4. Synthesis of Biodiesel from Palm Fatty Acid Distillate

Research Article

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Abstract

Palm fatty acid distillate is a by-product of palm oil refining industries and it consists of 83% fatty acids and 12% glycerides. Biodiesel was synthesized using palm fatty acid distillate (PFAD) as raw material in two steps. The first step involved hydrolysis of PFAD to convert glycerides into free fatty acids (FFA). The second step was esterification of these free fatty acids using methanol and homogeneous acid catalyst (sulfuric acid) to give methyl esters (biodiesel). Hydrolysis was studied at two different catalyst loadings. Esterification reaction was executed by recycling methanol and sulfuric acid in the aqueous phase. Recovery of methanol and sulfuric acid from aqueous phase of esterified PFAD was carried out by distillation. Biodiesel was purified firstly by water washing followed by neutralization of unreacted FFA. Neutralization was studied with different bases like aqueous sodium hydroxide, aqueous sodium carbonate, sodium hydroxide in 80:20 and 90:10 glycerol:water mixture.

Keywords: Biodiesel, esterification, neutralization, free fatty acid, PFAD.

1. Introduction

Biodiesel, an alternative fuel similar to conventional diesel, is produced from vegetable, and/ or animal oils/fats such as rapeseed, soybean, palm, lard, pork etc. No engine modifications are needed. Although diesel is part of its name, there is no petroleum or other fossil fuels in biodiesel. This environment-friendly fuel reduces emissions, smoke and odors. Biodiesel can also be used in blends with conventional diesel still achieving substantial reductions in emissions. Technically, biodiesel is Fatty Acid Methyl Ester (FAME). It is formed by replacing the glycerol from each triglyceride molecule of vegetable oil with methyl from methanol (that is by the reaction of free fatty acid and methanol). But there is some notable difference. The biodiesel molecules are simple hydrocarbon chains, containing no sulfur, ring molecules, or aromatics that are associated with fossil fuels. Biodiesel is made up of almost 10% oxygen, making it a naturally oxygenated fuel [12].

The Benefits of Biodiesel

Biodiesel has many environmentally beneficial properties. The main benefit of biodiesel is that it is carbon neutral, i.e., no net output of carbon in the form of carbon dioxide (CO_2). This effect occurs because when the oil crops grow they absorb the same amount of carbon dioxide as is released when the fuel is combusted. Biodiesel is rapidly biodegradable and completely non-toxic. Biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash. Biodiesel production process is straightforward and methodical and can produce consistent results. That is to say, in technical terms, the method of producing biodiesel is feasible.

2. Materials and Methods

2.1. Materials

The palm fatty acid distillate (PFAD) was procured from ROYAL ENERGY, Mumbai, as a yellow color solid having melting point of 40°C. Methanol (AR grade), potassium hydroxide, oxalic acid and phenolphthalein indicator were procured from S.D.Fine Chemicals, Mumbai. HPLC grade acetonitrile and acetone were procured from Thermo Fischer Scientific for analysis.

2.2. Experimental Methods

2.2.1. Hydrolysis of Palm Fatty Acid Distillate

PFAD was firstly washed with water in order to remove water soluble impurities. For this 100 g PFAD was taken in 250 ml glass reactor placed in oil bath maintained at 90^oC and washed with water at an agitation speed of 1500 rpm for about an hour with an overhead stirrer. Water to PFAD ratio was 2:1 (v:v) so as to keep water as a continuous phase with PFAD as dispersed phase. The organic (PFAD) and aqueous (H_2O) phases were separated out using separating funnel.

The washed PFAD was then taken for hydrolysis.

Hydrolysis reaction was conducted in a stirred batch reactor of volume 250ml equipped with a six blade turbine impeller running at 1500 rpm. In a typical reaction, 100g of PFAD was first melted in the reactor at 90°C for 10 minutes. Water (30% wt of PFAD) and sulfuric acid (1 and 2% wt of PFAD) as catalyst were added to the melt. The reaction temperature was maintained using an oil bath and the reaction mixture was vigorously agitated at 1500 rpm for an hour. Samples were collected at specific intervals of time (10 minutes). After the completion of reaction, reaction mixture was allowed to stand in an oil bath for 5 minutes to separate out the two phases. The two phases were separated from each other using separating funnel. Pretreated organic phase was subsequently used for the esterification reaction.

