A STATISTICAL APPROACH TO UNDERSTANDING THE ROLE OF REACTION CONDITIONS IN BIODIESEL PRODUCTION

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ABSTRACT

Understanding the reaction processes for transesterification of oils to biofuel is essential for bio refineries, but inconsistent results in the literature make understanding of this processes difficult. To solve this problem, statistical tools were used to interpret the results obtained from varying reaction conditions such as reaction temperature, time and methanol to oil ratio. It was observed that there is variation regime where changing the methanol to oil ratio has no effect on the biodiesel yield. The yield decreases significantly after reaching the maximum at 4:1. The optimum reaction temperature and time were 60 ℃ and 2 h, respectively. The biodiesel produced is within the acceptable range approved by ASTM. *[African Journal of Chemical Education—AJCE 9(2), July 2019]*

INTRODUCTION

Biodiesel is a liquid fuel produced through a process called transesterification of oil with alcohol (methanol or ethanol) in the presence of a catalyst. Recently, biodiesel has been considered as a promising potential substitute for conventional petroleum based diesel. It is the mixture of mono alkyl esters, which can be sustainably derived from vegetable oils or animal fats, hence, it is termed as a renewable source of energy [1,2]. In terms of properties and performance, biodiesel possesses many advantages such as high flash point, high cetane number, high lubricity, biodegradable, lower carbon monoxide, particulate matter and sulfur (IV) oxide during the combustion compared to conventional fossil fuel [3, 27. 28]. The use of 1 kg biodiesel (for compression engine or household purposes) leads to a reduction of about 3 kg of CO_2 emissions. Therefore, the use of biodiesel leads to a significant reduction in CO_2 emission of 65% to 90% compared with the use of conventional diesel.

In industries nowadays, biodiesel is produced via homogeneous base-catalyzed transesterification and the common alkaline homogeneous catalysts used are sodium hydroxide and potassium hydroxide [4, 5]. Alkaline homogeneous catalysts are preferred as they proceed about 4000 times faster than the acid catalyzed transesterification [6]. These alkaline homogeneous catalysts are cheaper in cost and give higher yields at modest operation conditions [7]. Nevertheless, the biodiesel and glycerol produced from this transesterification process need to be purified and washed with lots of hot water to remove any trace of catalysts and unreacted alcohol [8].

The emergence of solid (heterogeneous) catalysts provides an alternative catalyst to biodiesel industry. Heterogeneous catalysts are non-corrosive, green and environmentally friendly [9]. They can be recycled and used several times [9], thus offering a more economic pathway for biodiesel production. Solid catalysts (basic or acidic) greatly simplified the downstream purification of biodiesel, where the catalysts can be separated physically and no further purification and washing are required for the end product (biodiesel and glycerol) [10]. Similar to homogeneous catalysts, solid basic catalysts are more active than solid acid catalysts [11, 12] and a perfect example of a solid basic catalyst is CaO, which shows a promising result in transesterification process with oil conversion of more than 95 % [13,14]. Although CaO has a good performance in transesterification, it tends to leach out into the reaction medium and thus reduces its reusability [15]. Efforts has been made to prevent this leaching by varying the preparation methods [1]. Despite the achievements on transesterification processes, there are conflicting reports in literature as regards the ideal ratio of methanol:oil for maximum yield. For example, optimal ratios such as; 6:1, 10:1 and 3:1 had been reported by Sharma et al. [16], Patil and Deng [17] and Chouhan and Sarma [18], respectively. This difference in ratio may be related to the way various research group processed their results. To the best of our knowledge no effort has been made to validate results presented in literatures using statistical tools. Since it is statistically wrong to assume that a condition affect rate positively or negative without using ANOVA, least significance difference or/ and any other packages. The optimization of reaction conditions were done in this study and the results were analyzed using both one way ANOVA one way test, Duncan, LSD, Turkey, Turkey's-b, Sidak, and Scheff.

MATERIALS AND METHOD

To optimize the reaction conditions, experiments were performed by varying reaction parameters such as methanol/oil ratio, reaction temperature and reaction time. The methanol/oil ratio was varied from 2:1 to 26:1 and the reaction time was varied between 1 and 4 h, while the reaction temperature was fixed at 60 ^{o}C. The effect of reaction temperature was monitored by varying temperature between 30 and 60 ^{o}C. All experiments were done in triplicate and statistical analysis was done using SPSS to determine mean, ANOVA, Duncan and LSD test. The physical properties of biodiesel produced in this experiment were determined according to the ASTM standard (viscosity: ASTM D.445-10, [19]; pour point: ASTM D.97, [20]; flash point: ASTM D.93, [21]; and specific gravity: ASTM D.1298, [22]). The acid value was determined according to an established method [23].

RESULTS AND DISCUSSION

The result of biodiesel yield are presented in figure 1. In order to understand the role of methanol to oil ratio on the biodiesel yield, the triplicate results obtained for each ratio variations were subjected to ANOVA test and it was found that the results were statistically different from each other at $p = 0.05$. However, ANOVA only could not tell the sample which are different from the other, therefore the results were further subjected to Duncan, and LSD. LSD did not give comparison of mean (not shown), but Duncan test show that the result obtained for 2:1 (methanol:oil) was significantly different from others. The yield at this ratio was low because the reaction had no enough methanol to drive the reaction equilibrium to the right [24, 25]. The yield increased significantly when the ratio was changed from 2:1 to 4:1. However, there was a significant decrease when the ratio was increased to 9:1. Further increase in the ratio lead to significant decrease in the biofuel yield. Increasing the ratio from 13:1 to 17:1 has no significant difference on the biodiesel yield derived from the transeterification processes, but further increase lead to a significant decrease.

