



Production of Biodiesel Fuel from Used vegetable Oil

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Abstract

Used vegetable oil was introduced to transesterification reaction to produce Biodiesel fuel suitable for diesel engines. Method of production was consisted of filtration, transesterification, separation and washing. Transesterification was studied extensively with different operating conditions, temperature range (35-80°C), catalyst concentration (0.5-2 wt. % based on oil), mixing time (30-120 min.) with constant oil/methanol weight ratio 5:1 and mixing speed 1300 rpm. The concentration of Fatty acid methyl esters (Biodiesel) was determined for the transesterificated oil samples, besides of some important physical properties such as specific gravity, viscosity, pour point and flash point. The behavior of methyl esters production and the physical properties of Biodiesel were studied with the different operating conditions. The results show that increasing methyl esters concentration with increasing temperature and catalyst concentration and the transesterification is a second order reaction. The research aiming to recycle spent cooking oils to prevent pollution of soil and water, and converting them to Biodiesel fuel with low emissions.

انتاج وقود الديزل الحيوي من الزيوت النباتية المستعملة

الخلاصة

تم ادخال الزيت النباتي المستعمل لتفاعل الاسترة التبادلية لانتاج وقود حيوي مناسب لمكائن الديزل. ان طريقة الانتاج تضمنت الترشيح، الاسترة التبادلية، الفصل والغسل. درست الاسترة التبادلية على نطاق واسع بمختلف الظروف التشغيلية، مدى درجة حرارة (35-80°C)، تركيز العامل المساعد (0.5-2 % نسبة وزنية)، زمن خلط (30-120 دقيقة) بنسبة وزنية ثابتة زيت الى الميثانول 5:1 وسرعة خلط 1300 دورة بالدقيقة. حدد تركيز الديزل الحيوي لنماذج زيت الاسترة التبادلية، اضافة الى بعض اهم الخواص الفيزيائية مثل الكثافة النوعية، اللزوجة، نقطة الانسكاب و نقطة الوميض. لقد تم دراسة سلوك انتاج الاسترات المثيلية والخواص الفيزيائية لوقود اليزل الحيوي بمختلف الظروف التشغيلية. اظهرت النتائج زيادة تركيز الاسترات المثيلية بزيادة درجة الحرارة وتركيز العامل المساعد وان حركية التفاعل الاستري من الرتبة الثانية. البحث يهدف الى تدوير زيوت الطبخ المستهلكة لمنع تلوث التربة والماء، وتحويلها الى وقود الديزل الحيوي ذو الانبعاثات المنخفضة.

Key Word: Biodiesel Fuel, Transesterification, used vegetable oils

Introduction

Biodiesel is a mono alkyl ester of long chain fatty acids biodegradable, nontoxic fuel oil that is essentially free from sulfur and aromatics derived from renewable lipid such as vegetable oils and animal fats. It can also be produced from recycled vegetable oil or animal fat, which is generally referred to as waste vegetable oil. Used cooking oils and animal fats and the general set of products can be an excellent feedstock for biodiesel production depending on their condition and quality attributes (Guo, Y., 2002, Mark Hall, 2009). Used cooking oils or animal fats may be collected after cooking in the home or restaurants as well as from the commercial food industry. Frequently, this oil is placed in the solid waste stream and is deposited in landfills. Unfortunately, some of the oil is poured into sinks and finds its way into the sanitary sewer system and eventually becomes a burden on the wastewater treatment system (Mark Hall, 2009). Waste cooking oil is mainly composed of triglycerides, and contains some free fatty acids (Shigashida M., 2009). Most common method to produce biodiesel is by transesterification which means the reactions of catalyzed chemical involving vegetable oil and an alcohol to yield fatty acid alkyl esters and glycerol. Figure 1 shows a schematic representation of the transesterification of triglycerides with methanol to produce fatty acid methyl esters (Biodiesel).

