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Two-Steps Transesterification of *Hura Crepitans* Seed Oil using Polymer Based Catalyst

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Abstract

Sustainable energy management has become a high priority in Nigeria, as well as in many countries around the world. The majority of our energy stock comes from non-renewable fossil fuels, which are currently dwindling. Biofuels are one of the most promising solutions being researched to address this urgent problem. In particular, using transesterified Hura crepitans seed oil appears to be a promising method of producing biofuels, due to the availability of Hura crepitans trees in Nigeria, and the fact that it does not compete with food crops. The use of a polymer catalyst makes the separation and purification of the final product steps easier than catalysis in homogeneous conditions, but the high incidence of free fatty acid (FFA) in Hura crepitans seed oil shows the need for a 2-step transesterification process. Thus, this study investigated the transesterification of Hura crepitans seed oil using a methanol and polymer based catalyst. This study was achieved with a methanol/oil molar ratio of 3:1, 0.15 % catalyst (w/wt), 50 °C reaction temperature, for 1hr reaction times, resulting in an 82 % fatty acid methyl ester yield, a 0.520 mgKOH/g acid value, and a 235, 9 and –5 °C, flash point, cloud point, and pour point, respectively. The result further reveals a 912.40 kg/m^3 density, a 4.75 Cst kinematic viscosity, 0.021 mass% free glycerin, 0.280 mass% free glycerin, and 0.280 mass% total glycerin.

Keywords: Polymer catalyst, Hura crepitans, transesterification, biofuels, fatty acid, methyl ester

Introduction

In a search for new energy sources, much attention is focused on biomass as a reliable and renewable source that is able to satisfy a significant part of energy demands [1,2]. Currently, biodiesel is considered a real alternative to diesel fuel due to its advantages. Over the years, efforts have been directed towards salvaging our world through the provision of environmental friendly alternative energy sources. Biodiesel is a clean burning fuel derived from a renewable feedstock such as vegetable oil or animal fat [3,4]. It is biodegradable, non-inflammable, and non-toxic, and produces less carbon IV oxide than petroleum based fuel [5]. Currently, biofuel development focuses more on boosting feedstock production and development of novel heterogeneous catalysts [6]. The availability of feedstock and its production catalyst are the biggest challenges facing the biofuels industry worldwide [6-8]. In spite of this, most Nigerian oil crops have not yet been economically exploited; many of them are regarded as waste or underutilized [9]. The *Hura crepitans* plant is an evergreen tree of the *Euphobiaceae* family, commonly planted in the cities and villages in Nigeria; despite its abundance in Nigeria, it is still underutilized [9]. A number of seed oils have been characterized, but the vast majority has not been adequately evaluated [10]; this is particularly valid for Nigerian flora, which is one of the most extensive in continental Africa [11]. Hura crepitans falls into this group of underutilized species of plants in Nigeria [10,12].

Conventional biodiesel production is currently based on transesterification of vegetable oil or animal fats [4,13,14] using homogeneous an alkaline catalyst [15,16], with the major setback being the complexity seen in the catalyst separation stage [15]. Thus, this study investigates the transesterification of Hura crepitans seed oil using a polymer-based catalyst that does not dissolve in the final product mixture.

Material and methods

Material

Seeds of the Hura crepitans tree used in this study were collected from the premises of Auchi Polytechnics and its environs in the northern part of Edo State, Nigeria. All reagents used were of analytical grade, obtained from Sigma-Aldrich Chemical and Co, USA. The polymer-based catalyst used in this study was initially developed via a method of radiation-induced [8,17] graft polymerization of 4-chloromethylstyrene onto polyethylene substrates [6,8,18], as was earlier reported in [19].

Methods

1. Extraction of Hura crepitans seed oil (HCSO)

The hydraulic press method was used in this study in order to extract the oil of Hura Crepitans from the seeds [20]. In adopting this method, the hydraulic press screw handle was adjusted until a pressure of 25 N/m^2 was exerted on the sack containing a sample of the crushed Hura crepitans seeds. This was achieved by adjusting the screw handle to exert a pressure of 25 N/m^2 on the sack containing the crushed seed sample by moving the moveable plate closer to the fixed plate carrying the pan [21-23]. The oil in the crushed kernel was expelled through the perforation chamber in the pan into the reservoir, with the seed cake as a byproduct [23]. The extracted HCSO was further analyzed for its fuel properties before being used as raw material in the transesterification process.

