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MODERN METHODS OF BIODIESEL PRODUCTION: A REVIEW

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Abstract— Biodiesel is a clean alternative fuel to petrodiesel. This paper reviews the different methods of biodiesel production: pyrolysis, transesterification, Microemulsification and direct use. Many researches carried out to produce biodiesel continuously report that biodiesel is not competitive compared with petro-diesel due to the high cost of feedstock used for biodiesel production. Therefore, it is important that alternative production methods/feedstock be investigated.

Keywords— Biodiesel, Transesterification, petro-diesel, vegetable oils.

I. INTRODUCTION

Biodiesel is the monoalkyl ester of long fatty acids derived from renewable lipid feedstock such as vegetable oils and animal fats in a process called transesterification (reaction of triglycerides with an alcohol, mostly methanol, to produce fatty acid methyl esters (FAME) commonly referred to as biodiesel) for use in compression ignition (CI) engines Conley *et al.* (2006). According to Romano *et al.* (2011) biodiesel is mainly used as blends with petro-diesel and is denoted “Bx” where x is the percentage of biodiesel in the fuel. B100 therefore denotes pure biodiesel.

Biodiesel can be produced from edible, oils like palm, Soyabean, Rapeseed, and non-edible oils such as Pongamia, Jatropha, Mahua. it may also be produced from animal fat and marine algae Kumar *et al.* (2014).

Benefits of Biodiesel

The advantages relate to the use of biodiesel include

- Higher cetane number owing to its longer alkane chain
- It is a renewable fuel easily obtainable from vegetable oils and animal fats
- Higher solvency characteristics compared to petrodiesels
- Low toxicity, in comparison with diesel fuel.
- Completely biodegradable
- Lower Sulphur, nitrogen and metallic content which makes biodiesel much environmentally friendly (Gerpen *et al.* (2004); Knothe *et al.* (1997)).

Limitations of biodiesel.

- Biodiesel is of lower energy content, approximately 8% less energy per gallon.
- Biodiesel has higher cloud and pour points. This implies it will freeze more rapidly than conventional diesel
- Biodiesel is not compatible with some metals and plastics such as hoses and gasket materials, this may cause them to soften, degrade, and rupture Conley *et al.* (2006).

The rest of the paper is organized as follows. The feedstock for biodiesel production is discussed in section II. The different methods for biodiesel productions discussed in section III. Physical and chemical properties of biodiesel are discussed in section IV and lastly Concluding remarks are given in section V.

II. FEEDSTOCK FOR BIODIESEL PRODUCTION

Biodiesel can be produced from a variety sources such as: vegetable oils, animal fats and marine algae. Table 1 below shows a list of the different oils used for production and the preferred catalyst, methanol ratio, temperature and yield.

Table-1: Feedstock for Biodiesel production Moser (2009)

Feedstock	Catalyst	Methanol ratio	T/oC	Yield
Jatropha	KOH	5:1	60	99
Waste cooking oil	NaOH	9:1	60	90
Rapeseed	KOH	6:1	65	96
Canola	NaOH	6:1	40	93.5
Cotton seed	KOH	20:1	25	98
Sunflower	NaOH	6:1	60	97.1
Palm	NaOH	7:1	50	96
Madhuca indica	Pseudomona apacia	6:1	60	96



III. PROCESS OF BIODIESEL PRODUCTION

Biodiesel is mostly produced from vegetable oils (VO) and animal fats (AF). These oils were used in the past to power CI engines particularly in isolated areas where the supply of conventional fuel was becoming difficult but due to the modernization of the diesel engine these oils became unsuitable for direct use (Vrabie *et al.* (2016); Sidibé *et al.*, (2010)). Many transformation methods have been proposed aimed at rendering the oils better fuels for the CI engine as discussed below.

