Multi stage Transesterifications of High FFA Feedstock towards a High Conversion of Biodiesel in A Batch Mode Production Plant

Winardi Sani, Khalid Hasnan, Mohd Zainal Md Yusof, and Ishak Baba

***Abstract*—** Fossil fuel era will end. Biofuel can fortunately prolong its life span. This concern has stimulated globally, especially in the last two decades the search for an alternative energy source. Blending of both the fossil fuel and the biofuel counterpart is the most practical effort. However, the high feedstock cost is the major influence of the likely profitability of a biodiesel production plant. Hence, cheap cost feedstock such as used cooking oil might become an interesting material to produce biodiesel. Due to a high incidence of oxidation and polymerization products, used cooking oil will be more onerous, and the conversion yield is low compared to a raw material with the same high free fatty acid. In this research study, a raw material of crude palm oil (CPO) is used as the feedstock for biodiesel production. After pretreatment of CPO, transesterification reactions of the feedstock with methanol are carried out in stages. This multi stage transesterification carried out in pilot scale with the a capacity of 1 MT per batch results in a high conversion yield (> 96%) though the FFA level above 3%. Gas Chromatography (GC) is used to determine the methyl ester content following the EN 14103 testing methods to support the proposed multistage reactions towards a higher conversion. To assess the significance of the transesterification conducted in stages, various data showing the methyl ester profiles under different methanol to oil ratios are evaluated. Lowering the methanol to oil ratio in the first stage (2.5:1) and proceeding with a higher constant ratio (1.5:1) each for the subsequent two stages get better results (more than 98% conversion) compared to 3:1 and 1.25: 1 ratios.

***Keywords*—** *Biodiesel, Multi stage transesterification, Palm Methyl Ester, Conversion.*

I. Introduction

THE end of the stone age is not because of the stone was gone. The fact was that the people left this era. For more than two decades, petroleum has dominated globally as the fuel of major prime movers especially in the transportation section. The world consumption on petroleum has been increasing while its reserve decreases consequently and it will probably end. Blending of conventional diesel with biodiesel is a practical way to prolong the petroleum life time. The energy security perceptive is the significant driving force in the use of biodiesel although the environmental aspects play also an important role. Biodiesel is renewable and can be produced from a variety of resources such as vegetable oil. Because of the high cost in the feedstock, many efforts are mostly dedicated to produce biodiesel from used cooking oil. Biodiesel production in a commercial scale, however feedstock in form of raw material is more favorable. Less pretreatment processes and higher conversion are the technical and economical reasons. Quality standards are prerequisites for the commercial use of any fuel product. Since the implementation of the European standard specification EN 14214 in 2004, a standardized definition for biodiesel has been agreed as fatty acid methyl esters (FAME) from any kind of feedstock including palm oil based. In Universiti Tun Hussein Onn Malaysia (UTHM), an actual pilot plant for the biodiesel production at a capacity of 1 MT is utilized to study the reactors performance. Crude palm oil (CPO) with high FFA (> 3 %) and moisture content (> 1000 ppm) is used as the raw material. CPO in Malaysia is available in abundant. Producing biodiesel from this raw material can stabilize the market price fluctuations. It can sustain economically the inherently local strength. The block flow diagram (BFD) of the UTHM biodiesel plant is depicted in Figure 1.

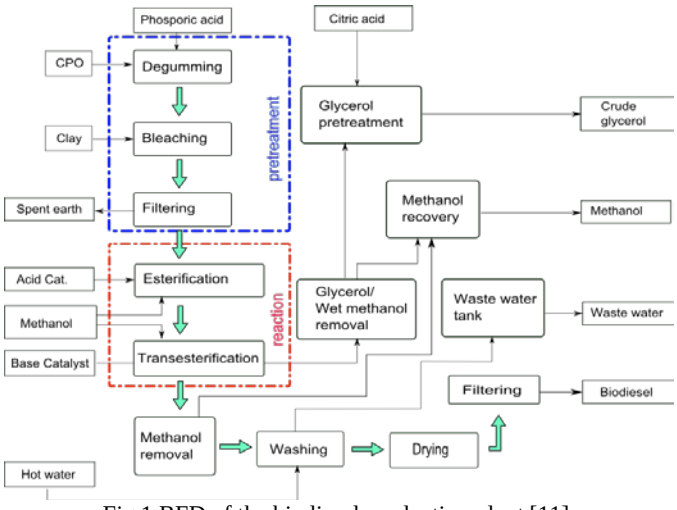

Fig.1 BFD of the biodiesel production plant [11]

