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Selective Characterizations of Crude Glycerol Co –Product with Biodiesel from Homogenously Alkaline Catalyzed Trans-Esterification of Neem Oil.

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Abstract: *Glycerol is a valuable byproduct in biodiesel production by Trans esterification reaction. The purity of glycerol obtained is low due to the presence of impurities such as residual catalyst, water, soaps, salts and esters formed during the reaction. In recent years that both purification and the transformation of glycerol into useful products have attained rising importance due to the rapid growth of the biodiesel industry. However characterization of crude glycerol is very essential to its value-added conversion. The physic-chemical characteristics of the neem oil feedstock was established in terms of acid value (33.21 mgKOH/g) ,iodine value(82.31g/mgKOH), viscosity (440500 Cp), saponification value (200.45mgKOH/g), cloud point (16^{o}C), pour point (6.8^{o}C) and density of 0.98g/cm3 against the standard. The high FFA esterified neem oil was Trans esterified with 1% oil weight KOH homogenous catalyst and 6:1 moles of methanol to neem oil. The crude glycerol achieved was characterized for its specific gravity (1.34), boiling point (321^{o}C), viscosity at 25^{o}C (1517Cp), pH (9.8), refractive index at 25^{o}C (1.552), acid value (2.16mgKOH/g), moisture (5.40%), iodine value (50.18g/mgKOH), colour (dark brown), ash content (2.11%) and free fatty acid of 1.35mgKOH/g. In addition, the FTIR of both the crude and pure/commercial glycerol affirmed the disparities between these two samples. The yield of the crude glycerol was estimated to be 8.63% from 86.27% of biodiesel.*

Keywords: Crude glycerol, biodiesel, KOH homogenous catalyst, esterification & Trans esterification.

1.0 INTRODUCTION

Biodiesel is a green resources that can be substituted as an unconventional synthetic fuel for fossil diesel engines from natural vegetable oils, animal lipids and waste cooking oils [1]. It is the product acquired when an alcohol is chemically reacted to a vegetable oil or animal fat to create alkyl esters of fatty acids [2]. While glycerol is a co-product, a homogenous catalyst like potassium hydroxide is required [3]. With every 100 kg of biodiesel, the estimated proportions of the reactants and reaction products contain 10 kg of crude glycerol. Recently, the world's output of glycerol has risen geometrically as a result of increased biodiesel processing. Crude glycerol as the result of biodiesel production is approximately 50 percent pure and of low economic benefit due to the presence of impurities such as catalyst, methanol and soap [5]. However, crude glycerol can be purified with treatment through fractional vacuum distillation [6], filtration [7], acidification [8], ion exchange [9] and chemical addition [10] to a number of applications in the processing of animal feed [11], cosmetics [12], Pharmaceuticals [13], plastics, and general scientific applications [14]. Neem oil is the vegetable oil compressed from neem seed (Azadirachta indica) and evergreen tree widely distributed across tropical Africa including Nigeria. It is undoubtedly the most useful neem products available commercially. Neem oil can be manufactured either mechanically or chemically by solvent from dried neem seed. Neem oil is endowed with essential fatty acids, triglycerides, calcium, and vitamin E [15]. Fatty acids found within neem oil are 21.4% stearic acid, 52.8% oleic acid, 2.1% linoleic acid, and 12.6% palmitic acid, [15]. The oil includes three bitter compounds namely nimbin, nimbinin, and nimbidin, which are primarily responsible for its medicinal qualities, in cosmetics formulation, and as an effective mosquito repellent [16]. Neem oil is characterized for its high free fatty acid components followed by a moisture content, both of which have a major impact on the trans-esterification of alcohol glycerides with a catalyst [16]. A cheaper and non-edible feedstock of fatty acids, such as waste food oil, animal fats, and processing by-products Using vegetable oil is recommended to monitor the demands of biodiesel production and food safety allowance. Nonetheless, there are some non-edible vegetable oil with high fatty acids which can be chemically regulated to an

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FFA content not exceeding 2%. [17]Therefore, the initial esterification process to decrease the amount of free fatty acid is important because the conversion of the oil to biodiesel and glycerol depends on the feedstock's quality, purity, and regulated FFA. This work characterizes therefore crude glycerol obtained from the processing of biodiesel with neem seed oil and potassium hydroxide as a catalyst, with an objective