2.2.2. Esterification of Palm Fatty Acid Distillate

100g of hydrolyzed PFAD was taken in 250ml reactor kept in oil bath at 60^{o}C. Methanol (PFAD:Methanol = 1:3 molar basis) and 98% sulfuric acid (5% by wt. of PFAD) were added to the reactor to initiate the esterification reaction. The reaction was carried out at agitation speed of 1500 rpm using an overhead stirrer for an hour. Samples were collected at specific intervals of time (10 minutes). When the reaction subsides, the organic phase was separated from the aqueous phase using a separating funnel. The esterification reaction was carried out as shown in Figure 1 in order to study the effect of recycling of aqueous phase on FFA conversion. The organic phase was further treated for neutralization of acid and aqueous phase was used for recovery of sulfuric acid and methanol.

2.2.3. Recovery of Methanol and Sulfuric Acid from Aqueous Phase obtained from Esterification

The aqueous phase was taken in a 250ml three necked round bottom flask. Dean-Stark apparatus was attached to one of the necks and the rest two were stoppered. The fractionating column of the apparatus was stoppered and its burette was attached to the condenser. The mouth of the condenser was connected to gas flow meter to check any formation of gas in the process. The gas flow meter was further connected to gas sampling tube to collect the gas coming out in the process. The round bottom flask was kept in an oil bath and heated stepwise from 65^{o}C to 150^{o}C. The methanol-water mixture was collected from the burette of the Dean Stark apparatus. The mixtures collected at different temperatures were analyzed in density meter and the composition of methanol and water in the mixture was calculated. Sulfuric acid thus recovered after removal of methanol and water was analyzed for its concentration.

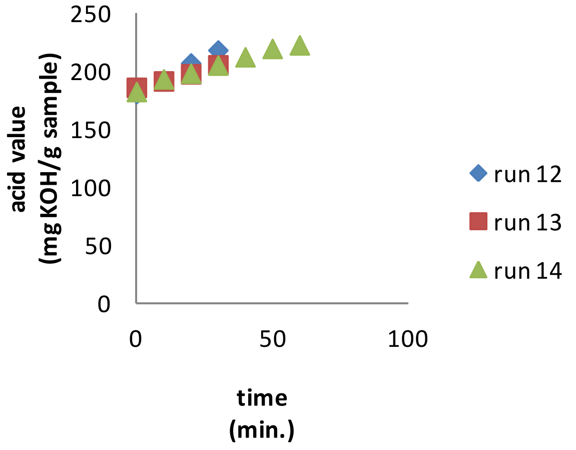
2.2.4. Neutralization of the Unreacted Fatty Acids present in the Organic Phase obtained from Esterification Stage

The entire organic phase was given water wash with excess water in order to remove methanol and sulfuric acid present in the organic phase. The sulfuric acid concentration of the organic phase before and after water washing was determined. The organic phase was then separated from the aqueous phase and its acid value was found out. Sodium hydroxide and sodium carbonate were used to neutralize (saponify) the unreacted FFA. Aqueous sodium hydroxide (50ml), aqueous sodium carbonate (50ml), sodium hydroxide in 80:20 and 90:10 (v:v) mixtures of glycerol: water (50ml each) were prepared. The unreacted fatty acids were removed by saponification reaction on the addition of above mentioned different bases to fixed quantity of organic phase taken in 250ml reactor at room temperature. The two phases were then separated using separating funnel and in case the phases did not separate, the reactor was kept in oil bath at about 60^{o}C till the separation is achieved.

3. Results and discussions

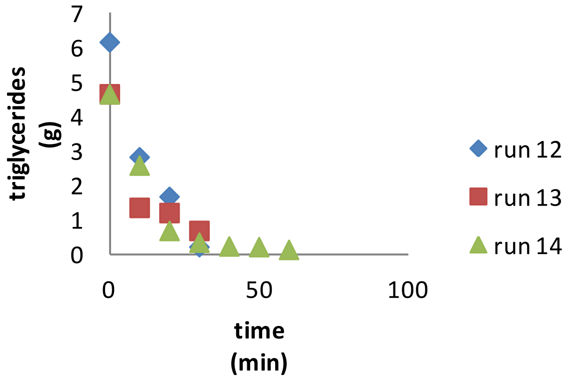
3.1. Hydrolysis of Palm Fatty Acid Distillate

About 100g of PFAD was taken in 250ml reactor kept in an oil bath at 90^{o}C. About 30g of water and 1g of 98% sulfuric acid was added to the reactor for the conversion of triglycerides in PFAD to fatty acids through hydrolysis reaction. PFAD was initially given water wash and water soluble impurities present in the PFAD were removed. The samples collected at intervals of 10 minutes were separated from aqueous phase, given water washing and analyzed for acid value. Also, HPLC analysis was done to find conversion of triglycerides, diglycerides and monoglycerides. Aqueous phase of the hydrolysis was analyzed for glycerol content. Following are the graphs representing the data. Graph 1 represents acid value increment of the PFAD during hydrolysis with time.