II. Process Description

1 MT of CPO stored in a heated storage tank is pumped into the pretreatment plant for the degumming and bleaching processes. In the degumming stage, phosphoric acid (0.5 kg) is added to condition gums together with the bleaching earth.

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The phospholipids, trace metals, oxidation products, and pigments are removed [2,3]. The operating conditions are kept under vacuum at a temperature of 90 – 110 ^{o}C to make the CPO free of moisture. The dried oil is treated with bleaching earth or clay (10 kg) to adsorb the residual colour. The mixture of oil is the passed through to the 10 µm filter for separation of the spent earth from the oil. The obtained oil refined in the pretreatment plant is a bleached, degummed, dry crude oil and yellow-reddish in colour. Researchers [1,2,8] reported that the esterification process is required if the feedstock has more than 0.5 % by weight of free fatty acid. The transesterification of the oil is used to convert the remaining oil completely into biodiesel. These two chemical reactions are the core processes in the biodiesel production. The downstream processes are employed for the purification of the crude biodiesel, the recovery of the methanol, and neutralization of the glycerol byproduct, along with the treatment of the waste water. Theoretically, under the appropriate conditions of pressure and temperature, in the presence of a catalyst, each mole of palm oil requires three moles of methanol to produce three moles of biodiesel and one mole of undesired glycerol. Since the reaction is reversible, the forward direction is in favour toward the desired product.

The esterification of FFA and the acid transesterification reactions hereby take place in one hour with water and glycerol as byproduct. After discharging the byproducts, the subsequent base-catalyzed transesterification is done in two steps. Removal of glycerol and soap formation by manually phase separation is done before proceeding to the second step. At the end of the last transesterification, hot water (80 ^{o}C) at 5 % (w/w) is introduced gently to the vessel to capture the remaining glycerol and a vacuum flashing follows thereafter to ensure the crude biodiesel being free of water.

III. Process Specification

Table I shows the process variables specified to the research study to obtain the maximum conversion. The parameters set at constant are the acid catalyst of 0.3 w/w %, and the base catalyst at 17.7 kg and 5 kg NaOMe each for the first and second transesterification reactions, respectively. Two samples are analyzed for the research purpose.

TABLE I
REACTION SPECIFICATION /1000 KG OF OIL

Reaction	Sample	Transesterification		
		Acid	First	Second
MeOH [mol]	#1	3	1.25	1.25
	#2	2.50	1.50	1.50

Para toluenesulfonate, $C_7H_8O_3S$, abbreviated with PTSA, is employed as the catalyst for the acid tranesterificatio and sodium methoxide ($NaOCH_3$) 30 % for the alkaline catalyst in the first and second transesterification.

Fig. 2 UTHM biodiesel production plant

In the UTHM biodiesel pilot plant as shown in Figure 2, the heat is supplied by saturated steam generated by a fire tube boiler at a flow rate of approximately 500 kg/hr at 2-4 barg. The isothermal conditions inside the reactors are controlled and monitored automatically using a Supervisory Control and Data Acquisition system (SCADA). Purging system such as nitrogen must be introduced before and after the chemical reaction for the process safety purpose. Due to the transesterification processes occur at a nearly boiling point of the methanol, introducing nitrogen gas into the reactor will also prevent any phase change of methanol due to a slight increment in the operating pressure. It makes the methanol boiling point higher and all methanol is maintained in the liquid phase during the reaction progress.