2.0 MATERIALS AND METHOD

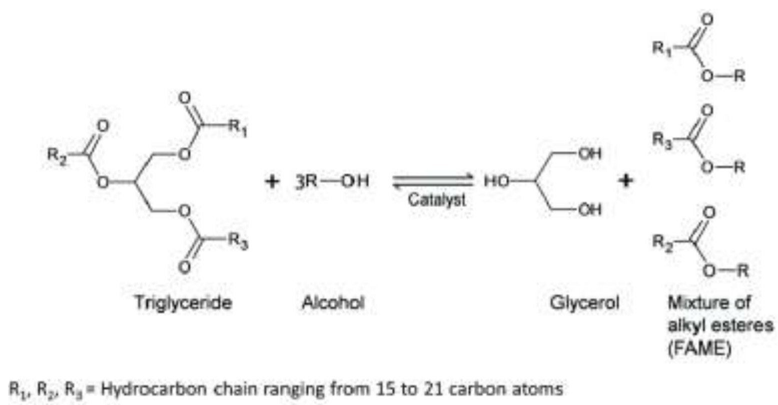
Filtered neem oil, glycerol (commercial grade) methanol, KOH pellets, distilled water, concentrated sulphuric acid, carbon tetrachloride, wij's reagent,10% potassium iodide, starch indicator, 0.1M sodium thiosulphate, phenolphthalein indicator,0.5M hydrochloric acid, 95% ethanol, diethyl ether, 0.1M ethanolic potassium hydroxide, analytical balance, 500ml separating funnel, soxhlet apparatus, burette, pipette, conical flask, and volumetric flask

2.1 Esterification of neem oil

200ml neem seed oil was measured and transferred into the reaction flask and preheated by the hot plate to the desired reaction temperature before the reaction started. The methanol to oil ratio was 6:1 and 1% wt/wt sulphuric acid catalyst was added. The mixture was continuously stirred at a temperature of 65^oC for a few minutes, poured into separating funnel and allowed to settle for one hour. Afterward, the top layer which a component of methanol, water, sulphuric acid, and other impurities was removed. The lower layer which is the oil phase is ready for trans esterification reaction with an alkali catalyst

2.2 Trans esterification.

The trans esterification reaction for neem seed oil was conducted using a 6:1 molar ratio of methanol to oil and potassium hydroxide catalyst concentration of 1% by weight of the oil at 65^oC under a reflux condenser with a mechanical stirrer. After two hours of reaction time, the mixture was transferred to a 500ml separating funnel. Two distinct layers were formed after allowing the reaction mixture to stay overnight for 12 hours. The upper methyl esters (Biodiesel) layer with the lower crude glycerol layer were separated and use as required for the study. The methyl ester layer was heated at 85^oC for 1 hour to remove the methanol [19].



[34].

2.3 Physico-chemical parameters of Neem seed oil

Acid value, iodine value, saponification value, cloud point, pour point and density and viscosity of the neem oil were determined with respective standard methods.

2.4 Physico-chemical parameters of the crude glycerol

pH, ash content, moisture content [20], specific gravity[21],free fatty acids [22] , iodine value and acid value were determined [23]. Viscosity by viscometer, refractive index by refractometer, density, colour, and boiling point [33] were also determined. All measurements were in triplicates.

2.5 FTIR spectra

The crude sample and the commercial-grade were scanned with Shimadzu FTIR-8400S with a range of 4000-500nm wavelengths.

3.0 RESULTS AND DISCUSSION

Table 1. Yields of neem oil biodiesel and crude glycerol.

Yield	Biodiesel	Crude glycerol
Volume(ml)	172.54	17.25
Percent /%	86.27	8.63

Table 2. Physico-chemical properties of neem oil

Property	Crude glycerol	Reference	
		Citation	Value
Physical state at room temperature	Golden yellow	-	
Acid value (mgKOH/g)	33.21	[31]	44
Iodine value (g/mgKOH)	82.31	[31]	82-98
Viscosity(centipoise)	440500	[32]	358300
Saponification value(mgKOH/g)	200.45	[31]	191-202
Cloud point (°C)	16.00	[32]	19
Pour point(°C)	6.80	[32]	10
Density(g/cm^3)	0.98	[32]	0.92

Table 3. Physico-chemical properties of crude glycerol against the commercial grade

Parameters	Crude glycerol	Commercial (purified) glycerol	
			Reference
Specific gravity	1.34	1.25	[24]
Boiling point (°C)	321	290	[25]
Viscosity (Centipoises at 25°C)	1517	1412	[26]
pH	9.8	6.7	[27]
Refractive index (25°C/D)	1.552	1.4730	[27]
Acid value (mgKOH/g)	2.16	2.00	[28]
Moisture content (%)	5.40	≤ 5.00	[29]
Iodine value(g/mgKOH)	50.18	90	[29]
Colour	Dark brown	Colourless	[29]
Ash content (%)	2.11	< 0.002	[29]
FFA (mgKOH/g)	1.35	0.05	[30]