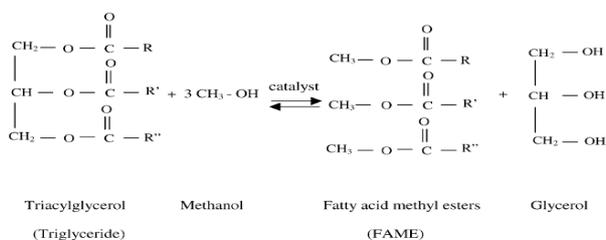


Fig.1. Transesterification Sketch

Triacylglycerol is the main component of vegetable oil, consists of three long chain fatty acids. As shown in Figure 1 when triacylglycerol reacts with an alcohol the three fatty acids chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid methyl ester (Y. Zhang, 2003). The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content

have an influence on the transesterification (UlfSchuchardt, 1998). Biodiesel is renewable with energy efficient and also displaces petroleum derived diesel fuel, it can be used in most diesel equipment and no or only minor modifications and reduce greenhouse gases emissions and tailpipe emissions, including air toxics and smogs (Pongsiri Jaruyanon, 2007). The lifecycle production and use of biodiesel produces approximately 80% less carbon dioxide emissions, and almost 100% less sulfur dioxide. Combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons, and a 75-90% reduction in aromatic hydrocarbons. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. The most common blend is a mix of 20% biodiesel with 80% petroleum diesel (Douglas G., 2002).

This paper focused on production of Biodiesel fuel from used cooking vegetable oil to establish a concept for recycling spent vegetable oils by using small pilot plants for production as in Europe and southeast Asia where the production cost of one gallon Biodiesel Fuel from used oil is 1.09\$. It is a fuel from a cheap source, has 90% of petroleum diesel fuel efficiency in addition to its features as fuel friendly to environments by preventing soil and water from direct pollution and gives low emission of combustion gases. The effect of catalyst concentration, temperature and mixing time were studied, and the purity of Biodiesel with its physical properties was determined at various operating conditions.

Experimental Work

Materials

- 1. Used vegetable oil** collected from the kitchen frying oil with boiling point 200°C, free fatty acids less than 5% and free acid methyl esters less than 1%.
- 2. Methanol** analytical reagent A.R. assay (GC) 99.8% supplied by LAB-SCAN analytical sciences
- 3. Sodium hydroxide** 98% supplied by RIEDEL-DEHAENASEELZE-HANNOVER.

Biodiesel Production

In general, Laboratory transesterification was carried out in a conical flask equipped with a magnetic stirrer. Either low or high base concentration dissolved in methanol and added to vigorously stirred recycled vegetable oil at 35 to 45°C with stirring for 60 min. (Fröhlich A., 2005). In this work Biodiesel was produced at various operating conditions, temperature range 35-80°C, ,

catalyst concentration range 0.5-2 wt. % and mixing time range 30-120 minute with constant oil/methanol weight ratio 5/1 and fixed mixing speed 1300 rpm. The operating conditions at which obtained optimum production is 65°C, 1wt. % NaOH and 1 h mixing time. The procedure of production was divided to three stages:

1. Pre-treatment

Used vegetable oil was exposed to thermal treatment 120 °C for 2 h and filtered under vacuum filtration to remove the impurities and contaminants, medium speed filter paper was used in a Buchner funnel which equipped to vacuum filtration system consist of 1 liter vacuum flask, trap and vacuum pump.

2. Transesterification

The Transesterification reaction was carried out in a 250 ml three neck flask, the two side necks equipped to a high efficiency condenser and a separating funnel, while a thermocouple was attached to the middle neck. A digital magnetic stirrer with hot plate (STUART CD 163) was used, able to read and control temperature automatically. In addition to a chiller (GALLENKAMR REGD) supplied the condenser with cold water. A 150 g of used vegetable oil was poured in the flask which set in a constant reaction temperature (35-80°C) with intensive stirring 1300 rpm (Jon Van Gerpen, 2005). Sodium methoxide solution was prepared by dissolving sodium hydroxide in methanol according to fixed oil/methanol weight ratio 5:1 and sodium hydroxide (0.5-2 wt. % based on oil), solution was transferred to separating funnel and poured into oil gradually and mixed for 30-120 minute. Mixture was quenched to stop reaction at once.

3. Separation and washing

The transesterification mixture was placed in a separating funnel for at least 6 h to ensure complete separation of Biodiesel (yellow) from glycerol (red to orange). The upper layer (Biodiesel) was drained and then washed by mixing with one volume of distilled water for about 15 minute to remove remained unreacted catalyst. The foggy solution poured into a separating funnel and left for 3 h. Biodiesel was placed in a furnace at 120°C for 1 h to ensure removing the remaining methanol and water (Fröhlich A., 2005).