1. Pyrolysis (cracking)

Pyrolysis is the direct thermochemical decomposition of organic material at high temperatures in the absence of oxygen. The process is complex and consists of both simultaneous and successive reactions. In this process, thermal decomposition of organic components in biomass starts at 350 °C–550 °C and goes up to 700 °C–800 °C. The long chains of carbon chains in biomass break down into smaller molecules in the form of gases, condensable vapors and solid charcoal under the pyrolysis conditions. However, the rate and extent of decomposition of biomass depends on the process parameters of the reactor such as temperature; pressure; reactor configuration; type of feedstock Jahiru *et al.* (2012). Pyrolysis can be catalytic or non-catalytic

1.1 Thermal cracking

The gross pyrolysis of saturated/unsaturated triglycerides (TG) at 300°C results in the formation of fatty acids (FA). At higher temperatures 400-500°C cracking of FA occur giving rise to short chain hydrocarbons (HC). A variety of reactions could be put to play to produce solid (char), liquid and gaseous fuels. Based on the reaction conditions, T, P, retention time and whether or not a catalyst is used, either diesel-based fuels or gasoline-based fuels are produced Oladeji *et al.* (2015).

1.2 Catalytic cracking

In the presence of catalysts such as transition metal catalysts or molecular sieve catalysts (activated alumina) the efficiency of conversion of TG to biofuels increases. Most commonly used catalysts for the pyrolysis of biomass include NaOH and KOH Mohamed *et al.* (2017).

2. Micro-emulsification

A micro-emulsion is a system of water, oil and amphiphile (surfactant + co-surfactant) in the liquid state having thermodynamic stability and isotropic property. The amphiphile is located at the boundary between oil and the aqueous phase giving the emulsion a definite microstructure with dimensions generally in the range 1-150nm Fangrui *et al.* (1999). They could be prepared from VO with an ester and dispersant or from VO + alcohol + surfactant + co-surfactant +

cetane improvers. μ -emulsions increase the spray characteristics of VO by explosive vaporization of the low boiling constituents in the micelles (Sandeep (2012); Ashish *et al.* (2014)). Alkyl nitrate is the most common cetane number improver added to vegetable oils. If micro emulsified diesel is used directly in a compression ignition engine, some problems arise such as incomplete combustion, carbon deposit, poor cold performance, dilution of lubricant and possibly nozzle failure Rajalingam *et al.* (2016).

3. Direct use and blending

In this method VO are mixed with diesel and used directly. This method remains archaic and very inefficient as it doesn't take into account the high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricant thickening on the performance of the CI engine and the emission properties Gebremariam *et al.* (2017).

3.1 Transesterification (TransE)

According to Schuchard *et al.* (1998), TransE is a chemical reaction where an ester is converted to another through the interchange of the alkoxy moiety when the original ester is made to react with an alcohol in the presence of a catalyst. In the process of biodiesel production, TransE (alcoholysis) Meher *et al.* (2004) is the chemical reaction between TG (esters of glycerol with three chains of paraffinic or olefinic free FA of variable lengths) and alcohol (mainly methanol) in the presence of a catalyst to produce monoalkyl esters and glycerol. The overall process is usually a sequence of 3-consecutive steps of reversible reactions González *et al.* (2020). Though the stoichiometry of alcohol/TG is 3:1, an excess of alcohol is always needed. Based on the type of catalyst used different types of TransE processes result as discussed on the sections that follow

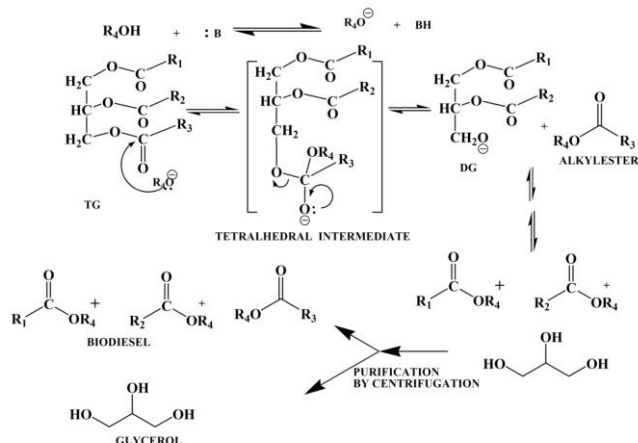
3.1.1 Base-catalyzed transesterification

