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STUDY ON HETEROGENEOUSLY CATALYZED TRANSESTERIFICATION REACTION

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Abstract: *The commercial process of heterogeneously catalyzed biodiesel production process is in its final steps due to its advantages over the old homogeneously catalyzed one, and in order to provide an economic and fast way to investigate the vegetable oil conversion into biodiesel, a relation between conversion and a parameter that can be easily measured like viscosity is developed in this paper. The variation of viscosity with increasing conversion was proved to be exponential.an equation was developed to predict conversion from dynamic viscosity values based on the experimental data. A conversion of 91% was obtained at 60 °C reaction temperature, 12:1 methanol to oil molar ratio, 600 rpm in 2 hours of reaction time. The method reported in this paper is meant to save time and money since the most widely used chromatography methods are expensive and time consuming.*

Keywords: biodiesel analysis, viscosity, Calcium oxide.

INTRODUCTION

The continuously rising energy demands and the limited fossil fuel resources have driven the researchers around the world toward the investigation and development of alternative fuels of renewable resources. Biodiesel is the term used to refer to a blend of fatty acid methyl esters with significantly lower exhaust emissions than its rival petro-diesel [1]. Biodiesel has some notable properties that attracted the attention to it as a promising alternative to petro-diesel like its biodegradability, low toxic emissions especially CO2 gas, decent properties of storage and transportation and the fact that it’s derived from renewable resources [2].

Biodiesel is derived from vegetable oils by esterification or transesterification of vegetables oils and animals fats[3].during the previous years the dominant process for biodiesel production was homogeneously catalyzed using mainly potassium hydroxide or sodium hydroxide for transesterification and sulfuric acid for esterification, primary alcohols are used to react with oils in both esterification and transesterification processes(mainly methanol for its favorable properties and low price)[4-6].the homogeneously catalyzed process has proven its acceptance, however it comes with its disadvantages like catalysts corrosiveness, soap formation, glycerol phase contamination with catalyst, requirement of large amount of water for biodiesel washing and requirement of energy for biodiesel drying which makes this process time and labor consuming [7-10].

The corrosion and purification steps associated with the homogeneous process were a key factor to the transformation to the more reliable and time conserving heterogeneous process which was reported as the solution to the homogeneous process problems [11,12].

Calcium oxide has been reported as a cheap and effective catalyst for the transesterification process of low free fatty acids oils, its resources basically consists of calcium hydroxide or calcium carbonate that can be calcined at different temperatures to obtain calcium oxide of specific properties (basicity, surface area, pore volume, etc..)Depending on calcination temperature and time, CaO was categorized as a solid basic catalyst with decent reusability with or without regeneration depending on its origin [13-16].

Different analytical systems have been utilized for the quantification of FAME in transesterification product including thin layer chromatography (TLC), Gas chromatography (GC), high performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR), IR spectroscopy and gel permeation spectroscopy (GPC) [17]. These systems are very accurate, sensitive and also measure the content of by-product glycerol as well as the remaining unreacted glycerides (tri di and mono) in the produced FAME. However, the on-line application of these systems in a biodiesel production plant is very difficult due to the requirement of sample preparation and usually chemical modification and most of the times the analysis will continue to more than 30 minutes to get accurate results [17].

When Triglycerides in vegetable oils are converted to fatty acid methyl esters there will be a remarkable decrease in the value of viscosity, normally from (40-60) cp to (2-8) cp, according to oil’s fatty acid’s profile. Since biodiesel is a mixture of different fatty acid methyl ester, each methyl ester will contribute to the overall viscosity of the produced biodiesel [18].

The objective of the current work is to develop a method that is acceptable, cheap and quick to estimate the conversion of triglycerides and quantify the FAME content in the product of a heterogeneously catalyzed transesterification process plant. The method is based on the difference in dynamic viscosity values between the fatty acid glycerides and the corresponding fatty acid methyl esters since methyl esters have lower viscosity values than glycerides. The dynamic viscosity value can be determined with not much effort, time and expenses using an on-line viscometer and thus the content of FAME will be continuously measured and the process will be monitored.

