Treatment And One Parameter Modelling Of Activated Carbon On Crude Glycerol Co-Product Of Biodiesel From Homogenously Catalyzed Waste Groundnut Oil.

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Abstract: *Crude glycerol as a by-product of biodiesel production is technical of low grade with significant levels of impurities in the form of carboxylic acids emanating from catalyst, alcohol, soap, and water. Selected parameters of the crude to treated glycerol with 12g activated carbon after acidification (12ml) with 1.19M sulphuric acid to the pH of 7 at $60^{O}C$ for 30minutes with extra characterization (FTIR) reveal pH of 11.24 to 6.57, the relative density of 1.0504 to 1.2120, the refractive index of 2.4185 to 1.4540, the viscosity of 1026Cp to 940Cp, the water content of 9.27% to 0.23%, the ash content of 6.14% to 0.04% and the glycerol content of 15.56% to 95.96%. One parameter adsorption isotherm (Henry's model) was applied in the adsorption pattern of the crude glycerol impurities on the activated carbon with viscosity as an index of performance. This model supports the adsorption process by $y = 1.7833x - 1583.9$ with the regression of (R^2) 0.7731.*

Keywords: Biodiesel, crude glycerol, activated carbon, henry's adsorption model and viscosity.

1.0 INTRODUCTION

Approximately eighty percent of global energy supplies come from carbon-based fuels, such as petroleum, coal, and biomass. Liquid biofuels are energy distributors from these collections of feedstock, to biodiesel, bioethanol, bio methanol, or bio-oils. They are considered liquid fuels from biomass, such as forestry and agricultural byproduct that undergo bio and thermo-chemical processes [1].Biodiesel is an applicable renewable energy source that can be achieved through the Trans esterification of methanol glycerides, consisting of methyl esters (FAME) of fatty acid. The production of biodiesel takes the form of a triglyceride Trans esterification with three methanol molecules around a basic or acid catalyst at one or two-phase reaction systems, under high-pressure and temperature to achieve biodiesel with glycerol byproduct [2]. Considering the cheap demand for glycerol, its purification remains a costly process, specifically with the medium-scaled enterprises; thus engaging, researchers in seeking various methods for incorporation in different application crude glycerol, optionally with a very simple purification step. There are potentials of crude glycerol for bio-refineries under the cheaper prices of crude glycerol that provides value-added products. There are far more than 1500 glycerol end products, as the supply market and price determinants are challenging protocols [2]. The massive influx of unrefined glycerol can make new applications with the contribution that offset the variations in biodiesel prices to fossil diesel, and also drop the energetic demands for production of biodiesel. In 2012, the global crude glycerol production was about 4 million tons with a forecast of 4200 million in 2020.

This rapid expansion was a reflectance, of a significant decline in the costs of treated glycerol from about $3200 per ton in the EU and $2000 per ton in the US in 1995 to less than $500 per ton and $600 per ton in 2010[2]. Crude glycerol prices were reduced by a triple factor as its price was restored to about $900–965 per ton, with the associated crude glycerol price crash on a four-fold scale [2]. Naturally, the low prices of glycerol assist to enhance the prospects of possible applications as they are largely dependent on biomass for biodiesel technology. Theoretically, Glycerol which is propane-1, 2, 3-triol by IUPAC nomenclature is an organic multifunctional compound with both hydrophilic and hydrophobic properties on a stable chemical structure with three groups of hydroxyls. And with the thermal conductivity, it demands sufficient energy that will break bonds for the formations of other compounds [4]. The by-product however includes contaminants like soap, methanol, fatty acids, water, and residual catalyst [5]. Glycerol is used in cosmetic, pharmaceutical, and petrochemical industries with highly marketable products [5]. The Trans esterification reaction is among the methods for producing glycerol by-products with biodiesel at ten to twenty percent volume [6]. The application of acidic and basic agents allows the by-product to retain the capacity to be reused through physical and chemical treatment. The introduction of acids can transform the soap mixture into free fatty acids with salt. Free fatty acids in glycerol are insoluble and therefore give a distinct layer over glycerol with salt at the base as residual reactants like methanol and water generate a soluble glycerol mixture. Through evaporation, approximately 85 percent