In base catalyzed TransE, homogeneous catalysts such as NaOH, KOH Arun *et al.* (2011), NaOCH_3 , Na_2CO_3 , K_2CO_3 , $\text{NaOCH}_2\text{CH}_3$ could be used. The reaction proceeds by deprotonation of the alcohol by the base to produce an alkoxide and the protonated catalyst. The alkoxide then attacks the carbonyl group of the TG to form an alkyl ester and the corresponding anion of DG through a tetrahedral intermediate (TI). The same process repeats until all the TG is converted to a mixture of alkylesters and glycerol through DG and MG Jain *et al.* (2011). this is shown by Fig 1 above. Base catalysis is the most industrially employed TransE process. At the end of a homogeneously catalyzed base TransE, H_3PO_4 is often added to neutralize the base resulting in the production of vast quantities of undesired wastes. Also, the process is very sensitive to the presence of impurities like water and free fatty acids (FFA). This shortcoming is often overcome with the use of



heterogeneous catalysts (solid basic material) such as MgO. Narasimharao *et al.* (2007). Figure 1 below shows the process of base catalyzed transe

Fig. 1. Mechanism of base-catalyzed TransE of VO. Schuchard *et al.* (1998).



3.1.2 Acid-catalyzed transesterification

It is the second conventional method for biodiesel synthesis by TransE in the presence of a Bronsted acid like H_2SO_4 , HCl or sulfonic acid (RSO_3H), Parawira. W. (2010). This method is used when the VO has high FFA and H_2O contents. The reaction proceeds by the protonation of the carbonyl group of the ester to produce a carbocation which after nucleophilic attack by the alcohol produces a TI which in turn eliminates glycerol to form the ester and regenerate the catalyst. Canakci *et al.* (1999) carried out an Acid-catalyzed transesterification and noted that it is much slower than alkali-catalyzed and that the ester conversion efficiency is strongly affected by the molar ratio of alcohol to oil. In acid-catalyzed esterification, a higher molar ratio is required than that of alkali-catalyzed. Fig 2 gives an illustration

3.1.3 Enzyme-catalyzed Transesterification

Lipases are enzymes that catalyze the hydrolysis and synthesis of a variety of acyl glycerols at interface of lipid and water. This method is not applied for the commercial production of biodiesels due to unfavorable retention time and reaction yields but remains a promising method for the synthesis of high purity biodiesel due to the regioselectivity and stereoselectivity of lipases. This could eradicate problems encountered in downstream processing of biodiesel such as separation of catalyst, unreacted methanol, glycerol recovery, removal of inorganic salts, risk of FFA and water contamination as well as soap formation, Venkates *et al.* (2014)

3.1.4 Supercritical methanol transesterification

Supercritical TransE is the non-catalytic synthesis of biodiesel from methanol and TG at a T and P above the critical point of

the mixture. The reaction mechanism is the same as that of acid-catalyzed in that the H-bond of methanol is weakened at high temperatures ($>200^\circ\text{C}$) to form a free alcohol monomer which directly attacks the carbonyl carbon of the TG or FFA to form a TI which then decomposes to produce the methylester. The shortcoming of this method is the high cost of production due to the use increased T and P which also contribute to the high temperature degradation of the FAME formed (Silva *et al.* (2014; Somkiat *et al.* (2011)).

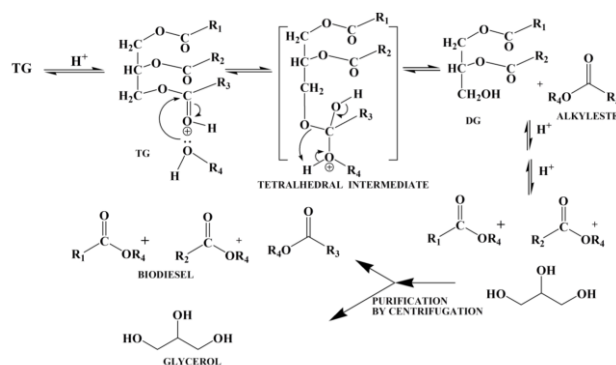


Fig. 2. Mechanism of acid-catalyzed TransE of TG. Ejikeme *et al.* (2009)

3.1.5 Conclusion

There are basically four different methods for the production of biodiesel namely; Microemulsification, direct use and blending, pyrolysis and transesterification. The section that follows throws more light on the physical and chemical properties of biodiesel.

IV. PROPERTIES OF BIODIESEL PRODUCED FROM DIFFERENT FEEDSTOCKS

4.1 Physical properties

The important physical properties of biodiesel from any given source include; density, kinematic viscosity, flash point, cloud point, pour point, specific gravity Ved *et al.* (2013). According to the study carried out by Thangapandian *et al.* (2015), the properties of biodiesel greatly depend on the feedstock used, this is further substantiated by table 2 below.