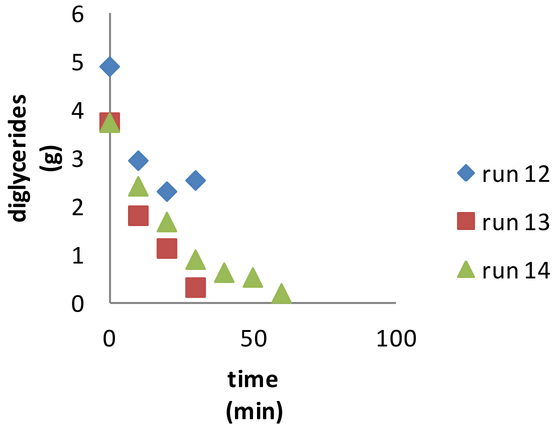


Graph 1: Acid value increment of the PFAD during hydrolysis with time

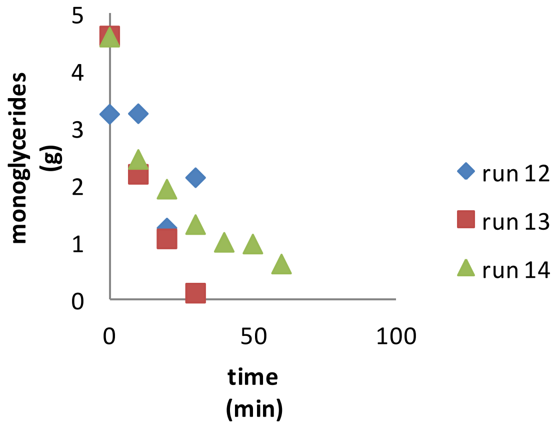
In run 12, 2% sulfuric acid was used to obtain acid value of 218 for reaction time of 30 min and in run 13, 1% sulfuric acid was used to obtain acid value of 205 for reaction time of 30 min. In order to check the conversion of acid value, run 14 was performed using 1% sulfuric acid for an hour and the acid value attained is 222 (nearly same as acid value achieved after half an hour using 2% sulfuric acid).



Graph 2: Conversion of triglycerides into fatty acids



Graph 3: Conversion of fatty diglycerides into fatty acids



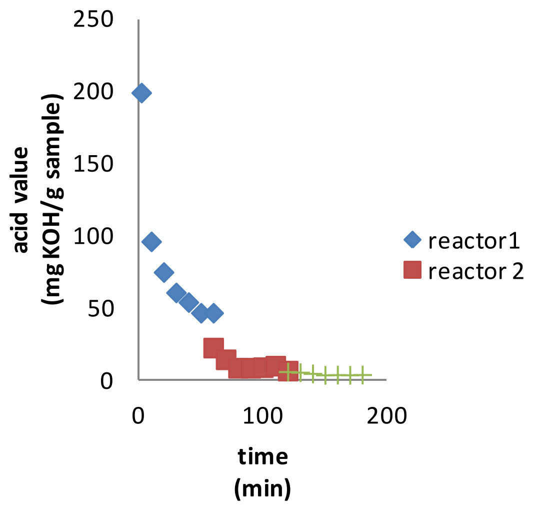
Graph 4: Conversion of monoglycerides to fatty acids

Graphs 2, 3 and 4 represent the conversion of triglycerides, diglycerides and monoglycerides reaction into fatty acids during hydrolysis reaction.

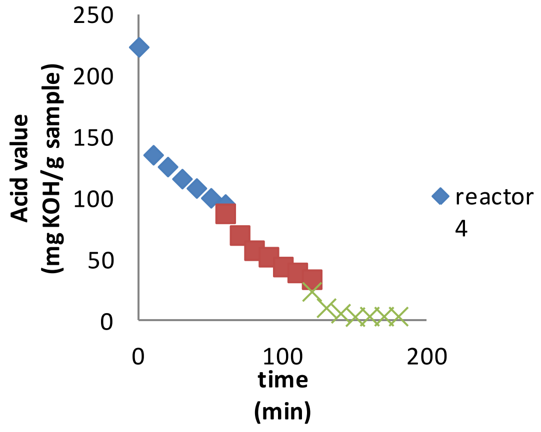
Glycerol content in the aqueous phase =2.004 g/lit (0.0307 mol/lit)