2. Polymer catalyst production

The polymer catalyst used in this study was freshly produced using the method described by Ueki *et al.* [8], as reported in Otokhian *et al.* [19].

3. Production of biodiesel from HCSO using polymer catalyst

The reactions were carried out in a specially-designed 1000 ml 3-necked flat bottom flask equipped with a reflux condenser, a thermometer, and a stopper to add the catalyst solution. The reaction mixture was heated and stirred by a hot plate with a magnetic stirrer.

Two step acid-polymer catalysts based catalyzed transesterification

With the aim of increasing the methyl ester yields, a 2-step acid catalyst esterification was employed [24 -26]. The high free fatty acid value initially present in the Hura crepitans seed oil was first pretreated with methanol in the presence of dilute sulfuric acid as catalyst, in an esterification process, to reduce the initial high FFA value to less than 1 % in order to make the HCSO suitable for transesterification. Transesterification reaction using a polymer-based catalyst was further carried out on the pretreated HCSO to convert it into its biodiesel.

(a) Acid-catalyzed esterification [24-26]

One thousand ml of the oil was precisely quantitatively transferred into a reaction flask and preheated using the hot plate to the desired reaction temperature of 60 °C before the reaction started. The sulfuric-methanol solution was freshly prepared with 5 % sulfuric acid being used and heated to the reaction temperature. The reaction was conducted at 60 °C and 400 rpm agitation rate for 1 h. After the required reaction time, the reaction mixture was poured into a separatory funnel and was allowed to settle for 2 h. The excess methanol, together with sulfuric acid and impurities, was moved to the top layer after settlement. The lower layer (HCSO phase) was withdrawn for transesterification.

(b) Polymer catalyzed transesterification [6,8]

The acid pretreated HCSO was used in this second step to produce biodiesel using a polymer based catalyst. 300 ml esterified HCSO was transferred to the reaction flask and preheated to the desired reaction temperature of 50 °C. 0.15 g of the catalyst was dissolved in the 900 ml of methanol required. The solution of polymer catalyst and methanol was preheated to the reaction temperature of 50 °C before being finally added to the esterified HCSO. The acid-esterified HCSO from the first stage was used as triglyceride in this second stage to produce biodiesel, using a polymer-based catalyst as the biodiesel production catalyst. In the process, 300 ml portion of esterified HCSO was measured, turned into a reaction flask, and preheated to a 50 °C reaction temperature. A 0.15 g portion of the polymer-based catalyst was weighed and mixed with 900 ml of methanol. The heterogeneous mixture of methanol-polymer based catalyst was then added to 300 ml of esterified HCSO.

Transesterification reaction proceeded at a stirring rate of 300 rpm for a period of 1 h. The reaction temperature was maintained at 50 °C throughout the reaction time. The product was then left in a separating funnel and allowed to settle overnight. The top layer (biodiesel) was withdrawn, washed with distilled water, and heated on a hot plate until it turned clear. A portion of the biodiesel produced from Hura crepitans seed oil (BHCSO) produced was examined and analyzed for its fuel properties.

Results and discussions

Table 1 Fuel Properties of ASTM D93-6751 Standards, HCSO and BHCSO, showing the results of the fuel properties of ASTM D93-6751 standards, HCSO and BHCSO from a polymer-based catalyst.

Property	Units	Method	ASTM limits	HCSO	BHCSO
Acid value	mgKOH/g	ASTM D664	0.8 mgKOH/g	8.49	0.52
Flash point	°C	ASTM D93	130 °C min.	249	235
Cloud point	°C	ASTM D2500	Report	11	9
Pour point	°C	ASTM D97	Report	–6	–5
Density	kg/m^3	-	-	919.38	912.4
Kinematic viscosity	Cst	ASTM D445	1.9 - 6.0	59	4.75
Total sulfur	wt%	ASTM D5453	0.050 max.	0.0174	0.004
Water and residue	%volume	ASTM D2709	0.050 max.	2.686	0.21
Colour	-	-	-	Brownish	Greenish yellow
Free glycerin	mass%	ASTM D6584	0.020 max.	0.614	0.021
Total glycerin	mass%	ASTM D6584	0.240 max.	8.253	0.28
Refractive index	-	-	-	-	1.473
% yield of biodiesel	-	-	-	38.40	82
Iodine value	g/100	ASTM D5554	-	164	104
Saponification value	mgKOH/g	ASTM D5558	-	236	212