IV. Phase Regions And Reaction Progress

In the biodiesel making through the transesterification processes, the process initially two phase liquid systems separating the oil and methanol exist. Because oil and methanol are not miscible at normal conditions. the reaction commences as two phases. These are an upper methanol phase, in which the catalyst is dissolved, and a lower oil phase. Stirring initiates the reaction, which transforms to another two-phase system comprising an ester-rich phase and a glycerol-rich phase. When stirring is stopped, the glycerol-rich phase settles to the bottom. Since the production of biodiesel standard fuel requires extremely high conversion and efficient isolation of the ester from the glycerol by-product, it is particularly important to characterize the steady-state compositions of the final phases. The Figure2 illustrates the different phase regions accompanying with the concentration profiles of the reactants and the products in the reaction progress [7].

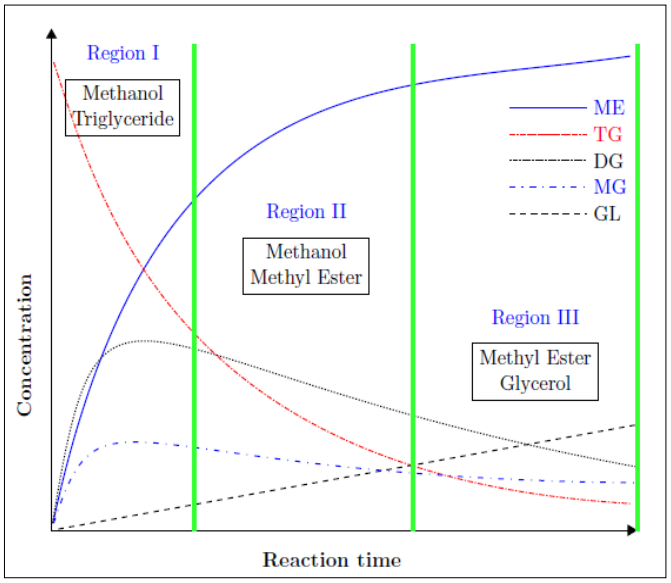

Fig. 2 Phase Regions and the Concentration profiles

In the Region I the reaction is identified as the diffusion-controlled region as described in [3,4,6,10]. To enable the reaction taking place, a mass transport occurs between the phases. One of the immiscible liquid diffuses to the other liquid to make the reaction. Whereas the mixing of solid particles go usually smoothly through a simple stirrer, the liquids being dispersed must be reduced into smaller droplets because of the different phase densities. Otherwise, they will return back to the singly phases. To overcome the interfacial tension of the liquid, a mechanical power must be introduced to the system. A mechanical system such as a mechanical agitator, vibrator or ultra sonic generator is required hereby for emulsification to bring these liquids in contact for the necessary reaction. The contact area between the phases is significantly enlarged. Furthermore, the oil concentration in the methanol phase is low at the start of the reaction, leading to mass transfer limitations. As the mixing proceeds, the concentration of oil in the methanol phase increases, leading to higher rates.

In Region II the mixing of the methanol and the triglyceride generates droplets which consequently enhances the phase contact area between them . The mechanical power introduced sustains the surface tension in the contact area of the liquids. The shear stresses reduce continuously the size of the droplets. Beside methyl ester, the partial products such as diglyceride (DG) and monoglyceride (MG) and also glycerol (GL) are formed in the Region II. These side products are called as emulsifier. The surface tension of the phases goes down drastically due to the emulsifying agent due to its polarities. As result, the contact area between the phases decreases. The formed partial glycerides prevent the doplets to coalesce each other and brings accordingly the system in almost single phase system of emulsion. In this region the rate of reaction is at a highest level and kinetically controlled. Therefore, the reaction progress in the region II can be approached with quasi homogeneous reaction.

In the region III the partial glycerides decay and the glycerol strengthened precipitates. Because glycerol and methyl ester are immiscible, the region III is a two phases system. To drive the reaction progress in the direction of the desired product, the glycerol must be removed from the system. The rate of reaction in this region proceeds slower.