3.2. Esterification of fatty acids:

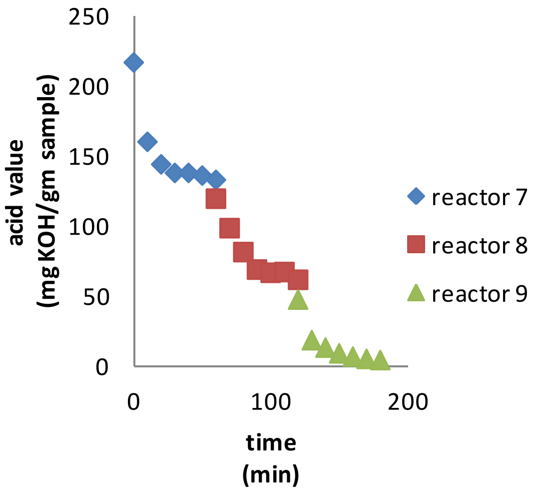
In the following explanation, each reaction was expressed in terms of a run. The block diagram is as shown in figure 1.



Graph 5: Decrease in acid values of the organic phase with progress in time



Graph 6: Decrease in acid values of the organic phase with progress in time



Graph 7: Decrease in acid values of the organic phase with progress in time

Graphs 5, 6 and 7 represent the decrease in acid values of the organic phase with the progress in time as the fatty acids were converted to methyl esters. Three batches in a row are shown in the same graph. The graphs indicate that, as the aqueous phase was recycled the rate of conversion of fatty acids to methyl esters decreased. The rate of conversion of FFA to methyl esters in reactors 6 and 9 increased.

3.3. Recovery of methanol and sulfuric acid from aqueous phase of esterification.

The aqueous phase obtained from esterification stage was taken in 250 ml three necked round bottom flask.