purity of methanol can be separated from the mixture and be the process to 99 percent [5]. Usually, a clear volume of crude glycerol could be reacted with 85 percent phosphoric acid solution to the pH of ± 2.5 and to be allowed to stabilize within 24 hours till the development of three phases. The top layer will be a free fatty acid, glycerol in the middle layer, and inorganic salt in the lower layer. The filtrate of crude glycerol is isolated from the salt deposits after vacuum filtration [5]. Whereas, using adsorption to obtain pure glycerol would require an excellent adsorbent with good absorption properties in terms of concentration, surface area, temperature, particle size, pH and contact time as factors that affect the method. Activated carbon selection is therefore very rational and necessary, since it is an adsorbent that is used in many fields, such as liquid and gas purification, as a catalyst or co-catalyst with its active adsorption capacity [7]. This material has a well-established porosity and a great internal substrate with a relatively high content of carbon with few inorganic compositions [8]. The nature of pores dimensions in activated carbons are functions of the pore shape distributions with the surface chemistry which are determined by the physical and chemical properties of the raw materials, the activation method, and the activation conditions [9]. They can be produced using both physical

methods and chemical methods of activation. The former method entails a two-step operation. First, under high temperatures and inert atmosphere, the raw material is carbonized with high temperatures and inert conditions. In the second stage, activation was done at elevated temperature of 800-1000°C with air, steam, or CO_2 and subsequently with the addition of activating reagents such as sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$), potassium carbonate (K_2CO_3) or potassium hydroxide (KOH) [9]. At an inert atmosphere and reasonable temperatures, the absorbing material is then subjected to thermal decomposition [9]. But the technique of chemical activation has some significant benefits to the technique of physical activation as it needs to reduce temperatures for activation and fewer periods for activation. Activated carbon is obtained in high yields with an active surface dimension and well-developed micro porosity only in a single step [10], [11]. Unfortunately, because of the activating agents' use, this method is expensive. Some impurities are created during this process, and they require intensive washing to remove them. Activated carbon obtained with the use of $ZnCl_2$ is the most generally used adsorbent because it has an excellent high surface area and high organic compound adsorption capacity [12].

2.0 MATERIALS AND METHODS
Crude glycerol [13], laboratory-grade activated carbon (Reagent Grade), distilled water, beakers, conical flask, separating funnel, stirrer magnetic heater, analytical balance, measuring cylinder , methanol, sodium hydroxide, sulphuric acid, sodium meta periodate, pH meter, and molecular sieve.
2.1 MSDS of lab grade activated carbon [14]
2.2 Acidification and characterization of Crude Glycerol
200g (33.34ml) of crude glycerol from biodiesel byproduct with used groundnut oil was characterized (pH, relative density [15], refractive index [16], a viscosity [17], water content [18], ash content [19], glycerol content [20] and with FTIR spectrum), heated and stirred by using magnetic stirrer followed by H_2SO_4 1.19 M addition drop wise until the pH is 7 while the heating temperature was maintained at 60°C. Afterward, the crude glycerol mixture (74.82ml) was cooled and left for 30 minutes.

2.3 Treatment of Crude Glycerol with Lab. Grade Activated Carbon

20ml of the acidified crude glycerol was added into 12 g lab-grade activated carbon and stirred for 30 minutes at room temperature with the allowance of 24hours. Afterward, the entire filtrate was agitated with some molecular sieve and finally obtained with vacuum filtration [21].

2.4 Henry's Adsorption modelling
3.0 RESULTS AND DISCUSSION

This is the simplest isothermal adsorption where the percentage of surface adsorption capacity is proportional to the partial pressure of the adsorptive gas this model defines an acceptable adsorption fit at relatively low doses, such that all adsorbed molecules are isolated from their closest available neighbors [22]. The balance thus adsorbs concentrations in the liquid with the adsorbed phases in a linear relationship as;

$$q_e = K_{HE}C_e,$$

Where qe is amount of the adsorbate at equilibrium (mg/g), KHE is Henry's adsorption constant, and Ce is equilibrium concentration of the adsorbate on the adsorbent.

$$q_e = K_{HE}C_e, \quad\text———\quad \boxed{1}$$

$$q_e = \frac{(C_i - C_e)V}{m} \quad\text———\quad \boxed{2}$$

2, 4, 6,8,10 and 12g lab-grade activated carbons were reacted with the 10ml of the acidified crude glycerol mixtures respectively at each quantity of the adsorbent with stirring for 30 minutes at room temperature. The individual filtrates were collected using vacuum filtration and analyzed for viscosities as an index of treatment.

