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Effects of Reaction Time on Biodiesel Yield

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ABSTRACT

The reaction time affects the conversion efficiency of the transesterification process of converting oil to biodiesel. In this study, the effect of reaction time at different time interval was examined on biodiesel yield for both alkali and acid transesterification. For alkali transesterification, the dependency of reaction time studied at different time intervals ranging from 0.5-6 hours revealed that about 2 hours of reaction was sufficient for the completion of the alkali transterification process and optimum conversion of oil to biodiesel (80%). For acid transesterifictation, reaction time was studied at time intervals ranging from 2-10 hours. About 8 hours of reaction was sufficient for the completion of acid transesterification and optimum conversion of oil to biodiesel (60%). Increase in reaction temperature speeds up the reaction rate and shortens the reaction time, hence, methyl ester yield increases with increase in reaction time. Further increase in reaction time beyond this point will subsequently lead to decrease in yield.

Keyword: *Biodiesel, Methyl ester, Reaction Time, Transesterification, Yield.*

INTRODUCTION

Biodiesel is a mixture of mono-alkyl esters of long chain (C16-18) fatty acids that can be obtained from a variety of vegetable oils and animal fat [1] by a process known as transesterification. Vegetable oils needs to be transesterified to biodiesel because of its high viscosity and cold flow properties by reacting it with alcohol in the presence of basic or acidic catalyst to form esters and glycerol [1] [2] [3].
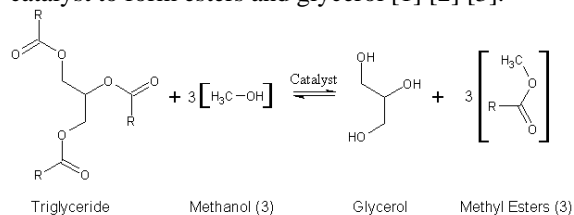

Fig 1 Transesterification Process

Methanolysis process occurs via three reversible consecutive reactions from triglycerides to diglycerides, diglycerides to monoglycerides and finally methyl esters, but side saponification .reactions have also been included into the reaction mechanism. [4].

The total reaction between triglycerides and methanol to give biodiesel is a sequence of three sequential reactions.

Triglycerides   + CH_3OH → Diglycerides   + Fatty acid methyl esters   *(1)*

Diglycerides   + CH_3OH → Monoglycerides + Fatty acid methyl esters *(2)*

Monoglycerides + CH_3OH → Glycerol   + Fatty acid methyl esters   *(3)*
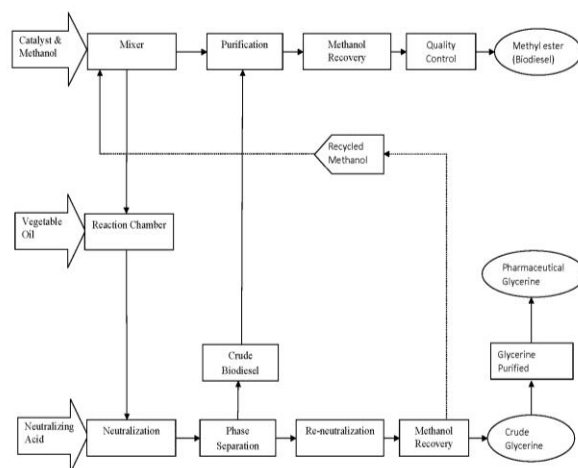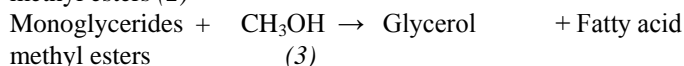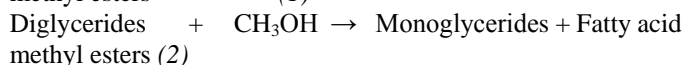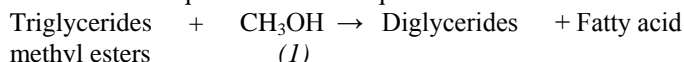

Fig. 2: Schematic of transesterification process of Biodiesel Production

The studies of methanolysis reaction kinetics identify three regimes: a slow initial mass transfer controlled regime, a fast chemically controlled regime followed by a slow final regime close to equilibrium [5]. The initial slow regime is attributed to the formation of a bi-phase reaction mixture due to the immiscibility of the methanol and the oil. In this stage of the process, the mass transfer of triglycerides from the oil phase to the methanol–oil interface limits the rate of methanolysis reaction and controls the kinetics initially. During the chemically controlled stage, the reaction rate increases rapidly which has been explained by increasing the concentration of oil in the methanol phase [6]. As methyl esters are formed they act as a mutual solvent or co-solvent for the reactants so that the reaction mixture becomes pseudo-homogeneous [5].