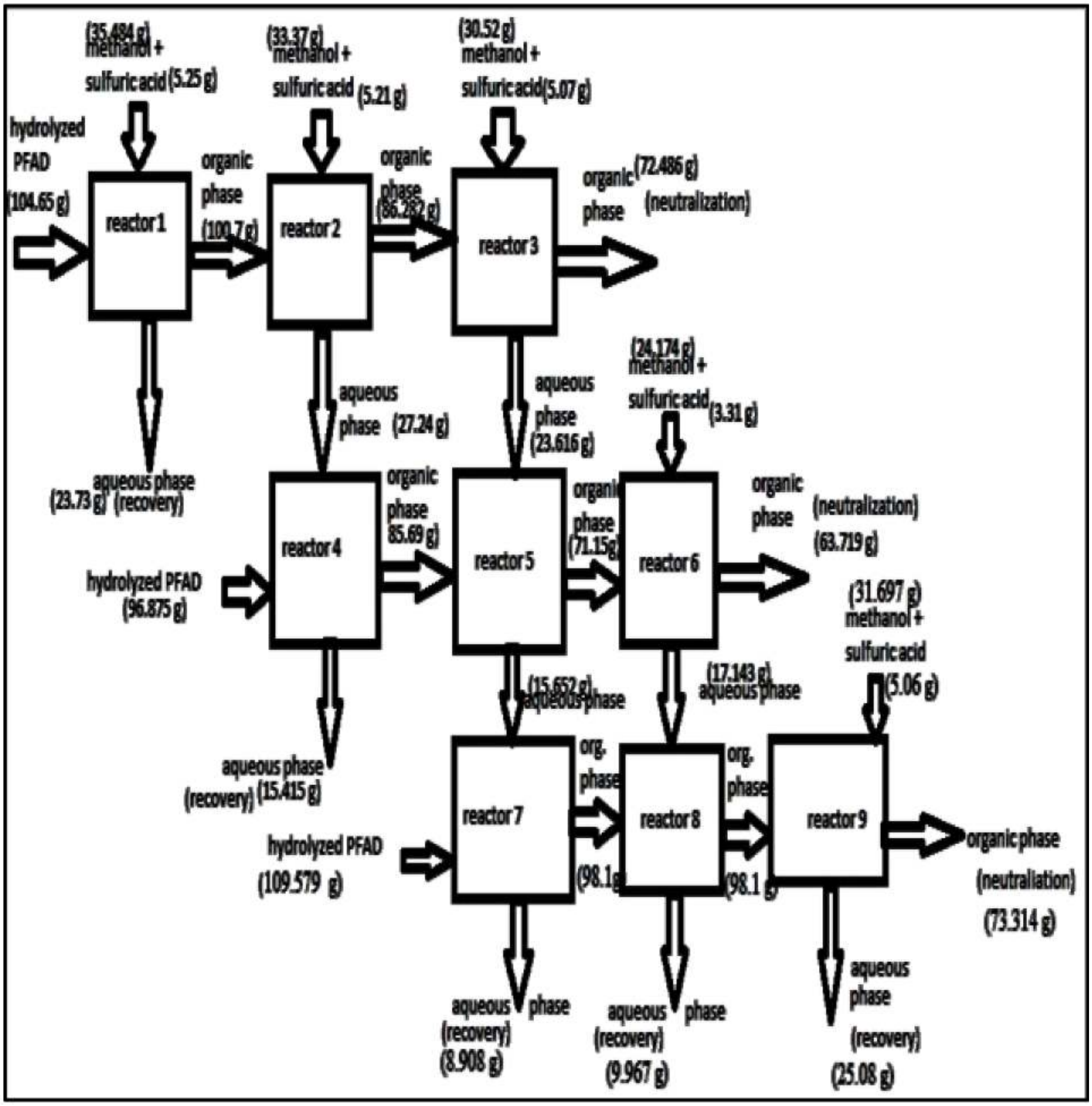


Figure 1: Esterification reaction

The setup has Dean Stark apparatus, condenser, gas flow meter, gas sampling tube. The Dean Stark apparatus along with condenser is shown in figure 2. The glycerol, if present in aqueous phase, will get dehydrated by sulfuric acid and gases will be trapped in gas sampling tube. The gas collected in the gas sampling tube was analyzed by gas chromatography. The analysis showed presence of carbon dioxide. The samples collected at different temperatures were weighed and analyzed in density-meter. On the basis of density of the mixture achieved, composition of the mixture was found out. The methanol content was given by,

Percentage of methanol

$$= \frac{(1-\text{density of mixture})}{(1-\text{density of methanol})} * 100$$

Density of methanol was found in density meter to be 0.787.

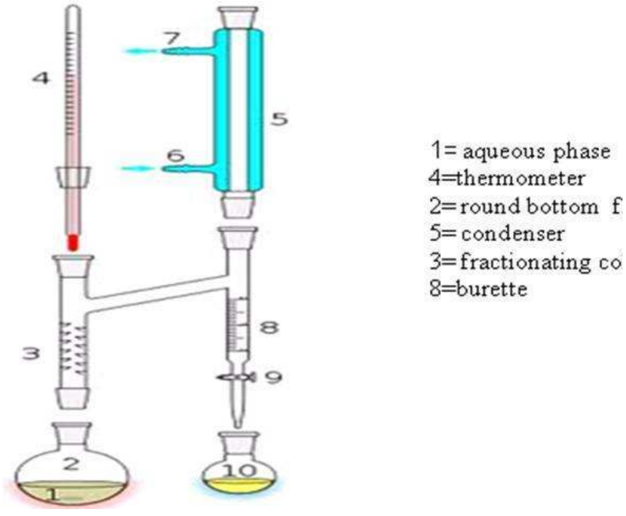


Figure 2: Dean Stark apparatus along with condenser

Following were the observations and calculations:

The concentration of sulfuric acid recovered =16.974N

Recovery of sulfuric acid =83.52%

Total amount of carbon dioxide present in the gas = 0.45 ml (in 150 ml of gas)

3.4. Neutralization of fatty acid in organic phase of esterification

The acid value of the organic phase was calculated to be 2.125.

Exact amounts of sodium hydroxide and sodium carbonate required to neutralize the fatty acids was calculated and 50 ml of these aqueous solutions were prepared. Also, sodium hydroxide solution in 80:20 and 90:10 mixture of glycerol: water was prepared. The bases were added to the organic phase containing methyl esters and fatty acid in a reactor of 250 ml using a six bladed impeller for 30 minutes at room temperature.

50 ml of aqueous solutions of sodium hydroxide (56.0 mg of NaOH pellets) was added to 37.487 g of organic phase in a reactor at room temperature. On the addition of the base, the aqueous phase changed its color from colorless to turbid yellow. When the agitation was started at 1500 rpm, the two phases appeared to be homogenous (pale turbid yellow) and foam formation took place at the top of the phases. The phases were allowed to separate for about 1 hour 15 minutes, yet the organic phase showed presence of soap (a whitish layer present in organic phase). The aqueous and

organic phases were allowed to separate in separating funnel. The organic phase was given water washing in a reactor for the removal of soap in heating condition at 60^{o}C by placing the reactor in an oil bath. A clear phase separation was observed and the organic phase appeared completely reddish. Acid value of the organic phase was calculated to be 0.548. The organic phase was separated by using a separating funnel.