1. EXPERIMENTAL

1.1. MATERIALS

Analytical grade methanol and n-hexane were purchased from RDH , 96% purity calcium oxide was supplied by CDH which is then activated by calcination at 900^oC for 2 hours and sunflower oil was purchased from local market.

1.2. TRANSESTERIFICATION

The experiments were conducted using a 250 ml flask connected to a reflux condenser, a specific amount of oil was added in the flask and when the desired reaction temperature was reached methanol and catalyst are added according to specific methanol to oil molar ratios and stirred at 600 rpm. Experiments are carried out with different reaction temperatures, residence times and methanol to oil molar ratios specifically to investigate different oil conversions and reaction products with a broad range of FAME content to get a clear idea about how conversion and dynamic viscosity are related. Schematic diagram of the system which is composed of a 250 ml flask (batch reactor), 3 way connection, thermometer an a condenser is shown in **figure (1)** .

1.3. FAME ANALYSIS

The FAME product samples were analyzed first by gas chromatography using GC-shimadzu 2010 with sp-2840 Column and flame ionization detector (FID), samples are first diluted with n-hexane then injected for the analysis. The injector temperature was fixed at 280°C and the detector temperature was fixed at 310°C, column oven temperature was raised from 140 °C (hold 1 min) to 160 °C (10 °C/min), 160 °C to 290 °C at a rate of (10 °C/min) (hold 3 min), 280 °C to 300 °C at a rate of (3 °C/min) (hold 11 min)

After GC analysis the dynamic viscosities of each of these samples was obtained at 38 °C using a Brookefield viscometer which consists of holder for the cylinder sample, spindle, adapter and a water jacket.

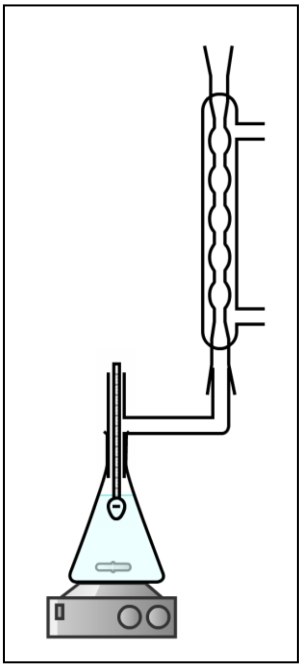

Figure 1: schematic diagram of the system.

2. RESULTS AND DISCUSSION

2.1. XRD ANALYSIS

XRD analysis of calcium oxide catalyst was carried out to obtain some structural information about it. CaO major peaks are clearly indicated in **figure (2)** and are indexed to CaO (card number: 00-037-1497). No peaks of calcium carbonate or calcium hydroxide are present due to strict storage and transportation of the samples (all samples are stored in vacuum sterile tubes).