Furthermore, increasing the ratio from 22:1 to 26:1 had no significant difference in the yield. This observation suggested that there is a range where changing methanol to oil ratio will not have any significant effect on the biodiesel yield. The stoichiometric molar ratio of alcohol:oil in transterification process is 3:1, which gives 3 moles of fatty acids methyl esters and 1 mol of glycerine [25]. Addition of methanol to oil above a particular level may not lead to an increase in the yield of product [17, 26, 27]. At high methanol:oil ratio (> 4:1), the glycerine would largely dissolve in excessive methanol [28]. Subsequently, it reduced the amount of methanol and inhibited the reaction of methanol to the reactants and catalyst, which resulted in a lower biodiesel yield [29]. Furthermore, the polar hydroxyl group in methanol acting as emulsifier making it more difficult to separate the biodiesel product from glycerol, which eventually reduce the yield of biodiesel [29].

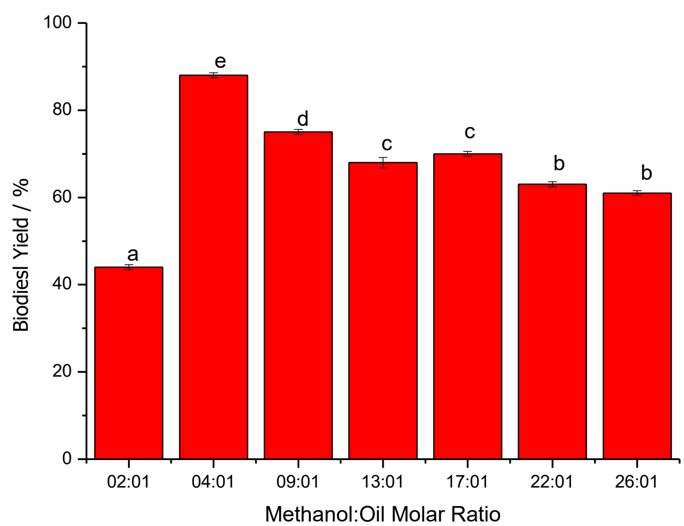

Figure 1: Effects of methanol:oil ratio on the biodiesel yield
The yield value with same alphabet were not different significantly.

At 30 ^{o}C, the reaction products solidified and subsequent increase in the temperature from 40 ^{o}C to 60 ^{o}C cause a significant increase in the yield of biodiesel (Table 1). Varying the reaction time has a significant effect on the yield of biodiesel produced. Increasing reaction time from 1 h to 2 h led to a significant increase in the yield of the product. Further increase in the time leads to a significant decreased in the yield of the biodiesel produce (Table 2). The yield of the biodiesel increased with time because the reaction has not reached equilibrium [30]. The decreased in yield observed after 2 h could be due to solubility of biodiesel in glycerol [31].

Table 1: Effect of temperature on biodiesel yield

Temp (^oC)	Yield ± SE (%)
30	-
40	$61.00{\pm}0.37^a$
50	$65.00{\pm}0.37^b$
60	$85.00{\pm}0.37^c$

Table 2: Effect of time on biodiesel yield

Time (h)	Yield ± SE (%)
1	$44.00{\pm}0.58a^b$
2	$90.00{\pm}0.58^c$
3	$44.00{\pm}0.58^b$
4	$25.00{\pm}0.58^a$

The flash point (table 3) of the biodiesel obtained was tested to know the temperature at which it will ignite, and the result indicates that the biodiesel produced is safe to handle, store and transport [25, 32]. The lower the flash point of a fuel, the lower the temperature at which the fuel can form a combustible mixture. Low flash point may indicate presence of methanoic impurities [25, 33]. Methanol contamination might occur due to insufficient purification of esters after biodiesel production. The biodiesel can be used in cold regions because the cloud point is just one, hence, it is safe for any region. High cloud point fuel is known to blocks fuel filters and injectors in engines. The density, acid value and specific value given in table 2 show that the biodiesel is within the allowed specification by ASTM.

Table 3: Physico-chemical properties of biodiesel

Parameter	Amount	ASTM
Density at 15 ^{0}C (kg/m^3)	878.4	860-900
Flash point (^{0}C)	116.8	<130
Acid value	0.78	<0.8
Specific gravity	0.851	0.88
Cloud point (^{0}C)	1	---

CONCLUSION

The reaction conditions that determine the yield of biodiesel produced through transesterification can better be understand using simple statistical tool such as ANOVA, Duncan, LSD, Turkey, Turkey's-b, Sidak, and Scheff. However, LSD is not significantly sensitive compare to Duncan, Turkey, Turkey's-b, Sidak, and Scheff. There was a methanol:oil ratio regime were there were no significant difference in the yield of biodiesel produced. Other reaction factor such as reaction time and temperature were also determining factor in optimizing biodiesel yields significantly. The biodiesel produced in this study is suitable for diesel engine because it is within the acceptable limit by ASTM.

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Author contributions statement

Femi F. Oloye and Victor O. Olumekun designed the study, while Isaac A. Ololade supplied the reagents. Afolabi Owoloye did the statistical analysis. FFO wrote the first draft. All authors read and approved the manuscript.