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Transesterification Reaction of Palm Kernel Oil (PKO) on a Bed of Crushed Cashew Nut Shell (CCNS)

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ABSTRACT

Biodiesel (GA1) was produced by the transesterification reaction of palm kernel oil (PKO) and methanol catalysed by crushed cashew nut shaft. Biodiesel samples GA2 – GA4 were also produced from the palm kernel oil using conventional base catalysis by NaOH and crushed cashew nut shaft combined with NaOH. The physico-chemical properties and spectroscopic data of the four samples were found to be similar and compared favourably to those of standard biodiesel.

Keywords: Transesterification, palm kernel oil, cashew nut shell, methanolysis, biodiesel.

INTRODUCTION

Gerpen (2005) used four methods to reduce the high viscosity of triglycerides including blending with petro diesel, pyrolysis, micro emulsification (co-solvent blending) and transesterification in order to enable their use in common diesel engines without operational problems such as engine deposits. Only the transesterification reaction, which is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety leads to the products commonly known as biodiesel i.e. alkyl esters of oils and fats. Transesterification reaction also called alcoholysis (Schuchardt *et al*., 1998) is similar to hydrolysis except that alcohol is used in the displacement of an –OH group from an ester instead of water.

Satisfactory results from literature has shown that production of biodiesel from triglycerides like vegetable oil (Schuchardt *et al*., 1998; Demirbas, 2003; Issariyakul *et al*., 2008; Alonso *et al*., 2008), animal fats (Goodrum *et al*., 2003; Liu *et al*., 2004) or used cooking oils (Demirbas, 2003) is possible since they are environmental friendly, renewable in nature and can be produced on a very large scale (Patil and Deng, 2009). Biodiesel is produced industrially by base or acid catalysis. A catalyst to be used for synthesis of biodiesel should be selective, specific, and result in transesterification with high conversion and yield. In recent time, development of heterogeneous solid acid catalysts (HSACs) has been a relative area of interest in transesterification reaction of triglycerides (Pua *et al*., 2011). The efficiency of the heterogeneous process however depends on several variables such as type of oil, molar ratio of alcohol to oil, temperature and catalyst type (Chopade *et al*., 2012). The mechanism of conversion of oils to biodiesel is a single step process unlike the homogenous-catalyzed reaction where reduction of acid value occurs in one step followed by the conversion of oil to biodiesel in the second step (Semwal *et al*., 2011). Simultaneous esterification and transesterification of high acid value feedstock on solid acid catalysts is also an added advantage. This becomes very important as the non-edible oils and waste cooking/frying oils commonly employed for synthesis of biodiesel have high acid value (Díaz and Brito, 2014). However, a few works have been reported in literature in the use of organic solid acid catalyst in the transesterification reaction of triglycerides which is the foundation of this work. A solid acid catalyst (SAC) should possess high stability, numerous strong acid sites, large pores, a hydrophobic surface providing a favourable condition for reaction, and should also be economically viable (Mondal *et al*., 2018). With HSACs catalyst removal procedures are generally simplified, corrosion problems associated with the process nearly eliminated and purification protocols largely reduced. As a result, HSAC processes are regarded as more environmental friendly.

The base-catalyzed transesterification process is suitable for feedstock with low free fatty acids; however, not all feedstock have low free fatty acid content like in the case of palm kernel oil (Canakci and Gerpen, 2001). However, solid acid catalysis has proven to have the potential to successfully catalyze a transesterification reaction (Fang and Yihang, 2014). Moreover the use of SACs has not been fully explored as expected given the different variety of catalytic materials that are available. A handful of existing studies on the topic are without decisive conclusions about its potential (Lotero *et al*., 2008).

Cashew nut shell (CNSL) is the by-product obtained after the removal of the edible nuts from the seed. In Nigeria, the environment and probably so elsewhere, is littered with cashew nut shafts and their seeds in many cashew nut processing industries as wastes. This constitutes threat to the environmental and therefore needs to be removed from the environment. The performance of cashew nut shells was therefore investigated as catalyst for the conversion of palm kernel oil (PKO) into biodiesel. The cashew nut shell is readily available, biodegradable, almost cost-free and can easily be found in large quantity in the southern parts of Nigeria. The quality of the biodiesel obtained using this catalyst system is compared with products from other techniques and the results are discussed in this paper.