Figure 1. The three layers seperation

Figure 2. Crude glycerol

Figure 3.Acidified CG

Figure 4. Acidified CG with AC

Figure 5. Vacuum filtration of the acidified CG from AC

Figure 6. Treated CG as filtrate with 3A mol. sieve

Figure 7. Treated and purified glycerol

Table 1. Selected physicochemical properties

Property	Crude glycerol	Treated glycerol	Pure glycerol	
			Value	REF
Colour	brown	colourless	colourless	[23]
pH	11.24	6.57	6.84	[23]
Relative density	1.0504	1.2120	1.2613	[23]
Refractive index	2.4185	1.4540	1.4720	[23]
Viscosity (Cp)	1026	940	954	[23]
Water content (%)	9.27	0.23	0	[23]
Ash content (%)	6.14	0.04	0	[23]
Glycerol content (%)	15.56	95.96	99.90	[23]
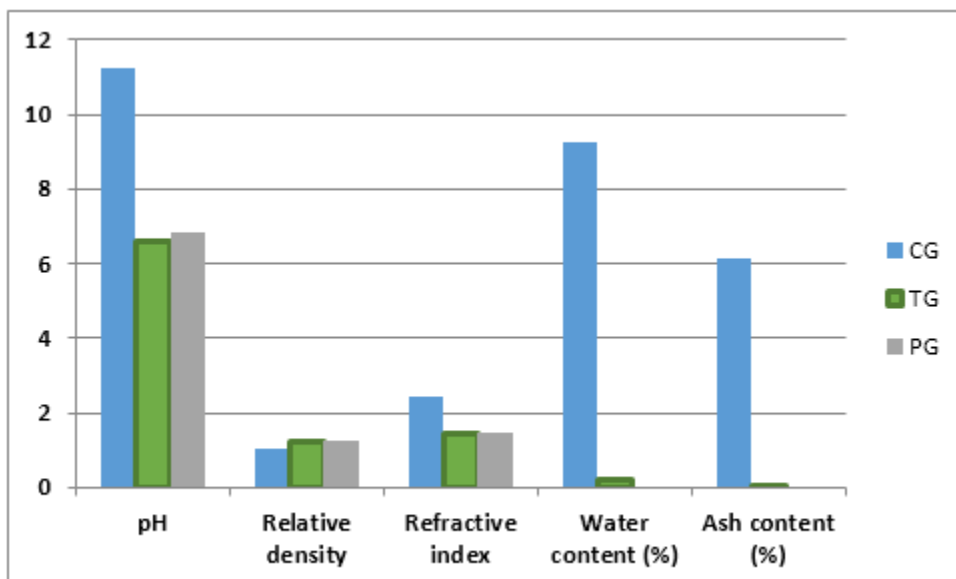
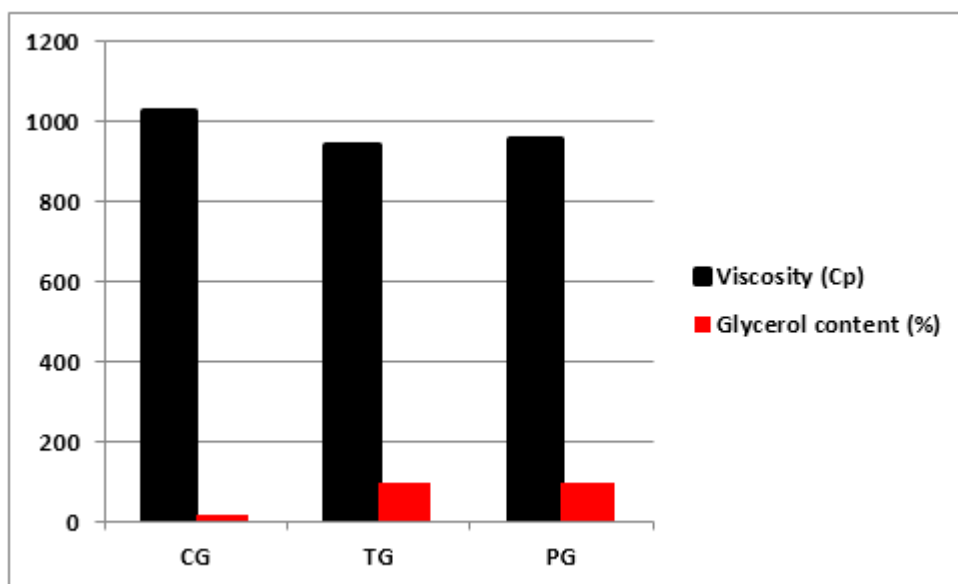Figure 8.Comparative physicochemical properties of crude (CG), treated (TG) and pure (PG) glycerol.