Feedstock and Products Tests

Gas Chromatography analysis

Fatty acid methyl esters (Biodiesel) composition of samples was determined by gas chromatography (UNITED TECHNOLOGIES-PACKARD) using a column SE-30, and flame ionisation detector. The initial column temperature, 200 °C, was held for 6 min, and then increased to 325 °C at 1°C/min. Injector temperature was 300 °C and detector temperature was 350 °C. The flow rates of gases helium (carrier gas), hydrogen and air were 30, 30 and 250 ml/min respectively (Nezihe Azcan, 2008). Figure 2 shows gas chromatography analysis of Biodiesel produced at 65°C, 1wt. % NaOH and 1h. mixing time. It is shows that the concentration of fatty acid methyl esters is 94%.

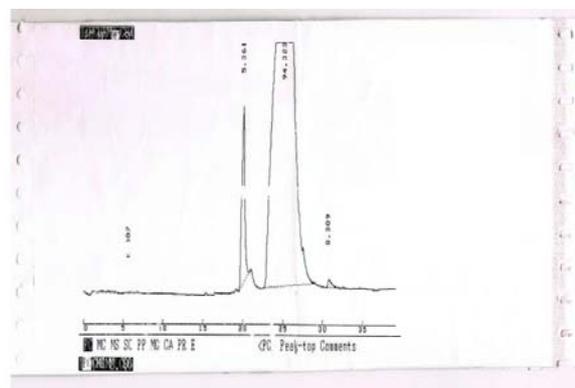


Fig.2. Gas Chromatography Analysis of Biodiesel

Density and Specific Gravity

The density and specific gravity of feedstock and products was determined by (ASTM D1217 - 93(2007)).

Viscosity

The viscosity of feedstock and products was determined by (ASTM D445 - 09).

Flash Point

The flash point of feedstock and products was determined by (ASTM D93 - 08).

Pour Point

The pour point of feedstock and products was determined by (ASTM D97 - 09).

Results & Discussion

Effect of Catalyst Concentration

The present result shows the effect of catalyst concentration (NaOH wt. %) on Biodiesel volume percentage in the transesterificated oil with mixing time 30 minute at different temperatures.

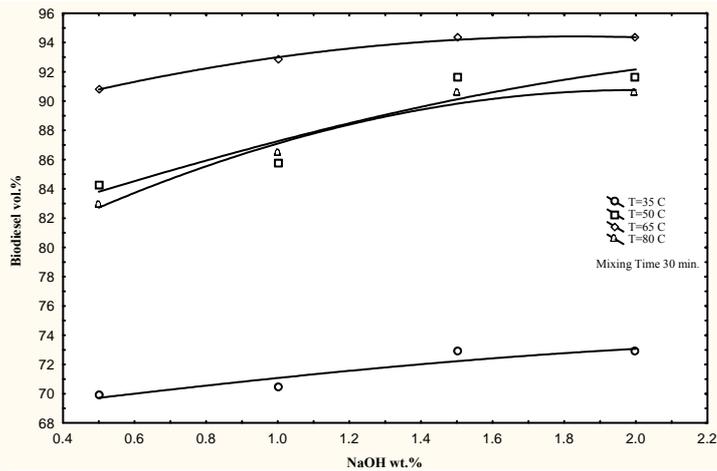


Fig.3. Effect of NaOH Concentration on Production of Biodiesel at Different Temperatures

Figure 3 results show that Biodiesel percentage (methyl esters) increased with increasing sodium hydroxide concentration at different temperatures. Catalyst concentration has an effective role in Biodiesel production, methyl esters increased with increasing sodium hydroxide concentration at different temperatures and that restricted according to the saturation level of NaOH in methanol if it above saturation or not. The concentration of methyl esters becomes constant beyond 1.5 wt. % NaOH and there is no significant increase, that matter qualifying this percentage to be the optimum, but some of NaOH was remained insoluble in the transesterification mixture at this percentage and that never note at lesser concentrations, that because NaOH became above saturation in sodium methoxide solution so can consider the optimum is 1wt. %. In general, methyl esters increased with increasing temperature up to 65°C (Yong W., 2007) at which maximum Biodiesel concentration was obtained 94 vol. %. At temperature 80°C the concentration of methyl esters was decreased which indicated that the optimum transesterification temperature is reflux temperature. Solubility of sodium hydroxide in methanol increased with increasing temperature which creates an efficient homogeneous sodium methoxide solution responsible on converting the triglycerides to fatty acid methyl esters, which mean that at high temperature an efficient sodium methoxide produced, so high Biodiesel was yield.