MATERIALS AND METHODS

Catalyst preparation

The nuts of the cashew obtained were washed thoroughly and sun dried. The nuts were then cracked open to separate the Shaft from the edible nut. The shafts were washed and sun dried. The shafts were then grinded to a fine free-flowing syrupy slurry (CNSL, slurry) using a Thomas Scientific hand operated mechanical grinder Model 3371H20 Worm Feed. This action breaks the cell walls and increases the surface area to promote a fast and more cohesive reaction. The surface area of the resultant syrupy slurry was then determined using the Sears' method (Sears, 1956; Shawabkeh and Tutunji, 2003).

Transesterification Catalysed by Crushed Cashew Nut Shaft (GA1)

The transesterification reaction was in the ratio of 3:1 (alcohol:oil). Cashew nut shaft slurry (10 g) was mixed with 120 g of methanol under continuous stirring for 30 minutes and 40 g of palm kernel oil already pre-heated to 60°C was added. The mixture was stirred for further 3 hs in a paraffin oil bath at reflux. Filtration was carried out under suction to separate the partially spent cashew nut shell. Separation into biodiesel and glycerol was carried out in a separating funnel after standing for 24 h (Knothe *et al*., 2010). The excess methanol was then removed on a rotary evaporator.

Transesterification Catalysed by NaOH (GA2)

Different weights of NaOH ranging from 0.1, 0.5 and 1 g were used. The procedure is described here for 0.1 g NaOH. The NaOH was dissolved in methanol and stirred for 30 minutes after which the pre-heated palm kernel oil was added and the mixture was further stirred for 3 h under reflux. The mixture was allowed to cool and separated using vacuum pump. The methyl ester was transferred into the separating funnel and left for 24 h. The biodiesel was separated from the glycerol. Excess methanol was removed on a rotary evaporator at 60°C.

Transesterification Catalysed by Crushed Cashew Nut Shaft followed by Base Catalysis by NaOH (GA3)

A portion of palm kernel oil (40 g) was heated in a 250 ml round bottom flask to 60°C. CNSL slurry (10 g) was separately mixed with 120 g of methanol under continuous stirring. The pre-heated oil was then added and stirring was continued under reflux for 3 h at a temperature of 60°C in a paraffin oil bath. After the separation of the shaft of the cashew from the methyl ester, 0.1 g of NaOH was added before the removal of the glycerol. Stirring was continued under reflux for another 1 h, cooled and separated into biodiesel and glycerol in a separating funnel. Removal of excess methanol by distillation was carried on a rotary evaporator.

Transesterification Catalysed by NaOH followed by Crushed Cashew Nut Shaft (GA4)

A portion of palm kernel oil (40 g) was heated in a 250 ml round bottom flask to 60°C. In another set up, 0.1 g of NaOH was mixed with 120 g of methanol undercontinuous stirring. The pre-heated oil was then added and stirring was continued under reflux for further 3 h at a temperature of 60°C in a paraffin oil bath. Before the separation of glycerol from the biodiesel, the CNSL slurry was added and stirring was continued under reflux for another 1 hr. After cooling, the cashew nut shaft was separated using a vacuum pump. The glycerol was separated from the biodiesel and excess methanol was removed by distillation.

Statistical Analysis

The obtained experimental values for each parameter were compared with their corresponding standards to determine if a significant difference exists. A 95% confidence interval (C.I.) about the mean of the physico-chemical properties of the synthesized biodiesel was constructed. This shows the interval within which the true mean lies 95% of the time. This is calculated using the formula:

$$95\%\ \text{C.I.}\ (\mu) = \bar{X} \pm Z_{\alpha/2}\ \frac{\sigma}{(n)^{1/2}}$$

Where $\bar{X}$ = mean; $Z_{\alpha/2}$ = confidence coefficient; σ = standard deviation and n = sample size.

The percentage biodiesel yield was calculated using the equation:

$$\text{Biodiesel yield}\ \% = \frac{\text{mass (g) biodiesel recovered}}{\text{mass (g) of palm kernel oil}}\ \text{x}\ 100$$

RESULTS AND DISCUSSION

The analytical data for the palm kernel oil (PKO) derived biodiesels are presented in Table 1. The percentage yield of biodiesel sample produced from each process (90%) was in good agreement with the ASTM standard as reported in Table 1.