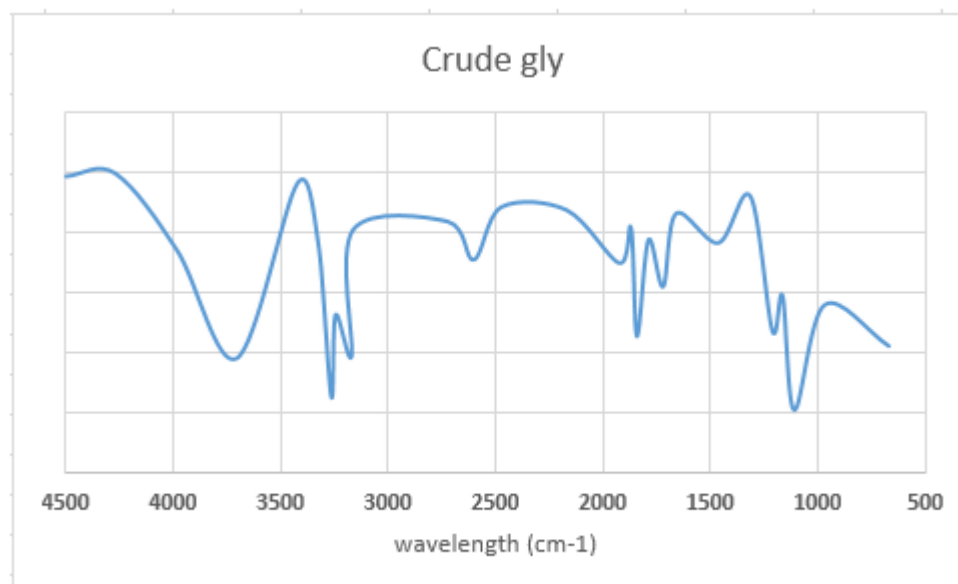Figure 9.Comparative physicochemical properties of crude (CG), treated (TG) and pure (PG) glycerol.
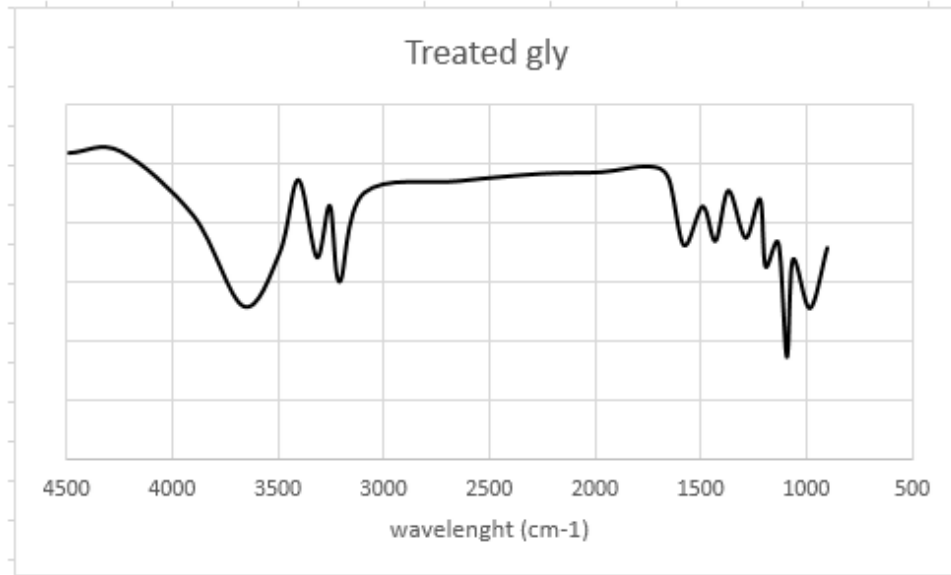

Figure 10. FTIR of crude glycerol

Figure 11. FTIR of activated carbon treated glycerol

Figure 12. FTIR of pure glycerol

Table 2. The FTIRs

Crude glycerol	Frequency	Assignment	Class	Structure
	1100	C–O stretch	Alcohol	R_2CHOH
	1560	C–O stretch	Carboxylic acids	RCO–O–
	3300	O–H stretch	Alcohol	R–OH
Treated glycerol	1100	C–O stretch	Alcohol	R_2CHOH
	3300	O–H stretch	Alcohol	R–OH
	3610	O–H stretch(free OH^-)	Alcohol	R–OH
Pure glycerol	1000	C–O stretch	Alcohol	R_2CHOH
	1100	C–O stretch	Alcohol	R_2CHOH
	3610	O–H stretch (free OH^-)	Alcohol	R–OH