While the reaction mixture is heterogeneous, the pseudo-homogeneous behaviour has been attributed to a self-enhancement of the interfacial area, due to the intensive drop breakage process during the fast reaction regime [7]. In the final part of the methanolysis process, the depletion of the reactants oil and methanol and the depletion of the catalyst in the biodiesel phase, along with the formation of the products enhance the reverse reactions and the equilibrium is approached [8]. Long transesterification tests run for about 4 hours at 65 °C with molar ratio 6:1 methanol to oil and 1–1.5% in weight of catalysts has shown that between 5.15% and 6.65% of the triglycerides, saponification which confirms the importance of the increment of side reactions as the methanolysis moves closer to equilibrium [9].

METHODOLOGY
Alkali-Catalysed Transesterification
Sodium hydroxide (NaOH) at different concentration of 0.6-1.6% to oil weight was mixed with 16 litres of methanol and the mixture (sodium methoxide) stirred in a mixer at an optimum speed of 200 rpm for 20 minutes to ensure a homogeneous mixture and that the catalyst dissolves completely.

The feedstock (palm olein vegetable oil) was pre-heated to a temperature of 120^0C in the reactor to remove any water vapour and other volatile impurities. The oil was allowed to cool to 60^0C which is below the evaporating temperature of methanol. Sodium methoxide was then added to the pre-heated oil in the reactor at a molar ratio of 6:1(sodium methoxide in excess) and stirred rigorously at 200 rpm for hours ranging from 0.5-6 hours at a temperature of 60^0C and ambient pressure. The product at each interval of time was discharged through a funnel and allowed to settle for 24 hours to enhance effective separation. A successful transesterification reaction produces two liquid phases: esters and crude glycerol [10]. After 24 hours, it was discovered that the product formed separated into two layers with the lighter methyl ester (biodiesel) at the top and glycerol at the bottom. The by-product (glycerol) was found to be heavier than biodiesel (i.e has higher density than the biodiesel formed), so biodiesel was carefully decanted. The crude biodiesel obtained contains some impurities which were separated by purification via methyl ester wash followed by drying process.

Acid Catalysed Transesterification
For this transesterification reaction, HCl is used as a catalyst because the performance of the acid catalyst (HCl) is not strongly affected by the presence of free fatty acids in the feedstock. The used frying oil was pre-heated to a temperature of 120^0C, in order to remove trapped water molecules in the oil and then allowed to cool to 60^0C. The acid catalyst (HCl) at a concentration of 0.8-1.8% of the weight of oil, was mixed with methanol to form methanolic HCl and the mixture was carefully added into the used frying oil in the mixer at a molar ratio of 8:1(Methanolic HCl in excess) and stirred at 200 rpm for time interval of 2-10 hours after which it was discharged into a funnel at each interval of time and allowed to settle for 24 hours. After 24 hours, it was discovered that the product formed separated into two layers with the lighter biodiesel at the top and denser glycerol at the bottom.

RESULTS AND DISCUSSION
Effect of Reaction Temperature on Yield
The biodiesel yields were determined when ambient temperature was varied between 20^0C-90^0C. Increase in reaction temperature speeds up the reaction rate and shortens the reaction time [1] [11].

According to Bello et al., (2013) [1], the optimum temperature was 64^0C (near the evaporating temperature of methanol). Increase in temperature beyond this point decreases the yield due to evaporation of methanol.