Acid value determines the acidic or basic constituents in petroleum products and lubricants, and for biodiesels, the acid value is an indicator of the quality of the product (Skiera *et al.*, 2014). Specifically, it detects the presence of any unreacted fatty acids still in the fuel, or of any acids that were used in the processing. This is also an indication of the condition of the stability of the fuel, because the acid value increases as the fuel ages (Bello and Otu, 2012). For biodiesel blends, the acid number will change as a result of the normal oxidation process over time (Skiera *et al.*, 2014). Once purchased, biodiesel fuel blends that will not be utilized immediately should be monitored for changes in acid number as an indicator of fuel degradation (Bello and Otu, 2012).

Table 1: Analytical data for the Palm Kernel Oil Derived Biodiesel

Physico-chemical Property	GA1	GA2	GA3	GA4	ASTM Standard	Mean	95% C.I.
Yield (%)	95	98	96	97	> 90	96.5	96.5±1.27
Density (g/cm^3)	0.84	0.86	0.85	0.86	0.82-0.90	0.85	0.85±0.01
Specific Gravity	0.85	0.88	0.87	0.87	0.80-0.90	0.87	0.87±0.01
Refractive Index	1.48	1.45	1.40	1.50		1.46	1.46±0.05
Viscosity (mm^2/s)	1.97	1.76	1.91	1.85	6.00 max	1.87	1.87±0.09
Acid Value (mg/KOH/g)	0.70	0.56	0.62	0.65	0.50 max	0.63	0.63±0.06
Iodine Value (gI$_2$/100 g)	151.8	101.6	150	150.5	120-150	138.5	138.5±24.10
Saponification Value (mg/KOH/g)	98	96	105	97	96 min	99	99±4.00
Ester Value (%mass)	97.30	97.44	104.38	96.35	96.5 min	98.87	98.87±3.63
Ash Content (%)	0.20	0.18	0.19	0.19	0.10 max	0.19	0.19±0.01

With the exception of the base catalysed process, the acid value obtained for the biodiesel in this study were slightly higher than the ASTM standard. Iodine value measures the degree of unsaturation and corresponds to the amount of iodine required to saturate the olefinic bonds in fuels (Haryati *et al*., 1997). High iodine value has been linked with formation of engine deposits and problems in the storage of fuels (Che Man *et al*., 1998). Iodine absorption occurs at double bond positions, thus the higher the iodine number in the sample the greater the quantity of double bonds, an indication of the greater potential to polymerize and hence becomes less stable (Gharby *et al*., 2016). The acceptable iodine value according to the ASTM specification should range between 120 and 150 (Garba *et al*., 2018), and the biodiesels produced in the present study meet this requirement.Ash content measures the amount of ash left after a sample is burned. The presence of ash may indicate undesirable impurities or contaminants. As such, it provides a measure of the suitability of a product for a given application. The maximum acceptable value of ash content in biodiesels which should be met is 0.01% (Schumacher *et al*., 1995).

FT-IR analysis

The selected FT-IR absorption bands of the Crushed Cashew Nut Shaft catalyst are given in Table 2. The peak of absorption of OH group that indicate the presence of phenolic compound appeared at a 3343 cm^{-1} frequency (Oliveira *et al*., 2016). The peaks that appear at frequencies range between 3008-2855 cm^{-1} indicate the presence of C-H branched chains of the phenolic compounds while the phenolic C–O groups were observed between 1260 - 1000 cm^{-1} in all the samples (Coates, 2000). Strong absorption bands due to aromatic and branched ring C=C bonds of cardanol were observed around 1595 cm^{-1}in the IR spectra of the catalyst (Risfaheri *et al*., 2009).The aromatic C=C absorption bands in the catalyst appeared around the 1458 cm^{-1}(Coates, 2000).