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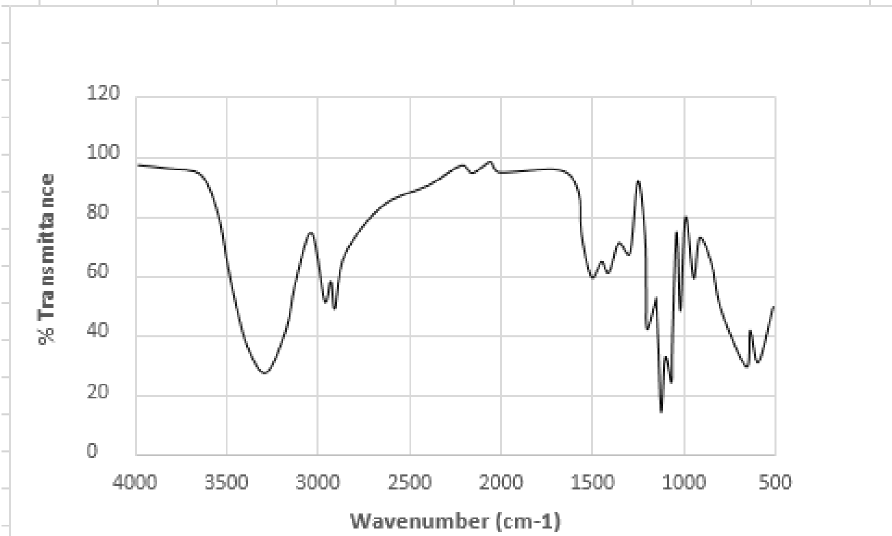

Figure 1. FTIR of pure glycerol.

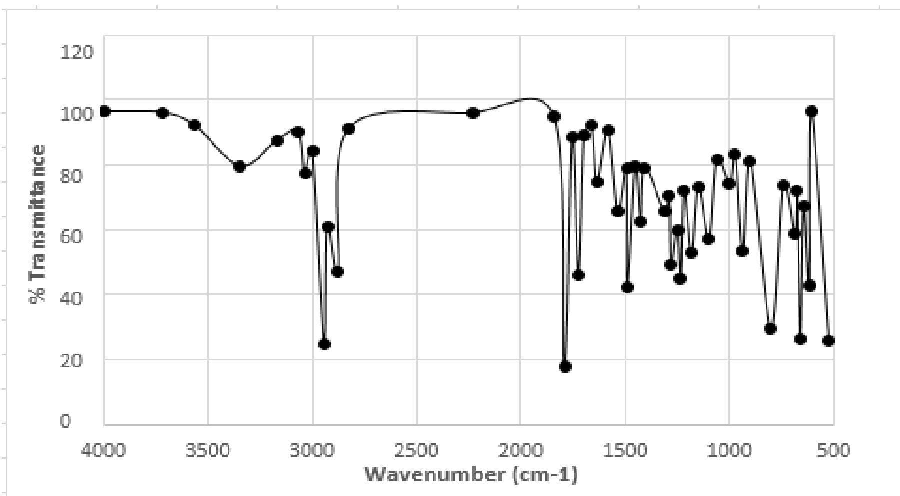

Figure 2. FTIR of crude glycerol

The yield of the methyl ester (Biodiesel) and the crude glycerol were disclosed in terms of volume and percentage (Table 1) and with selected Physico-chemical properties of neem oil as the feedstock the entire process. (Table 2). Specific gravity, boiling points, viscosity, pH, refractive index, acid value, colour, ash content, and free fatty acid of the crude glycerol co-product were the parameters that are significantly higher than the pure/commercial form. These are strong indications of the intrinsic physical and chemical natures of the crude glycerol by-product. The FTIR of both the pure/commercial glycerol (Figure 1) and crude glycerol achieved from this process (Figure 2) supported the aforementioned claims. The Absorption spectra of the crude glycerol were complex exhibiting peaks of many functional groups at 3321.58 cm-1, O-H stretching peak was registered and at 1737.61 cm-1,the sharp pronounced peak was assigned to C = O stretching of esters group resident in the crude glycerol. O-H bending was detected at 910.22 cm-1, while the COO group specific to soap contaminants demonstrated a peak at 1550.80 cm-1, reflecting dissolved salts in the crude glycerol. A spike at 3010.10 cm-1 is credited to C= C identity in the alkyl portion of the fatty acid chain [18]. FT-IR spectrum of the pure/commercial glycerol is shown in Figure 5. From the full spectrum, it was characterized that the functional groups observed in this continuum were similar to those mentioned in literature. The FTIR spectrum of the pure/commercial glycerol revealed O-H stretching at 3265 cm-1 while C-H stretching was disclosed by the peaks in the range of 2810-2947 cm-1. The C= O stretching group present in the crude glycerol at 1655 cm-1 was inactive in the pure/commercial glycerol spectra. The peak at 1556 cm-1 was already excluded in the refined glycerol reflecting the elimination of the salts. Twisting of the C-O-H group was also recorded in the range of 1350 to 1420 cm-1 of the C-O stretching of the primary alcohol, as seen at 1211 cm-1.

4.0 CONCLUSION

With trans esterification of triglycerides (neem oil) to make biodiesel with a catalyst, crude glycerol is generated in significant amounts. The advent of methyl ester production has significantly changed the global economy. Increasing volumes of glycerol have started dumping to the world market, while prices have begun to drop, approaching the smallest historical norms. Glycerol can be a very useful co-product of the biodiesel production process, with hundreds of applications when refined to a chemically pure material. However, purification at this stage is costly and typically out of the economic viability range for the medium and small-sized biodiesel sector. Alternative usage of crude glycerol to produce an increasingly competitive global economy for biodiesel should be investigated as it has been generally acknowledged as a renewable resource to the chemical industry.

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