Effect of Mixing Time

Figure 4 show the effect of mixing time on Biodiesel volume percentage in the

transesterficated oil with sodium hydroxide concentration 1wt. % at different temperatures.

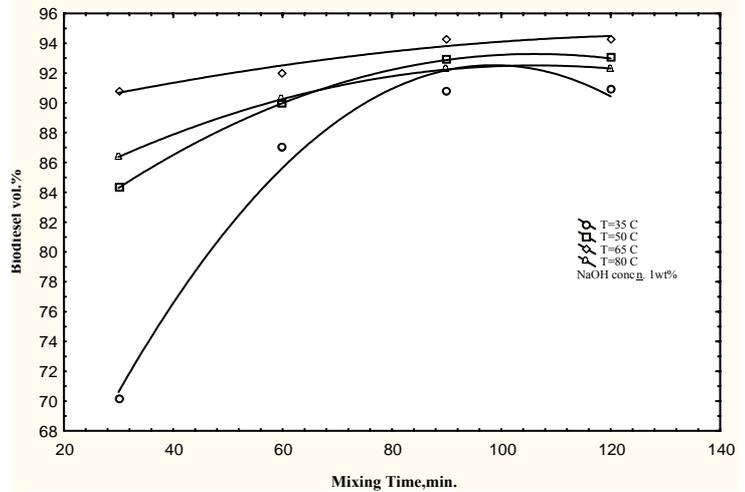


Fig.4.Effect of Mixing Time on Production of Biodiesel at Different Temperatures

Results show that methyl esters percentage (Biodiesel) increased with increasing mixing time at different temperatures (M.G.Devanesan, 2007). Biodiesel concentration increased clearly from 30 to 90 minute, and there is no significant increasing in Biodiesel concentration for longer extent of mixing time, this behavior was clear at minute 120. Mixing was necessary for commencement transesterification reaction, where sodium methoxide begin attack the triglycerides of used oil, and residence time is one of the most important parameters affect reaction, which can be expressed by residence time and conversion, so the transesterification is time dependence to get progressing in conversion until reaching equilibrium. From getting before, could be explain the reasons for increasing of Biodiesel concentration with increasing mixing time and the steadily concentration of methyl esters after 90 minute of mixing. Also, the concentration of methyl esters increased with increasing temperature at all times of mixing except at temperature 80°C where the Biodiesel concentration closed to concentration at temperature 50°C in mixing time 60 minute and then deviated to lesser concentration.

Effect of Catalyst concentration and mixing time on Biodiesel Physical Properties

1. Flash and pour Points

The flash and pour points are from the most important characteristics of engine fuel which restrict the safety and performance features of



fuel. Results show that biodiesel fuel had a flash point range between 180- 192°C, flash point decreased with increasing catalyst concentration, mixing time and triesterfication temperature but beyond 65°C was increased near to those at 50 °C caused by decreasing of methyl esters concentration at temperatures beyond 65°C as shown in figures 5 and 6 . While the pour point had a very narrow range begins from -9 to -12 °C and can say that no clear difference happened to pour point at different catalyst concentrations and transesterfication temperature. In general, pour point was recorded decreasing with increasing catalyst concentration and transesterfication temperature. From before, the produced Biodiesel fuel has high safety in storage and in engine combustion and can be workable even at low environment temperature (severe conditions).