50 ml of aqueous solution of sodium carbonate (76.6 mg of Na2CO3) was added to 37.696 g of organic phase in a reactor at room temperature. The observations were same as in previous case. Acid value of the organic phase was calculated to be 0.812. The organic phase was separated by using a separating funnel.

50 ml of 90:10 glycerol: water mixture was prepared and 58.6 mg sodium hydroxide was added to it. This solution was added to the reactor containing 37.91 g of organic phase. The neutralization was carried out at 60^{o}C with agitation of 1500 rpm provided by six bladed impeller. On the addition of the base, the two phases remained unchanged, i.e., aqueous phase remained clear and organic phase remained reddish. As the stirring was started, the two phases appeared as homogenous phase of red color and no foam and soap formation was observed. When the agitation was increased to 2500 rpm, bubbles of aqueous phase were observed in the system. On further increase in agitation to 3500 rpm, the reactor content turned turbid yellow and foam formation appeared at the top. When the agitation was stopped after half an hour, the reactor content showed phase separation slowly. After 85 minutes, phases separated out and organic phase was separated using a separating funnel. The acid value of the organic phase sample was calculated to be 0.438.

4. Conclusions

This two-step synthesis which is hydrolysis followed by acid catalysed esterification method reduces the overall production cost of the biodiesel, as it uses low cost unrefined feed. The initial water washing of PFAD is an important part of the synthesis because the water soluble impurities can cause problems with the conversion of glycerides to fatty acids.

Table 1

Time taken (min)	Temperature (^oC)	Weight (g)	Density (gm/lit)	Methanol (%)	Water (%)
138	85	9.718	0.803	92.50	7.50
83	90	8.119	0.803	92.50	7.50
69	100	9.634	0.812	88.30	11.70
42	120	9.057	0.830	79.81	20.19
112	150	11.79	0.891	51.20	48.80

The hydrolysis of PFAD with 2% acid catalyst loading shows the same results as 1% acid catalyst loading and takes half of the reaction time, comparatively. The esterification reaction was successfully performed by recycling the aqueous phase. The neutralization was best performed with sodium hydroxide in 90:10:: glycerol: water mixture. The analysis reveals that biodiesel from unrefined PFAD is quite suitable as an alternative to diesel.

References

1. Chongkhong S., Tongurai C., Chetpattananondh P., ‘Continuous esterification for biodiesel production from palm fatty acid distillate using economical process’, Renewable Energy, **34** (2009) 1059–1063.

2. Chongkhong S., Tongurai C., Chetpattananondh P., Bunyakan C., ‘Biodiesel production by esterification of palm fatty acid distillate’, Renewable Energy, **32** (2007) 1208-1211.

3. Ab Gapor Md Top, ‘Production and utilization of palm fatty acid distillate (PFAD)’, Lipid Technology, **2** (2010)11-13.

4. C. Pattamaprom*, N. Jantasuwanno, P. Kitkrimongkon .Comparative Study of Biodiesel Production from PFAD by Ion-Exchange Resin, Thammasat International

Journal of Science and Technology, (2008) 1429-1430.

5. P.Boonnoun, A.Maneesiri and C.Pattamaprom, Thammasat Int.J.Sc.Tech., **13** (2008) 32-37.

6. Eiji Minami, Shiro Saka, ‘Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process’, Fuel, **85** (2006) 2479-2483.

7. Fangrui Ma, Milford A, Hanna., Biodiesel producaiton: A review, Bioresources technology, **70** (1999) 1-15.

8. Gerhard Kevin, A comparison of used cooking oils: A very heterogeneous feedstock for biodiesel, Bioresource Technology, **100** (2009) 5796–5801.

9. P.D.Namdev, T.A.Patil, T.S.Raghunathan, and H.S.Shankar, Thermal Hydrolysis of Vegetable Oils and Fats,. Reaction Kinetics (Ind Eng Chem Res), **27** (1988)727-735.

10. R.Tesser, M.Di Serio, M.Guida., M.Nastasi and E.Santacesaria, Kinetics of Oleic Acid Esterification with Methanol in the presence of Triglycerides, Ind Eng. ChemRes., **44** (2005) 7978-79.