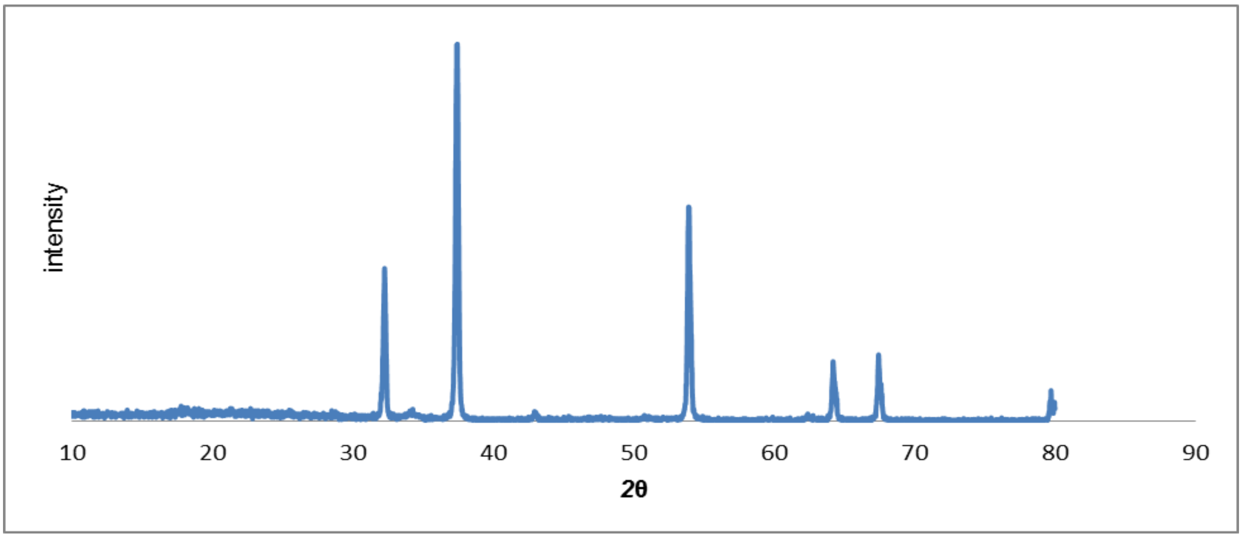

Figure 2: XRD analysis of catalyst CaO.

2.2. BET SURFACE AREA ANALYSIS

BET surface area analysis was carried out for the calcium oxide catalyst using the ASAP 2020. The test result showed a BET surface area of 3.7202 m^2/g, pore volume of 0.014526 cm^3/g, pore size equals to 156.1846 ^{o}A and an average particle size of 16128.160 ^{o}A.

2.3. RELATION BETWEEN CONVERSION AND VISCOSITY

As shown in the **figure (3)** a relationship between dynamic viscosity and conversion is obtained. The associated increase in conversion with the notable decrease of dynamic viscosity is attributed to the fact that fatty acid methyl esters has much lower viscosity than triglycerides initially present in the oil, this relation seems to be exponential however at conversions higher than 65% it can be seen from **figure (2)** that conversion started to vary kind of linearly with dynamic viscosity and this may be because the samples contain mainly methyl esters and less glycerides [18].

$$\%conversion = 156.99 * e^{(-0.137\mu)} \qquad (1)$$

μ : dynamic viscosity (cp) at 38 ^oC

Equation (1) can be used to estimate glyceride conversion as a function of dynamic viscosity at 38 ^oC.

Statistical analysis was carried out using statistica v10.202, analysis showed a level of confidence equals to 95% and a standard deviation of 6.58. observed values of conversion vs. predicted values of conversion are shown in **figure (4)**.

The results' operating conditions are shown in **table (1)**.

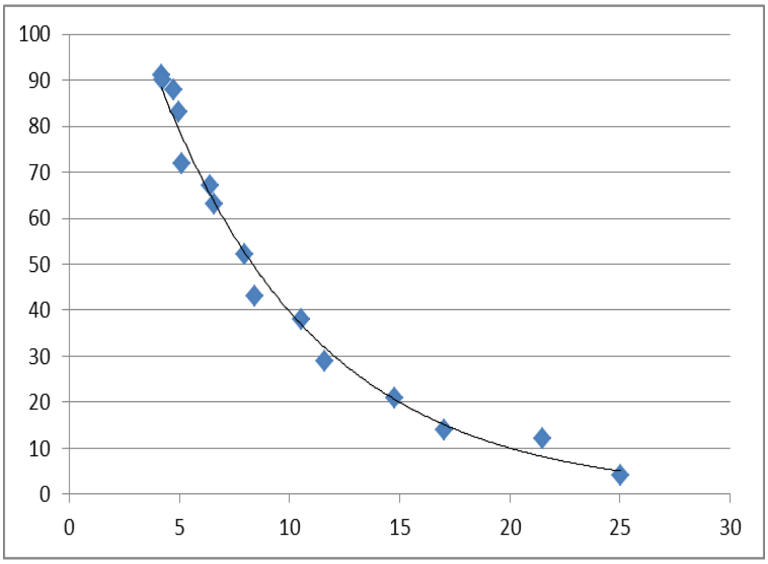

Figure 3: conversion vs. dynamic viscosity.