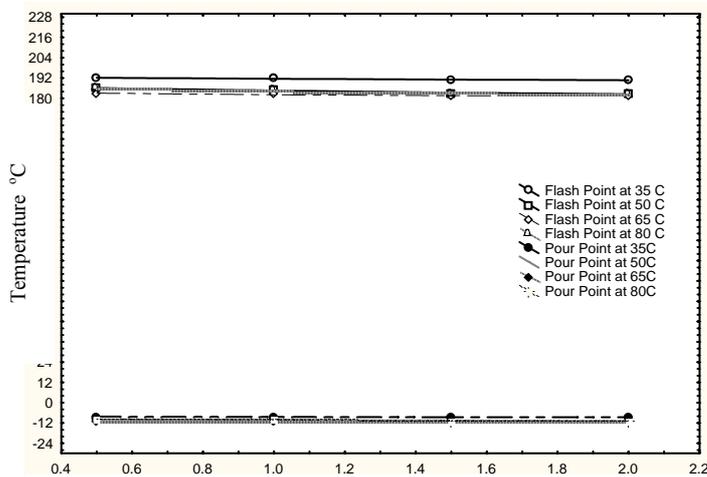


Fig.5. Effect of NaOH Concentration on Flash and pour points of Biodiesel

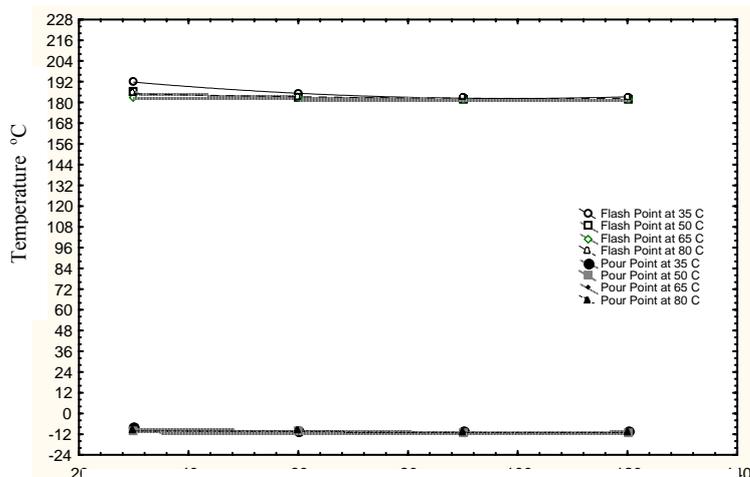


Fig.6. Effect of Mixing Time on Flash and pour points of Biodiesel

2. Viscosity and Specific Gravity

Figures 7 to 10 are showing the effect of catalyst concentration and mixing time on viscosity and specific gravity of Biodiesel fuel at different temperatures. Results show that viscosity and specific gravity decreased with increasing catalyst concentration, mixing time and transesterfication temperature. Increasing concentration of methyl esters with increasing catalyst concentration, mixing time and transesterfication temperature causes the decreasing in the viscosity and specific gravity of Biodiesel fuel, where long chains of triglycerides with high viscosity and high specific gravity converted to mono fatty acid methyl esters have viscosity and specific gravity lesser, which is responsible on this behavior. A viscosity range of Biodiesel fuel was distinguished from different operating conditions (1 - 2.6 cSt) at 100°C, but a very narrow specific gravity range was recognized (0.86 - 0.89).

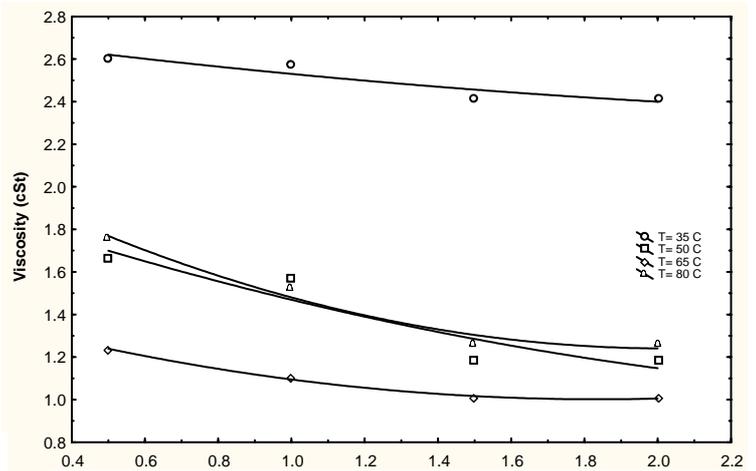


Fig.7. Effect of NaOH Concentration on Viscosity of Biodiesel at Different temperatures