Table 2: IR Spectroscopic analysis data for the Catalyst (Crushed Cashew Nut Shaft)

Peaks (cm^{-1})	Assignments
3386	OH of phenolic compounds
2985b – 2854	C–H branch of phenolic compounds
1689	C=O of carboxylic acid
1541	C=C of aromatic ring
1456	C–H of aliphatic
1207	C–O of phenol

Table 3 contains some selected absorption bands in the IR spectra of the biodiesels produced from the various processes. The spectra revealed the presence of OH groups of carboxylic acids with bands at 3382.59, 3385, 3431.48and 3456.55 cm^{-1} respectively for GA1, GA2, GA3 and GA4 biodiesels (Smith, 2018). The weak C=O stretch of the methyl ester observed respectively in the spectra of GA1 and GA3 at 1748.81 and 1716.70 cm^{-1} could be as a result of the cashew nut being highly acidic or that the reaction time may not be sufficient for the full conversion of all the free fatty acids present in the starting materials. Bands attributable to the signal of C=O stretch of carboxylic acid were found respectively at 1653, 1647.26, 1666.55 and 1666.55 cm^{-1} for GA1, GA2, GA3 and GA4. However, the signal strength for GA2 and GA4 appears very weak. Bands observed at 1454.35 cm^{-1}, 1458.23 cm^{-1}, 1462.09 cm^{-1} and 1458.23 cm^{-1} were assigned to C-H aliphatic stretch in GA1, GA2, GA3 and GA4 respectively (Smith, 2018).

The GC analyses

The methyl ester groups present in the biodiesels were determined using GC. The results of the GC analysis on all the biodiesel from the various catalysts are summarized in Table 4. It can be observed from Table 1 that there were sixmain characteristicpeaks attributable to fatty acid methyl esters (FAMEs) in GA1.The six identified FAMEs are lauric acid methyl ester (C12:0), methyl tetradecanoate (C14:0), hexadecanoic acid methyl ester (C16:0), 10-octadecanoic acid methyl ester

Table 3: The Main IR Diagnostic Absorption Bands and its Assignment for the Methyl Esters Produced through the Various Catalyzed Processes.

GA1 (cm^{-1})	GA2 (cm^{-1})	GA3 (cm^{-1})	GA4 (cm^{-1})	ASSIGNMENT
3382.59	3385	3431.48	3456.55	OH of carboxylic acid
2854.74	2852.81	2854.74	2852.81	Aliphatic C-H stretch
1748.81	1743.71	1716.70	1743.71	C=O stretch of methyl ester
1647.26	1647.26	1666.55	1666.55	C=O stretch of carboxylic acid
1508.38	1558.54	1585.54	1560.46	C=C Aromatic
1454.35	1458.23	1462.09	1458.23	C-H of Aliphatic

(C18:3), 9,12-octadecadienoic acid methyl ester (C19:0) and decanoic acid methyl ester (C11:0). Lauric acidmethyl ester appeared to be the most abundance in all the samples with percentage composition thehighest for GA3 at 48.612%. Myristic acid methyl ester and linolenic acid methyl ester were the next most abundant in this biodiesel sample. The % composition of the biodiesel produced through the various catalysed processes were in good agreement with the standard.

Table 4. Summary of the GC analysis data on the biodiesel produced through the various catalyzed processes.

Compound	GA1	GA2	GA3	GA4	MRT
Caprylic acid ME (C8:0)	4.86	2.97	2.60	2.74	8.95
Capric acid ME (C12:0)	3.81	4.70	3.87	2.91	11.20
Lauric acid ME (C12:0)	47.78	47.28	48.61	44.49	12.65
Myristic acid ME (C14:0)	16.27	16.13	16.51	21.39	13.80
Palmitic acid ME (C16:0)	7.17	6.67	7.06	8.40	15.25
Stearic acid ME (C18:0)	2.37	3.88	3.44	2.31	17.93
Oleic acid ME (C18:1)	10.08	14.61	14.95	15.63	8.85
Linoleic acid ME (C18:2)	2.09	3.75	2.97	2.18	19.65

The values are GC yield presented as % composition by mass; ME = methyl ester; MRT = Mean Retention Time in minutes

CONCLUSION

The results obtained from the present study shows that the slurry from cashew nut shaft has the potential to effectively catalyze transesterification reactions. Thebiodiesel produced through this process (GA1) has physico-chemical properties comparable to those of the standard diesel, and its quality compared well to those obtained from the other catalytic treatments as well as to that of ASTM specifications. The results suggest that crushed cashew nut shafts has the potential to replace strong liquid acids and bases commonly employed as catalysts for transesterification reactions.

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