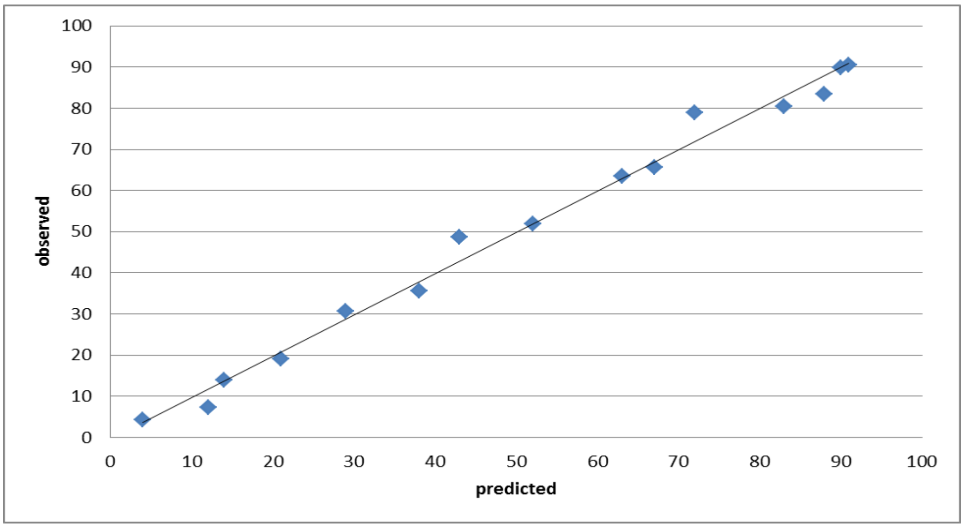

Figure 4: experimental vs. predicted data.

Table 1: details of experiments.

Conversion %	Methanol : oil (molar ratio)	T (^{o}C)	Residence time (h)	Dynamic viscosity (cp)
91	12:1	60	2	4.17
83	12:1	60	1.5	4.98
72	12:1	60	1	5.12

83	14:1	60	2	4.98
67	12:1	50	2	6.38
63	9:1	60	2	6.6
52	6:1	60	2	7.98
43	6:1	60	1.5	8.4
38	9:1	60	1	10.55
29	6:1	50	1.5	11.59
21	12:1	40	2	14.79
14	12:1	40	1.5	17
12	12:1	60	0.5	21.5
4	12:1	40	1	25.02

2.4. METHANOL : OIL RATIO

Alcohol (methanol CH3OH) to oil molar ratio highly affects the transesterification process. Experiments were carried at molar ratios of (6:1, 9:1 and 12:1) at 60^{o}C below the boiling point of methanol for 2 hours, a condenser is used to assure no (or extremely little) methanol loss during the reaction. It is clearly indicated in **figure (5)** that an increase in this ratio will positively affect the transesterification reaction and that is attributed to shifting the reaction equilibrium toward the forward reaction where glycerides react with alcohol producing more fatty acid methyl esters and resulting in achieving higher conversions. As shown in **figure (4)** increasing the methanol to oil molar ratio to 12:1 resulted in the highest glycerides conversion however, studies show that the addition of an excessive amount of alcohol will result in decreased conversions due to slower separation of produced glycerol and methyl esters [19]. It is suggested that glycerol is dissolving in the excessive amounts of alcohol (methanol CH3OH) and inhibits the transesterification reaction thus resulting in lower conversions [20-23]. Methanol to oil molar ratios higher than 12:1 resulted in lower conversion and thus biodiesel yield.

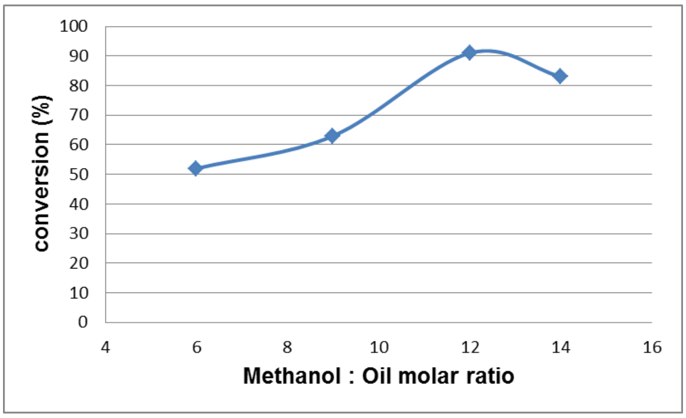

Figure 5: conversion(%) vs. methanol:oil (molar).

