane number is high for long-chain alkanes and low for short- and branched-chain alkanes (Madhumita Patel and Amit Kumar, 2016). Figure 1 depicts the production route of green diesel.



Figure 1: Production of green diesel.

Green diesel is a mixture of carbon chains (e.g.: alkanes) which are derived from lignocellulosic biomass and are naturally similar to the petrodiesel. Green diesel can be prepared from triglycerides-based biomass (e.g. vegetable oil and algae oil) by hydro-treating or hydrodeoxygenation. During this process, double bond and oxygen moieties (decarboxylation, decarbonylation, dehydration) present in the feedstock are broken and removed by treating the feedstock with hydrogen under an elevated temperature with the presence of catalyst in a refinery (Kordulis et al., 2016). Another less developed approach to produce green diesel is by zeolite catalyst pyrolysis, where bio-oil produced by pyrolysis is directly upgraded to petrodiesel-like fuel by using zeolite catalyst in the pyrolysis reactor (Ahmad and Oki, 2015).

In addition, the fuel properties of green diesel compared to Ultra Low Sulphur Diesel (ULSD), and Fatty Acid Methyl Ester (FAME) which known as biodiesel shown in Table 1 (Hoekman, 2009). Impressively, green diesel has a higher cetane value and has excellent storage stability with good cold flow properties. The factor that determines the usefulness of this biomass is the calorific value. Higher calorific value indicates it is more efficient as an energy source (Bran and Crnkovic, 2014). Biodiesel contains about 11 wt.% oxygen, and has lower mass energy content than petroleum diesel. Meanwhile, the green diesel contains zero oxygen, and has mass energy content (44 MJ/kg) similar to petrodiesel (43 MJ/kg).

Fuel Properties	Petrodiesel (ULSD)	Biodiesel (FAME)	Green Diesel					
Oxygen (wt%)	0	11	0					
Carbon (wt%)	86.8	76.2	84.9					
Hydrogen (wt%)	13.2	12.6	15.1					
Cetane Number (CN)	40	50-65	70-90					
Kinematic Viscosity	2-3	4-5	3-4					
(mm²/s) at 40°C								
Specific Gravity	0.84	0.88	0.78					
Sulphur (ppm)	<10	<1	<1					
Cloud Point (°C)	-5	-5	-5 to +15					
Distillation (°C)	200-350	340-355	265-320					
Stability	Good	Marginal	Good					
Energy Content - Low Heating Value (LHV)								
Mass Basis, MJ/kg	43	39	44					
Mass Basis, BTU/lb.	18,500	16,600	18,900					
Vol. Basis. 1000 BTU/gal.	130	121	122					

Table	1: Com	parison	of	petrodiesel	biodiesel	and	areen	diesel
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1.2 Biomass Resources

First-generation bio-fuels are derived from edible feedstock from the agricultural sector such as corn, wheat, sugarcane, and oil seeds. First generation biofuels have limitation of food versus fuel issue. Second-generation bio-fuels are non-edible and comprise of raw materials derived from lignocellulosic biomass and crop waste residuals from various agricultural and forestry activities. Third generation biofuels are based on algal matter (micro- and macro algae) and cyanobacteria, which yield carbohydrates, proteins, vegetable oils (lipids), and, subsequently, biodiesel and hydrogen gas, are gaining considerable interest.

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Figure 2: Biofuels from biomass (Rawel et al., 2016)

Green diesel as second generation diesel is produced from abundant plant waste biomass. Figure 3 shows two types of biomass resources. The resources are divided into two categories: food and non-food/lignocellulosic biomass resources. Lignocellulosic biomass refers to collection of resources for green diesel which can be obtained through hydrolysis, fermentation and gasification which classified into two groups, starch sugar crops and oil seed vegetable plants. Bioethanol and biodiesel are formed from starch sugar crops through fermentation and transesterification, respectively, using different catalysts.

Non-food biomass also known second-generation biomass can be divided into four categories. They are mainly agricultural, forest, municipal waste feedstock and energy crops. Lignocellulosic biomass resources potentially to produce green diesel but additional thermo chemical processes must be carried out prior to hydrotreatment via pyrolysis or by thermal or catalytic depolymerisation. With a systematic knowledge of relation between feedstock element characteristic and production yield and quality, data can be used as a platform to select optimum biomass resources planning system for the green diesel production (Lim et al, 2015). This simple literature focuses on the production pathway of biomass to green diesel. The synthesis route will be focused is the thermo chemical synthesis of green diesel.



Figure 3: Classification of biomass (Naik et al., 2010)

2. Thermochemical Conversion

Green diesel is one of the most promising and economic solutions to mitigate air pollution issues while retaining or even improving the performance of petrodiesel. Several studies have clearly demonstrated that oxygenated biofuels are able to enhance the combustibility of diesel fuel in the engine combustion chamber, and hence, reduce the particulate matters and soot in the exhaust stream (Mwangi et al., 2015).

There are numerous biochemical/biofuels available today. Figure 4 provides a schematic of an integrated production routes for some common biofuels/biochemical, which are potentials to blend with petrodiesel. Figure 5 is drawn based on the information provided by (Barret et al., 2006). Furfural and levulinic acid are the most important intermediates and precursor of various potential fuel compounds. The possible chemicals which are derived from furfural and levulinic acid are illustrated in Figure 5 and Figure 6, respectively.



Figure 4: The possible production routes of potential diesel blending agents from biomass



Figure 5: The possible chemicals derived from furfural (Barret et al., 2006)

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Figure 6: The possible chemicals derived from levulinic acid (Yan et al., 2015)

3. Production of Green Diesel: Hydrodeoxygenation

There are several methods of conversion of biomass such as mechanical, chemical, biochemical and thermochemical processes. Chemical processes carry out a change in the chemical structure of the molecule by reacting with other substances. These processes include the wide class of chemical reactions where a change in the molecular formula occurs. One of the promising green diesel production routes is hydrodeoxygenation.

Hydrodeoxygenation or Catalytic Hydrothermal Liquefaction is the mainly thermochemical process for conversion of biomass to green diesel. The hydrodeoxygenation of liquid biomass converts the contained triglycerides/lipids into hydrocarbons at high temperatures and pressures over catalytic material under excess hydrogen atmosphere. Hydrodeoxygenation is a themochemical process that can remove oxygenated compounds from water molecules using catalyst such as nickel and zeolite materials.

The hydrodeoxygenation of liquid biomass process is quite similar to the typical process applied to petroleum streams, as shown in Figure 7 (Stella, 2013). The higher oxygen content of vegetable oils (50 wt%) has unfavourable effects such as low heating value, thermal and chemical instabilities, corrosion, immiscibility with fossil fuels and increase in tendency towards polymerization. Hydrodeoxygenation can be a promising process to remove oxygen content of the fuel thus aiding in the production of biofuels. Consequently, the production of green diesel from biomass-derived carbohydrates must involve reactions for oxygen removal (Johannes et al, 2016).



Figure 7: Schematic diagram of the catalytic hydrodeoxygenation of liquid biomass (Stella, 2013)

4. Conclusions

Overall, biomass-derived green diesel has the potential to replace fossil fuels and the only renewable neutral carbon resources. Consequently, the study on green diesel is gaining attention in this decade. Choice of biomass resources for the studies should be based on the local availabilities of the biomass resources and its

chemical properties. This paper has discussed the second generation advanced biofuels (biomass-derived diesel), the production routes and the hydrotreatment process to convert the biomass to green diesel. This commitment to green diesel will make the transition to the second generation diesel more economically convenient.

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