Table 1: Parameters compared include:

Methyl ester yield: Biodiesel yield (%) was found to be 82 % after a reaction period of one hour. The value, when compared with biodiesel from rapeseed oil produced with other catalysts from the literature, was found to be lower than 98.7, 84.0, and 89.0 %. Ulf *et al.* [26] reported on biodiesel obtained from rapeseed oil using NaOH, K_2CO_3, and TBD catalysts, respectively, at a similar reaction time of 1 h. The result was, however, higher than a 64.5 % yield, Jitputti *et al.* [27] reported on biodiesel obtained from palm kernel oil using a ZrO_2 catalyst with an alcohol: oil molar ratio of 6:1, at a reaction time of 1hour. The value was, however, also found to be 56.4 and 67.0 %, reported from brown grease oil using KOH and $NaOCH_3$ catalysts, respectively [28]. Comparison of the biodiesel yield result based on the molar ratio of Alcohol: Oil, showed that the yield (%) result attained showed better results, when compared with the 93 % yield Zhu *et al.* [29] reported for jatropha curcas seed oil biodiesel produced at a reaction time of 150 min and an alcohol: oil molar ratio of 9:1, using CaO catalysts, and the 98:9 % yield, Demirbas [30] reported for sunflower oil biodiesel produced using CaO catalysts at an alcohol: oil molar ratio 41:1.

Flash point: The flash point of the BHCSO produced was 235 °C, as indicated in **Table 1** above; this value, when compared with 249 °C of the initial HCSO, reveals the transesterification reaction of the HCSO to be higher than the temperatures of 176, 178, 164, 183, 172, and 96 °C Agarwal [31] reported for biodiesel produced from peanut oil, soybean oil, palm oil, sunflower oil, linseed oil, and tallow oil, respectively. The value was found to be in line with the ASTM D93 specification of 130 °C as a minimum.

Cloud point: The cloud point was found to be 9 °C; this value is said to be higher than the temperatures of 5, 1, and 1 °C Agarwal reported for biodiesel from peanut oil, soybeans oil, and sunflower oil, respectively, but lower than the 13 and 12 °C Agarwal [31] and Shimada [32] reported for biodiesel from palm oil and tallow oil, respectively.

Pour Point: The pour point was found to be −5 °C, and is comparable with the temperatures of −4 and −7 °C Shimada [32] reported for cotton seed oil and soybean oil biodiesel, respectively, but was found to be higher than the −7 and −15 °C Agarwal [33] reported for soybean and linseed oil biodiesel, respectively. This value was also found to be less than the 9 °C reported for tallow seed oil biodiesel [33].

Acid value: The acid value was found to be 0.520 mgKOH/g, and is in line with the 0.80 mgKOH/g ASTM D664 standard specified as acid value for biodiesel. This value was found to be higher than the 0.468 mgKOH/g Igbum *et al.* [34] reported for methyl ester produced from *Cucumeropsis manii* vegetable oil.

Density: The density of the biodiesel produced was found to be 0.9124 g/ml, and was found to be greater than the 0.885, 0.883, 0.880, and 0.860 g/ml Shruti *et al.* [35] reported for biodiesels produced from cotton seed oil, soybean oil, groundnut oil, palm oil, and sunflower oil, respectively.

Kinematic viscosity: The kinematic viscosity was found to be 4.750 Cst; this result is in line with the 1.9 - 6.0 Cst ASTM D445 range specified as the standard requirement for the kinematic viscosity for biodiesel, and was also found to be lower than the 4.9 and 5.7 Cst Agarwal *et al.* [33] reported for peanut oil and palm oil biodiesels, respectively. In contrast, it was found to be higher than the 4.51 Cst Xiaohu reported for methyl ester produced from recycled canola seed oil [2].

