



Original Research Article

DEVELOPMENT OF POLYMER CATALYST FOR THE PRODUCTION OF BIODIESEL FROM RUBBER SEED OIL

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ABSTRACT

Polymer catalyst for biodiesel production and the catalytic activity dependence of preparation condition, ranging from adsorbed radiation dose, reaction temperature and retention time were investigated in this study. The catalyst was synthesized by radiation – induced graft polymerization of acrylonitrile onto cassava starch substrate followed by amination with trimethylamine and the product was further treated with sodium hydroxide solution and washed in distilled water. The catalyst was characterized with X-ray diffraction (XRD) and Fourier transform infrared spectrophotometer (FT-IR). The X-ray diffraction analysis showed that the starch had a change in crystallinity. The FT – IR results with strong peak at 929 cm^{-1} revealed the presence of α -amylase in the polymer catalyst. The enzymatic degradation of cassava starch with α -amylase resulted in the disappearance of the intensity of bands at 1150 cm^{-1} and 1080 cm^{-1} . The high free fatty acid value of the rubber seed oil (2.8) necessitated the use of a two – step transesterification process for biodiesel production. The transesterification was carried out with methanol at a temperature of $50\text{ }^{\circ}\text{C}$ for 1 hour. Fuel properties of the biodiesel produced was evaluated following ASTM standard methods.

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1. INTRODUCTION

The depletion of world petroleum reserves and increased environmental concerns has stimulated the search for alternative renewable fuels that are capable of fulfilling an increasing energy demand (Clark *et al.*, 1984). Biodiesel is a clean burning fuel derived from renewable feedstocks such as vegetable oil or animal fat (Pahl *et al.*, 2005). Currently, more than 95% of world biodiesel is produced from edible oils (e.g., soya bean, rapeseed, canola, cotton, palm, and palm kernel oils) which are easily available on a large scale from the agricultural industry. However, the daily rise in human population has brought some short comings as the human population faces serious food

shortages and malnutrition arising from the extensive use of these edible oils for fuel and as a result drawing attention towards the inedible oils as an alternative (Gui *et al.*, 2008). The use of cheap and nonedible seed oils, animal fats, and waste oils as raw feed stocks for biodiesel production is an effective way to reduce the cost of biodiesel. Inedible oils generally have higher free fatty acid (FFA) content compared to edible oils; thus a pretreatment step is often required to reduce the FFA content to a workable level (Lam *et al.*, 2010).

Rubber seed oil (RSO) is a semi-dried oil that is a rich source of fatty acids such as oleic acid, linolenic acid, palmitic acid, and stearic acid (about 52% of total fatty acid composition) (Ghandhi *et al.*, 1990). Two products are obtained from rubber seeds which are the oil and the cake. The oil content in dried kernel varies from 35 to 45%. RSO has been found to have potential applications in many areas amongst which are in the production of biodiesel as fuel for compression engines (Ikwuagwu *et al.*, 2000; Ramadhas *et al.*, 2005), foaming agent in latex foam, in the synthesis of alkyd resin used in paints and coatings and several other uses (Iyayi *et al.*, 2007). RSO has also been used as partial substitute to mineral oil as carrier for copper fungicide in the management of abnormal leaf fall disease of rubber in an attempt to reduce cost without compromising on the efficacy of diseases control (Jacob *et al.*, 2007).

Excellent fuel properties of transesterification process depend mainly on the nature and quality of the catalyst used among other factors (Ueki *et al.*, 2011). Biodiesel is usually prepared in the presence of homogeneous base or acid catalysts. With homogeneous base catalysts (sodium and potassium hydroxides, carbonates, sodium and potassium alkoxides, principally), the reaction is faster compared with acid catalysts (sulphuric acid, phosphoric acid, hydrochloric and sulphonic acid) (Fangrui and Hanna, 1998). However, the main disadvantage of the aforementioned homogeneous catalysts is the undesirable production of soap and glycerol, and this increases the production costs. On the other hand, heterogeneous catalysts could improve the synthesis methods by eliminating the neutralization salts in the glycerol and therefore the number of separation steps can be reduced (MacLeod *et al.*, 2008).