V. GC Measurement And Parameter Setting

Gas chromatography (GC) or a high sensitive gas separating technique is a very important analytical technique in the biodiesel product analysis because it makes possible to separate the volatile compounds of a very small sample and quantify the amount of each component present in the biodiesel. A mixture being analyzed is loaded into the capillary column through the injection port via a micro syringe. The injection port is heated in order to volatilize the sample. Once in the gas phase, the sample is carried onto the column by the carrier gas or mobile phase, typically an inert gas such as helium or nitrogen.

The capillary column is where the components of the sample are separated contains the stationary phase. This phase is coated on the interior walls of a tubular column with a small inner diameter and made of a polysiloxane material. It has a high boiling point preventing it from evaporating off the column during the experiment. The components in the sample is separated on the column because they take different residence time to travel through the column depending on how strongly they interact with the stationary phase. As the components move into the column from the injection port they dissolve in the stationary phase and are retained. Upon re-vaporization into the mobile phase they are carried further down the column. This process is repeated many times as the components migrate through the column. Components that interact more strongly with the stationary phase spend proportionally less time in the mobile phase and therefore move through the column more slowly. Normally the column is chosen such that it's polarity matches that of the sample. Hence, the rate at which compounds move through the column depends on the nature of the interaction between the compound and the stationary phase. Other variables that affect this rate are column temperature and carrier gas flow rate.

If the column conditions are chosen correctly, the components in the sample will exit the column and flow past the detector one at a time. There are several different types of detectors common to gas chromatography instruments. The choice of detector is determined by the general class of compounds being analyzed and the sensitivity required. In this work, the gas chromatograph is equipped with a flame ionization detector (FID) and it is the most widely used detectors for organic samples. FID uses an air and hydrogen flame to pyrolyze the effluent sample. The pyrolysis of the compounds in the flame creates ions. A voltage is applied across the flame and the resulting flow of ions is detected as a current. The number of ions produced, and therefore the resulting current, depends on the flame conditions and the identity of the molecule. In other words, the detector shows a different response to each compound. For this reason,

separate calibrations must be performed for each compound analyzed.

The output of the detector is converted from current to voltage and sent to an integrating data acquisition system that plots, stores, and analyzes the data. The voltage from the detector is proportional to the number of molecules passing through the detector at any given time. For well-separated peaks, the total number of molecules of each component reaching the detector is then proportional to the area under the peak. The recorder determines the area of each peak by integration and reports this in the results table. Additionally, an internal standard is used in this research a the calibration method. In this method, a constant concentration of a non-interfering compound is added to each sample before it is analyzed. The ratio of the areas of the added compound and analyte are then used to construct the calibration curve The FAME analysis is carried out with a split injection onto an analytical column with a polar stationary phases and FID detector as specified in EN 14013-2003. The configuration used here is the PerkinElmer Clarus 500 Gas Chromatography fitted with a capillary column split/splitless injector and FID. Table 2 provides an overview of all the instrument parameters. The ester content , C, expressed as a mass fraction in percent, is calculated using the following formula as specified in [3]:

$$C = \frac{(\sum A) - A_i}{A_i} * \frac{C_i V_i}{m} * 100\% \quad (1)$$

Where $\sum A$ is the total peak area from the methyl ester in C_{12} to that in $C_{22:1}$. A_i is the peak area corresponding to methyl hepta decanoate, C_i is the concetration, in miligrams per ml, of the methyl hepta decanoate solution being used, V_i is the volume, in ml, of the methyl hepta decanoate solution, and m is the mass, in mg, of the sample.