Temperature influences the reaction rate and yield of methyl esters. Therefore, the reaction of vegetable oil with the mixture of methanol and sodium hydroxide was carried out close to the boiling point of methanol (70^0C) at atmospheric pressure. Further increase in temperature is reported to have adverse effect on the conversion process [12]. Generally, under transesterification with alcohol, the first step is the conversion of triglycerides to diglyceride, which is followed by the subsequent conversion of higher glyceride to lower glycerides and then to glycerol, yielding one methyl ester molecule from each glyceride at each step. The production process starts with the reactor charged with a given amount of palm olein vegetable oil or waste frying oil, which was pre-heated at different temperatures, meanwhile a solution of catalyst in methanol (CH_3OH) was added. The reaction condition was varied to obtain a large range of methyl ester yield. Heating and stirring was then stopped, neutralized with acetic acid and the product was allowed to separate into two phases. The optimum parameter involved in the process was determined while the rest of them remain constant. After each optimum was obtained, this value was considered to be constant during the optimization of the next parameter. Ester yields results (given as percentages) were related to the weight of the oil at the start. (weight of ester/weight of oil).

Effect of Reaction Time on Biodiesel Yield
The effect of reaction time on biodiesel yield was studied for palm olein vegetable oil.

For alkali transesterification, the reaction time studied at different time intervals ranging from 0.5-6 hours revealed that about 2 hours of reaction was sufficient for the completion of the alkali transterification process and optimum conversion of palm olein vegetable oil to biodiesel (about 80%). For acid transesterification, reaction time was studied at time intervals ranging from 2-10 hours. About 8 hours of reaction was sufficient for the completion of acid transesterification and optimum conversion of used frying oil to biodiesel (about 68%).
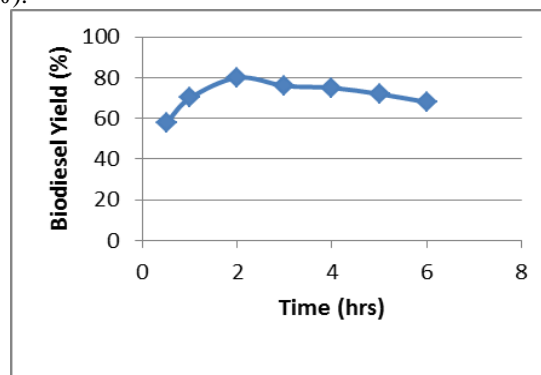
Figure 3: Biodiesel yield at different Time Interval for Alkali Transesterification

From Fig. 3, as temperature increases, the reaction rates increases and biodiesel yield was optimum (80%) at 2 hours after which there is decrease in yield as a result of evaporation of methanol.
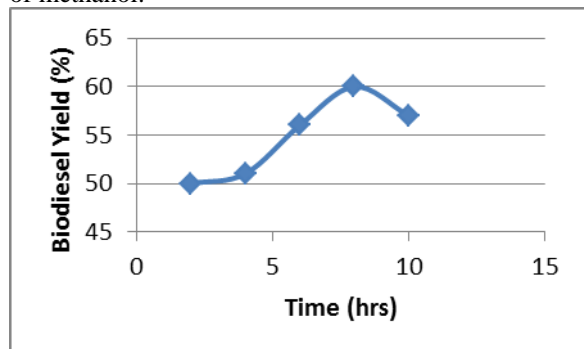

Figure 2.0: Biodiesel yield at different Time Interval for Acid Transesterification

Also from Fig. 4, as temperature increases, the reaction rates increases and biodiesel yield was optimum (60%) at 8 hours after which there is decrease in yield as a result of evaporation of methanol. The yield of alkali transesterification of palm olein vegetable oil to biodiesel was greater than the acid transesterification of used frying oil to biodiesel because of the virgin nature of palm olein oil. The presence of long chain free fatty acid in used frying oil decreases the yield compared to palm olein vegetable oil.

Determination of Biodiesel Yield

In order to ensure that the transesterification method employed results in optimum yield of biodiesel from its raw materials, the biodiesel yield was determined as follows:

$$Yield = \frac{Amount\ of\ biodiesel\ produced}{Weight\ of\ oil\ used} \times 100\% \qquad (4)$$

CONCLUSION

Increase in temperature; increase in amount of catalyst and stir speed speeds up the rate of transesterification reaction and reduces the reaction time for the conversion of oil to biodiesel. Excessive increase in temperature above the evaporating temperature of methanol will subsequently reduce yield due to gradual evaporation of methanol. Also, soap and gel may be formed when catalyst amount increases beyond the optimum, this prevents ester layer separation. Excessive increase in stir speed may cause splashing of raw materials due to excessive agitation hence decreasing the biodiesel yield.

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