Recent setbacks in biodiesel production processes arising from non-availability of vegetable oil feedstock coupled with competitiveness of most vegetable oil to foodstuff and separation problem encountered from the use of homogeneous catalyst as well as rate limitation experienced in most heterogeneous catalyzed transesterification processes (Hamada *et al.*, 2016) led to the development of polymer catalyst which was found not to dissolve in the reaction solution, is recoverable and possesses high catalytic performance with rubber seed oil. The successful production of polymer catalyst and transesterification of rubber seed oil into biodiesel suggest the use of the polymer catalyst as biodiesel heterogeneous catalyst.

2. MATERIALS AND METHODS

The Polymer Catalyst was synthesized using cassava starch (*Manihot esculenta*). Other chemicals used include acrylonitrile, polysorbate 20 (Tween 20), Trimethylamine (TMA), methanol, sodium hydroxide (NaOH) pellets and distilled water. The cassava tubers were obtained from the satana market at sapele road, Benin City and the chemicals were obtained from Rovet scientific limited, Benin city, Edo state, Nigeria.

2.1. Graft Polymerization of Cassava Starch

The monomer emulsion solution (MES) was obtained by measuring 50ml of Acrylonitrile solution into a beaker using a measuring cylinder, 10% of its equivalent volume amounting to 5 ml of polysorbate 20 (Tween 20) was measured and added to the content inside the beaker. Then 50 ml of distilled water was measured and added to the mixture and stirred vigorously (Ueki *et al.*, 2010). The functional group was introduced by measuring 100 ml of 0.25 mol/L aqueous trimethylamine solution into a beaker. The grafted substrate was then transferred into the beaker by dipping it into the solution and kept in the water bath. The temperature of the apparatus was maintained at a constant temperature of 50 °C for a retention time of two hours (Ueki *et al.*, 2010; Ueki *et al.*, 2011). The resulting substrate from the introduction of functional group above was transferred into a beaker containing 100 ml of 0.1 M solution of sodium hydroxide for the hydroxyl group substitution step. The reaction condition was maintained at atmospheric temperature and pressure for a retention time of 6 hours. Subsequently, the substrate was withdrawn and set for washing operation. The product from the previous step was washed with distilled water and then dried in a laboratory oven (Model DHG-9101) at a controlled temperature of 105 °C for a period of 10 minutes. The final product was analyzed and used as biodiesel catalyst.

2.2. Acid – Catalyzed Esterification

One liter of crude rubber seed oil required 200 ml of methanol for the acid esterification process. Methanol and 5% sulphuric acid was added with the preheated rubber seed oil and the reaction was conducted at 60 °C and 400rpm for one hour. On completion of this reaction, the product was poured into a separating funnel and was allowed to settle for two hours. The excess alcohol, with sulphuric acid and impurities moves to the top surface and is removed. The lower layer was left at the bottom of the flat bottom flask for further processing.

2.3. Polymer – Catalyzed Transesterification

The catalytic performance of the synthesized polymer catalyst was carried out via transesterification of the acid preheated rubber seed oil. This was carried out using 300 ml of esterified rubber seed oil. It was then transferred to the reaction flask and heated to the desired reaction temperature of 50 °C. The solution of polymer catalyst (0.15 g) and methanol (900 ml) were preheated to the reaction temperature of 50 °C before being added to the rubber seed oil in the reaction flask. The esterification was carried out on a hot plate at a constant stirring speed of 300 rpm. After a reaction period of one hour, the reaction mixture was then transferred into a separation funnel and allowed to settle and the biodiesel was removed (Ueki *et al.*, 2011).