Sulfur content: Sulfur content, an elemental compositional property of the produced biodiesel, was found to be 0.004 wt%, lower than the 0.050 wt% specified as the maximum value requirement as specified in ASTM D5453. The Sulfur content of the produced biodiesel was also found to be lower than the 0.0310 wt% [34] and 0.059 wt% Xiaohu *et al.* [2] reported for methyl esters produced from Cucumeropsis manii vegetable oil and recycled canola oil, respectively.

Water and residue content: Water and residue was found to be 0.21 %volume; this is less than the 0.050 %volume specified as the maximum value requirement for conventional biodiesel as specified in ASTM D2709. It was found to be higher than the zero %volume Xiaohu *et al.* [2] reported for biodiesel produced from recycled canola oil and the 0.05 %volume Igbum *et al.* [34] reported for biodiesel produced from Cucumeropsis manii vegetable oil.

Free glycerin: The result showed that a free glycerin content of 0.021 mass% obtained was within the standard maximum requirement of 0.020 mass% specified in ASTM D6584. The value was found to be higher than the 0.006 mass% Igbum *et al.* [34] reported for methyl ester of *Cucumeropsis manii* vegetable oil, and also higher than the 0.004 mass% [2], 0.004 mass%, and 0.002 mass% Canakci *et al.* [28] reported for biodiesels produced from brown grease using 0.82 g $NaOCH_3$ and 0.42 g $NaOCH_3$ catalysts, respectively. The free glycerin obtained from Hura crepitans biodiesel produced in this study using polymer catalysts was found to be higher than the 0.017 mass% Canakci *et al*. [28] reported for biodiesel produced from yellow grease oil using conventional NaOH catalysts.

Total glycerin: ASTM D6584 specified a 0.240 mass% as the maximum total glycerin requirement for biodiesel. Comparing the results of the total glycerin obtained from the biodiesel produced from Hura crepitans seed oil in this study, it was found to be 0.201 mass%, which was found to be in line with the ASTM D6584 standard requirement. The total glycerin value obtain was found to be higher than the 0.13 mass% Xiaohu *et al.* [2] reported for biodiesel produced from recycled canola oil, and the 0.119 mass% Igbum *et al*. [34] reported for biodiesel produced from Cucumeropsis manii vegetable oil. It was also found to be higher than the 1.91 and 9.22 mass% Canakci *et al*. [28] reported for biodiesel that was produced from brown grease oil using 1.01 and 0.50 gKOH catalysts, respectively.

Refractive index: A refractive index of 1.473 was evaluated as the produced biodiesel refractive index; this value when compared with those from the literature was found to be in line with the 1.471 Igbum *et al*. [34] reported for biodiesel that was produced from Cucumeropsis manii vegetable oil.

Iodine and saponification values: The iodine and saponification values of the biodiesel produced in this study were found to be 104 g/100 for the Iodine value; this was found to be in line with the 80 - 106 g/100 Shruti *et al*. [35] reported for ground nut oil biodiesel, and lower than the 35 - 61 g/100 Shruti *et al*. [36] reported for palm oil biodiesel. The saponification value obtained was 212 mgKOH/g.

Conclusions

The results from this study reveal that transesterification of HCSO to BHCSO was successful via the use of a polymer-based biodiesel heterogeneous catalyst. The results compared favorably with those of the ASTM D93-6751 biodiesel standard. Some of the benefits of the polymer-based catalyst observed during the study include its simplicity, effectiveness, easy separation process, and small amount of catalyst required. The results obtained from a methanol/oil ratio of 3:1 using a 0.15 % of the polymer-based catalyst revealed the high performance of the catalyst. Transesterification was achieved with a methanol/oil molar ratio of 3:1, 0.15 g polymer catalyst, at a 50 °C reaction temperature, for 1 h. The results showed 82 % fatty acid methyl ester yield, 0.520 mgKOH/g acid values, and 235, 9, and –5 °C flash point, cloud point, and pour point, respectively. The results further reveal a 912.40 kg/m^3 density, 4.75 Cst kinematic viscosity, 0.021 mass% free glycerin, and 0.280 mass% total glycerin.

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