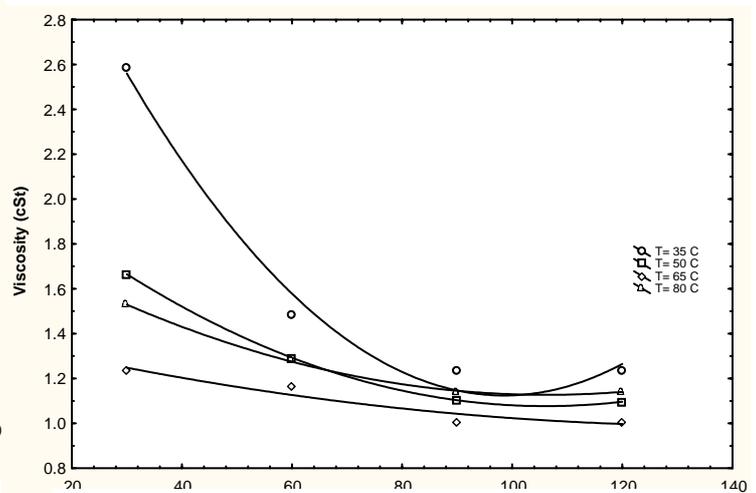


Fig.8. Effect of Mixing Time on Viscosity of Biodiesel at Different Temperatures

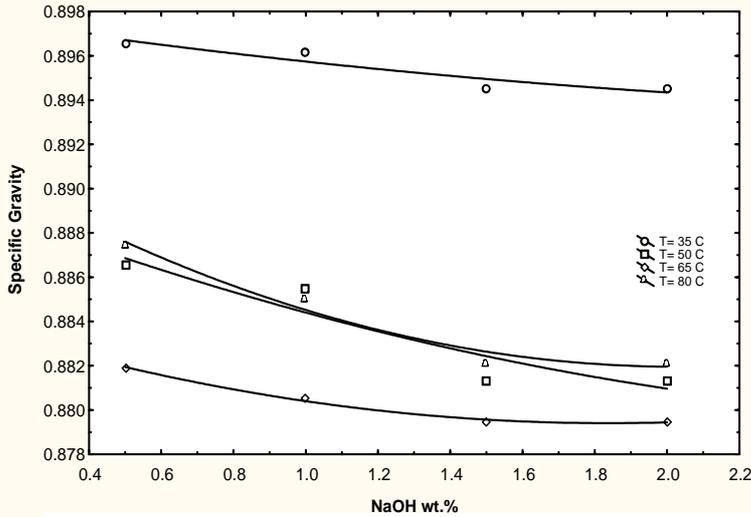


Fig.9. Effect of NaOH Concentration on Specific Gravity of Biodiesel at Different Temperatures

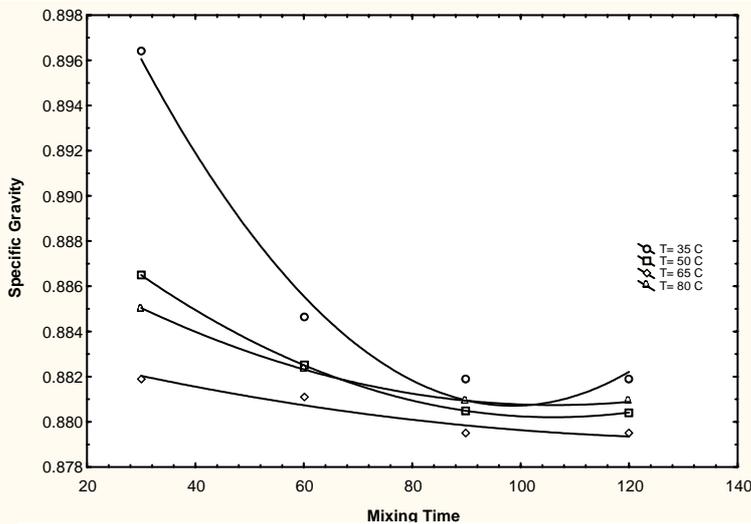


Fig.10. Effect of Mixing Time on Specific Gravity of Biodiesel at Different Temperatures

Kinetics of Transesterification Reaction

Transesterification reaction of triglyceride (backbone of used vegetable oil) with methanol and in presence of sodium hydroxide to produce fatty acid methyl esters (Biodiesel) was studied. Transesterification is a reversible reaction in which one molecule of triglyceride reacts with three molecules of methanol, the three fatty acids chains are released from the triglyceride skeleton and combine with the alcohol to yield fatty acid methyl esters and glycerol which is call “net reaction”. In fact, triglyceride react with the first molecule of methanol to produce diglyceride and ester of first chain of fatty acid then the diglyceride molecule react with the second molecules of methanol to produce monoglyceride and ester of second chain of fatty acid, finally the

monoglyceride molecule react with the third molecule of methanol to produce ester of third chain of fatty acid with glycerol. Transesterification reaction was carried out in a constant volume batch reactor without flow and the integral method was used for analysis of data. Some assumptions decided for simplifying determination order of reaction such as neglecting the effect of decomposition reaction. Thus, the irreversible reaction is simply the special case of the reversible reaction in which $C_{A_s} = 0$, or $X_{A_e} = 1$, or $K_c = \alpha$ (Octave Levenspiel, 1999). Results show that transesterification is a second order reaction. A plot of $\ln[(1.875 - X)/(1.865(1-X))]$ vs. t , as shown in Fig.11, gives a straight line through the origin for this form of rate of equation. The experimental data seems to be better fitted by a curve than by a straight line as shown in Fig.12, which indicated that this reaction is not first order reaction.