2.4. Analytical Procedure

The properties of the polymer catalyst was characterized with X –ray diffraction (XRD) and Fourier transform infrared (FT-IR) Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Characterisation of Catalyst

X-ray diffraction studies proved that the starch had a change in crystallinity as shown in Figure 1. Starches tend to present pertinent crystalline arrangements depending on their botanical origin (Cereda and Vilpoux 2003). The cassava starch had a C-type of X-ray diffraction pattern. The pattern of the cassava starch is recognized by the intensity of the corresponding band to one small peak 6° (2θ). There was more peak at $22^\circ(2\theta)$ suggesting a change in crystallinity after the treatment. The formation of the carboxyl groups in the amorphous part of cassava granules was caused by sodium hypochlorite.

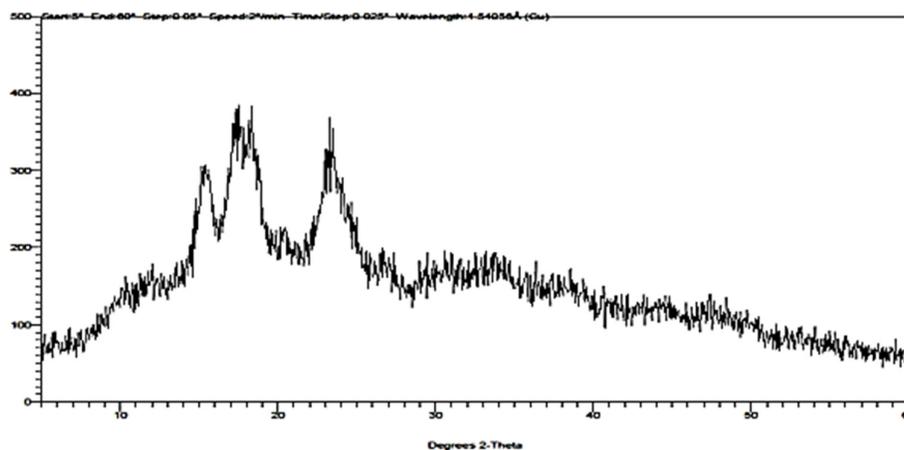


Figure 1: X-Ray diffraction analysis for cassava starch

The functional groups of the developed polymer catalyst was investigated via FT-IR spectra. Enzymatic degradation of cassava starch with α -amylase resulted in the decrease or disappearance of the intensity of bands at 1150 cm^{-1} and 1080 cm^{-1} while the intensity of the band at 1220 cm^{-1} was increased. These results suggest that the ordered structure of native starch was disrupted as a result of enzymatic degradation and the structure of the modified starch is more amorphous in nature. It is also interesting to note that the native starch has prominent band at 929 cm^{-1} , which is sensitive to water (Alexander, 1992). The results of the FTIR spectra (Figure 2) suggest the formation of amorphous structure in starch and decrease in the ordered structure of starch (Sevenou *et al.*, 2002).

3.2. Graft Polymerization Step of Polymer Catalyst

Variation of graft reaction temperature has no significant effect on the grafting of acrylonitrile onto cassava starch substrate (Figure 3). At various reaction temperature of 40°C , 50°C and 60°C , the uptake of monomer from monomer emulsion solution onto the main chain of the substrate decreased with increasing retention time and increased thereafter, which shows that irradiation dose absorbed affect significantly the grafting rate of the substrate. This shows that irradiation creates significant area on the surface of the substrate and produces unique effects that cannot be duplicated by other means (Ueki *et al.*, 2010).