Table-2: physical properties of biodiesel from various feedstock

V. CONCLUSION

The objective of this study was to review the different methods currently employed for biodiesel production. Currently there are four methods that are used: pyrolysis, direct use/blending, Microemulsification and transesterification (acid-catalyzed, base-catalyzed, enzyme-catalyzed and supercritical methanol transesterification). Different feedstocks such as; jatropha, canola, sunflower, palm, cotton seed rapeseed and waste cooking oils are used. Most of the researches reviewed indicate that biodiesel is mostly produced by the process of transesterification using vegetable oils as feedstock. However, the production of biodiesel from any of the vegetable oils is uneconomical due to the high prices of these oils. It is therefore important that, alternative production schemes requiring low cost feedstock be investigated.

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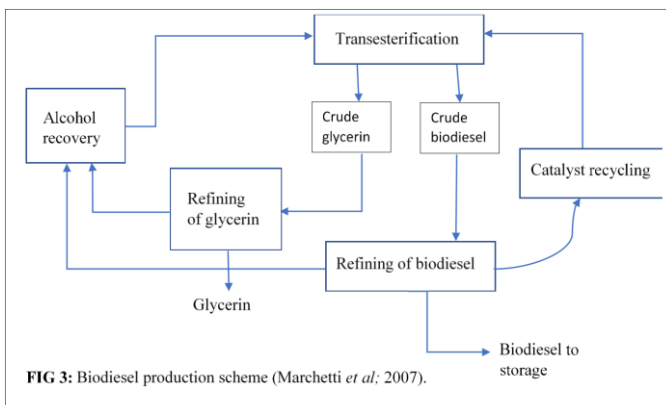
Feedstock	Density(Kg/m ³)	μ (mm ² /s)	Flash point/oC	Pour point	References
Diesel	850	2.6	68	-20	Parawira <i>et al.</i> (2010)
Biodiesel	880	4.29	182	-8	Jun <i>et al.</i> (2017)
Jatropha	880	4.8	135	2	Parawira <i>et al.</i> (2010)
Waste cooking oil	920	2.88		-12	Pati <i>et al.</i> (2014)
Rapeseed	930	4.56		-15	Azocar <i>et al.</i> (2016)
Canola	880	4.51	110	-5	Fan <i>et al.</i> (2009)
Cotton seed	874	4.27	142	-15	Madiwale <i>et al.</i> (2017)
Sunflower	870	1.9	183	1	Thirumarimurugan <i>et al.</i> (2012)
Palm	874.8	4.452	135	12.1	Borhanipour <i>et al.</i> (2014)

4.2 Chemical properties

From the studies carried out by Okullo *et al.* (2012) on the transesterification of jatropha and castor oils and Anguebes-Franseschi *et al.* (2019) on the transesterification of sailfin catfish biomass oil, the reported the most commonly studied chemical properties of biodiesels. These are; cetane number, metallic content, fatty acid composition, water content, ash content, acid content, calorific value, iodine index, peroxide index. Table 3 below gives a list of different oil feedstocks and their chemical properties. Whatever the starting feedstock and the choice of catalyst, the process of biodiesel production can be summarized as shown on figure 3 below Marchetti *et al.* (2007)

Table-3: chemical properties of biodiesel from different feedstocks

Feedstock	Water content (%)	Ash content (%)	Carbon residue (%)	Acid value (mgKOH/g)	Calorific value (MJ/Kg)	References
Diesel	0.02	0.01	0.17		42	Parawira <i>et al.</i> (2010)
Biodiesel	<0.05	0.01	0.05	0.5	39.48	Hoekman <i>et al.</i> (2011)
Jatropha	0.025	0.012	0.20	0.40	39.23	Parawira <i>et al.</i> (2010)
Waste cooking oil	0.033				44.4	Pati <i>et al.</i> (2014)
Rapeseed	0.031			0.77		Azocar <i>et al.</i> (2016)
Canola	<0.05	0.09	<0.05	0.14		Chhetri <i>et al.</i> (2012)
Cotton seed	0.52			0.3	36.8	Eevera <i>et al.</i> (2013)
Sunflower				0.5	33.5	Cervero <i>et al.</i> (2008)
Palm	0.0297			0.115	39.9	Borhanipour <i>et al.</i> (2014)





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