Table 3. Henry's one parameter adsorption factors

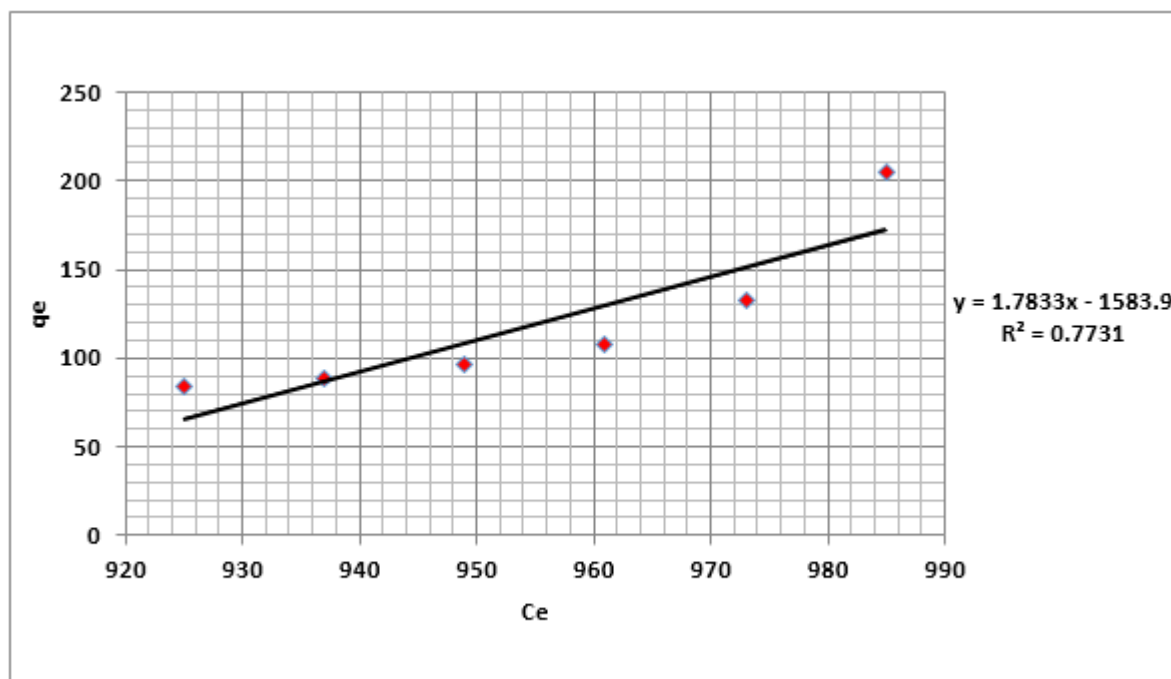| $C_f(Cp)$	$C_e(Cp)$	Adsorbent mass(g)	Volume (ml)	$Q_e(Cp)$
1026	985	2	10	205
1026	973	4	10	133
1026	961	6	10	108
1026	949	8	10	96
1026	937	10	10	89
1026	925	12	10	84

Figure 13. Henry's one parameter isotherm of activated carbons treated crude glycerol

The crude glycerol (Figure 2) was technically separated, acidified (Figure 3), treated with activated carbons (Figure 4), vacuum filtrated (Figure 5), and dehydrated (Figure 6) with molecular sieves in obtaining a better grade of glycerol (Figure 7). The comparative physicochemical characteristics of initial crude glycerol treated glycerol in the course of this project, and pure glycerol was disclosed in table 1, figure 8, and figure 9 accordingly. The high levels of pH, refractive index, water content, ash content, and viscosity of the crude glycerol were significantly controlled concerning pure glycerol. Meanwhile, the relative density and glycerol content was boosted with the treatment.FTIR of the crude glycerol (Figure 10), treated glycerol (Figure 11), and the pure glycerol (Figure 12) as evaluated in table 2. This reveals a band around 1560cm-1 that was attributed to the presence of impurities as carboxylic acids emanating from the formation of soap sediments as the treated and the pure glycerol lack absorption at this band, justifying the treatment efficacy of activated carbons. Also, absorption at 1100cm-1, 3300cm-1, and 3610cm-1 with the treated and pure glycerol confirm the identities of good grade glycerol. Table 3 presents the henry's adsorption isotherm with the varying amount of the adsorbent from 2 to 12 grams in batches with the effect of viscosity as the singular control factor with the treatment. The model was eventually defined as; $y=1.7833x-1583.9$ with a coefficient of 0.7731.

4.0 CONCLUSION

The objective of obtaining good grade glycerol from its crude form from biodiesel production through one parameter adsorption process of the activated carbons has been demonstrated as a valuable by-product.
The initial magnitudes of the selected parameters such as pH, refractive index, water content, ash content, viscosity, relative density, and glycerol content with the crude glycerol were remarkably controlled to the grade that can be used directly or further be processed into value-added chemical products industrially. This implies that it can contribute significantly to a sustainable environmental circular economy turning the biodiesel industry into a profitable one.

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