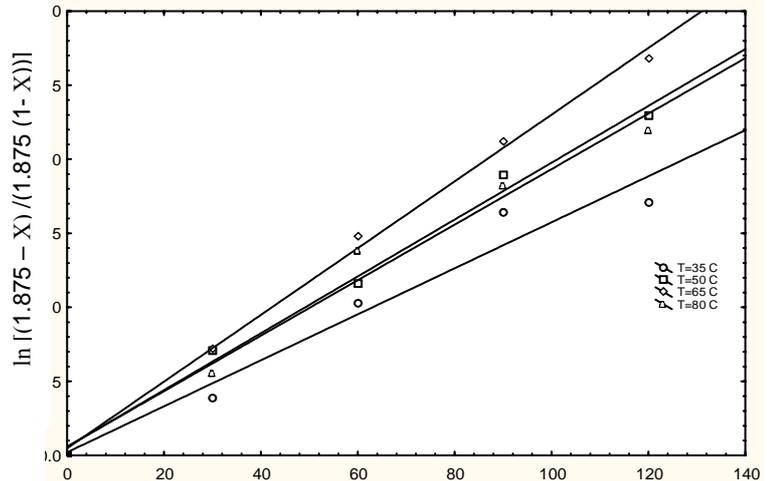


Fig.11. Second Order of Transesterification Reaction of Biodiesel Production at Different Temperatures

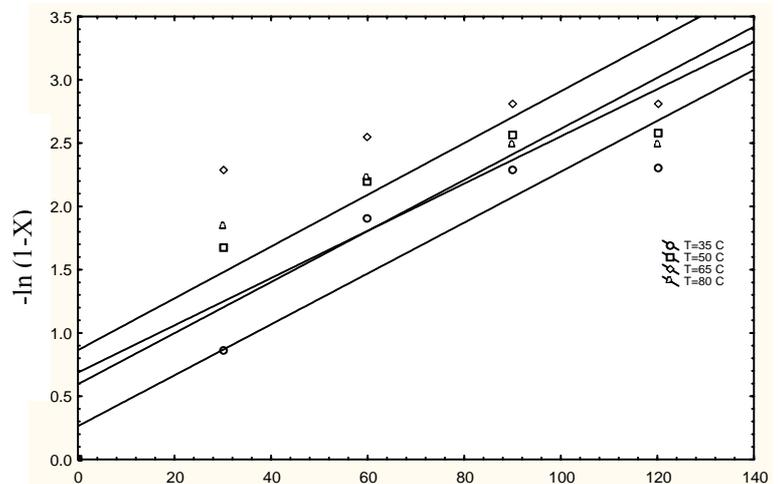


Fig.12. First Order of Transesterification Reaction of Biodiesel Production at Different Temperatures



Conclusions

Biodiesel fuel produced from waste vegetable oil was affected by catalyst concentration, temperature of reaction and mixing time. Result show that biodiesel was increased with increasing catalyst concentration and the best concentration was 1 wt % where higher catalyst concentration led to above saturation state. Also, the biodiesel increased with increasing temperature of reaction up to 65°C (boiling point of methanol) at higher temperature biodiesel was decreased. Biodiesel was increased sharply with increasing mixing time from 30-60 minute and the increasing was taking steadily behavior as reaching 90 minute. The physical properties of the biodiesel fuel were compatible with the standard specifications as shown in Table 1. The kinetics of transesterification reaction was examined and results indicated that this reaction is a second order.

Table 1 Physical properties of standard and obtained Biodiesel Fuel

Test	Standard	Obtained
Specific gravity@15.6°C	0.86-0.90	0.88-.89
Kinematic Viscosity at 40°C,mm ² /s	3.5-5	4.5-5
Flash Point,°C	minimum120	184-194
Pour Point,°C	< 3	-9/-12

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