2.5. Effect of reaction time

Reaction time is a key parameter in the study of transesterification reaction. Set of experiments at 12:1 methanol to oil molar ratio carried out at a reaction temperature of 60 ^{o}C and kept for (0.5, 1, 1.5 and 2) hours. As shown in **figure (6)** the conversion of triglycerides into fatty acid methyl ester remarkably increases with time and after 2 hours of reaction time, a conversion of 91% is obtained and increasing the reaction time beyond 2 hours did not affect the reaction which is attributed to catalyst activity, reaction temperature and the high methanol to oil ratio used in the experiments resulting in shifting the equilibrium reaction toward the forward reaction [20]. This result may differ from that reported in the literature because the activity of calcium oxide catalyst highly depends on its origin [13-16].

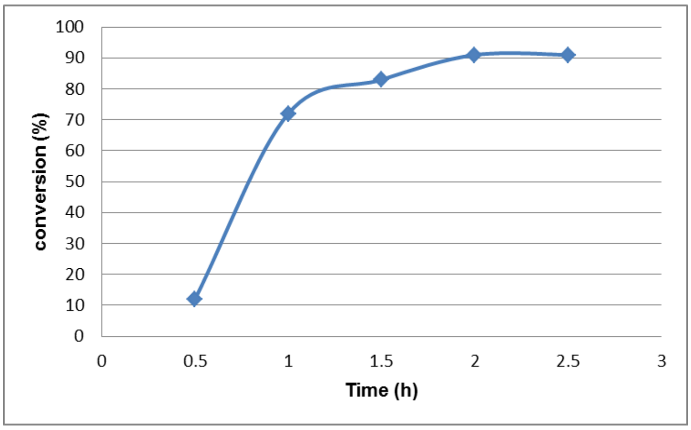

Figure 6: conversion(%) vs. reaction time (h).

2.6. EFFECT OF REACTION TEMPERATURE

Experiments are carried out with (40,50 and 60) ^{o}C reaction temperatures at atmospheric pressure using methanol to sunflower oil molar ratio of 12:1 and the reaction was allowed to continue to 2 hours. Reaction temperature was maintained constant during the reaction period and measured using a digital thermometer. As indicated in **figure (7)** , increasing the temperature from 40 ^{o}C to 50 ^{o}C and then to 60 ^{o}C at atmospheric pressure causes a significant rise in glycerides conversion which is expected since the transesterification reaction is endothermic and the temperature was under the boiling point of methanol where reaction temperatures higher than methanol boiling point will cause a reduction in glycerides conversion due to formation of methanol bubbles [24].

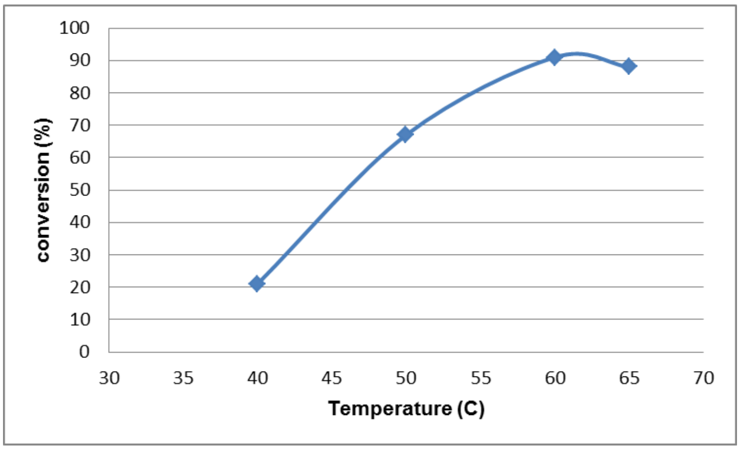

Figure 7: conversion(%) vs. Temperature.

CONCLUSIONS

A cheap and quick method to calculate glycerides conversion and estimating the FAME content is developed using viscosity measurements with the aid of gas chromatography analysis. A predicted data with 95% level of confidence was obtained using the developed equation (1). The exponential variation of dynamic viscosity as a function of conversion was proved and it is apparently as a result of tri, di and mono glycerides conversion into methyl ester. It was shown that increasing reaction time after the first 2 hours did not affect the reaction however increasing methanol to oil molar ratio and temperature beyond 12 molar ratio and 60 ^{o}C resulted in a decrease in the conversion.

BIODATA

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