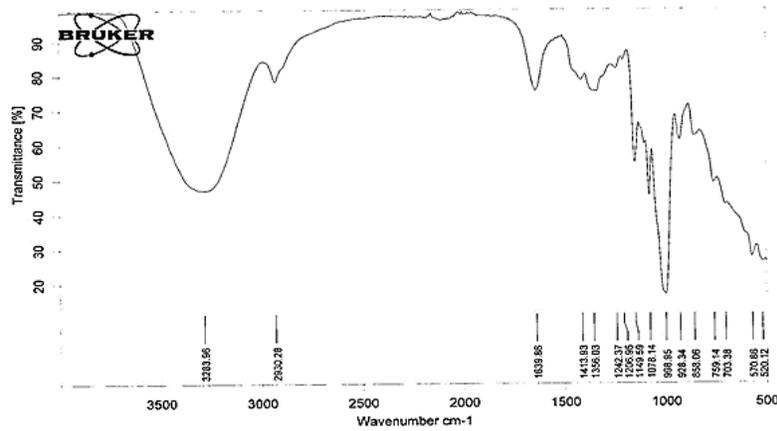


Figure 2: FT-IR spectra of cassava starch

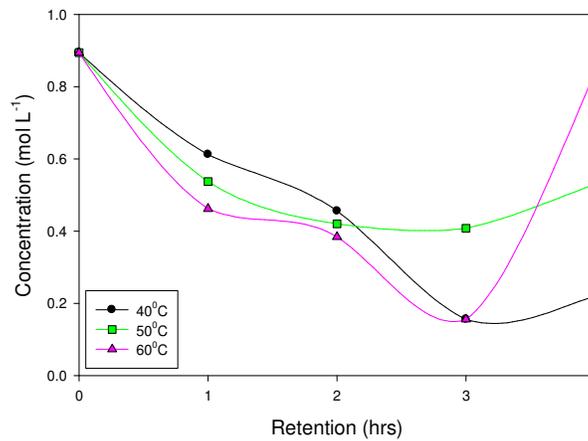


Figure 3: Effect of temperature on the concentration of monomer emulsion solution on the grafting of cassava starch

3.3. Characterisation of Rubber Seed Oil

The physiochemical properties of rubber seed oil used in the study compared to the physico-chemical properties of rubber seed oil from literature is shown in Table 1. The range of the parameters were almost the same except for the free fatty acid value which is high.

3.4. Characterisation of Rubber Seed Oil Biodiesel

The fuel properties of rubber seed oil methyl ester in comparison with literature is shown in Table 2. The results obtained show that the transesterification process improved the fuel properties of the oil with respect to specific gravity, viscosity, flash point and acid value. The flash point of rubber seed oil was lowered by transesterification.

Table 1: Physicochemical properties of rubber seed oil

Parameter	Rubber Seed Oil	Ramadhas et al. (2005)
Color	Dark brown	Dark brown
Clarity	Clear	Clear
Odor	Unpleasant	Unpleasant
pH	6.7	6.0
Specific gravity	1.011	0.92
Peroxide value	15	14.4
Saponification value(mgKOH/g)	182.3	193.61
Acid value	2.8	1.68
Melting Point	46 ^o C	45 – 48 ^o C
Viscosity(poise)	10.0	10.32

Table 2: Comparison between this research work and that of ASTM

Parameters	ASTM	Limits	Current work
Density (kg/m ³)	D1298	860 -890	850
Flash point (°C)	D93	Min 130	125
Specific gravity	D287	0.82 -0.89	1.02
Cetane number	D613	51 -	45
Acid Value (mgKOH/g)	D669	<0.50	1.12
Pour point (°C)	D97	-4 to -7	-5
Kinematic viscosity(mm ² /s) at 40 °C	D445	1.9 – 6.0	5.71

4. CONCLUSION

This results obtained showed that cassava starch can be used as a base polymer to produce a polymer catalyst for biodiesel production. The two-step transesterification method reduces the overall production cost of the biodiesel as it uses low cost non-edible rubber seed oil. At various reaction temperature of 40 °C, 50 °C and 60 °C, the uptake of monomer from monomer emulsion solution onto the main chain of the substrate decreased with increasing retention time. The produced biodiesel was characterized for its physicochemical properties and compared to that of literature and it was found that the properties were within range with literature.

5. ACKNOWLEDGMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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