TABLE II
GC PARAMETER SETTING

GC Parameter	Value
Inlet Temperature [°C]	250
Column Flow [ml/min]	1
Split flow [ml/min]	50
Injection Volume [µl]	0.5
Oven Program Initial Temp [°C]	210
Hold Time 1 [min]	13.0
Ramp 1 [°C/min]	5.0
Oven Program Final Temp [°C]	230
Hold Time 2	15.00
Equilibrium Time [min]	0
Column	30m x 320µm x 0.25µm film
Carrier Gas	Nitrogen
FID Temperature [°C]	250
Hidrogen Flow [ml/min]	45
Air Flow [ml/min]	450
Range	1
Attenuation	-5

Samples are collected during the plant operation at interval of 15 minutes and hot water is poured into the sample to stop the reaction. To prepare for GC analysis, each sample is washed and dried in an oven to remove the water and stored in a freezer.

VI. PLANT OPERATION PROCEDURES

in Figure 4 shows the implementation of the multi stage transesterification in form of the plant operation procedures. The acid-catalyzed (PTSA) transesterification takes place in a mechanical-agitated reacting vessel for 60 minutes retention time. FFA level and water content are the two significant parameters to be monitored after this reaction. FFA level above the specified value indicates an incomplete esterification and consequently a low conversion in the acid transesterification. The process continues to the base-catalyzed transesterification for the second 60 minutes. A new methanol and the methoxide catalyst are pumped into the second vessel for complete reaction. Glycerol and soap formed are discharged. The conversion after this reaction is higher but below the desired value (96.5 % minimum). The same procedure is performed for the subsequent base-catalyst transesterification. Experience shows that after the second step in this stage, a high conversion above the minimum level can be achieved by adjusting the methanol to oil ratio, see Table 1.

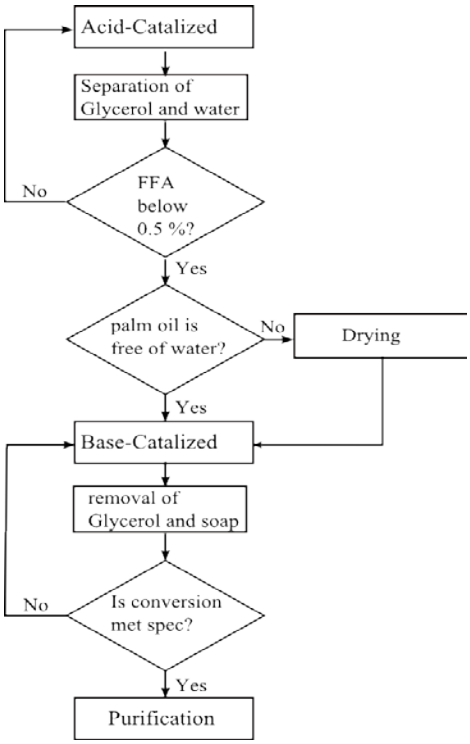

Fig. 4 Plant Operation Procedure

VII. GC REPORT DATA AND RESULTS

A selected report data and the associated chromatograph is shown in Table III and Figure 5, respectively. The chromatograph in Figure 2 plots the peak area (A_i) against the retention of each compound composition of the palm methyl ester ranging from methyl lauric to methyl linolenate

TABLE III
SELECTED GC REPORT DATA

FAME	C_{14}	$C_{16:0}$	$C_{18:0}$	$C_{18:3}$
Time[min]	8.304	9.904	12.72	15.277
A_i[mV]	3362028	24547873	1834005	886084

The entire report data of a sample begins with the first FAME (C_{12}) to $C_{18:3}$ ester family based on the internal standard (C_{17}) retention time. Table 3 shows only the selected data of the methyl esters due to space limitation.

A. Esterification and Acid-Catalyst Transesterification

The objective of esterification is to reduce the FFA level below 0.5% by converting the FFA to MG, DG, and palm methyl ester. Simultaneously, the acid catalyst can also catalyst both the esterification (FFA) and transesterification (TG) to biodiesel production at a certain conversion. The FFA level of 3.4% (w/w) needs to be reduced to 0.5% maximum to avoid saponification problem in the transesterification. The chromatograph shown in Figure 5 is a typical FAME analysis following EN 14103 where C_{17} is used as the internal standard. Biodiesel naturally contains only even number of

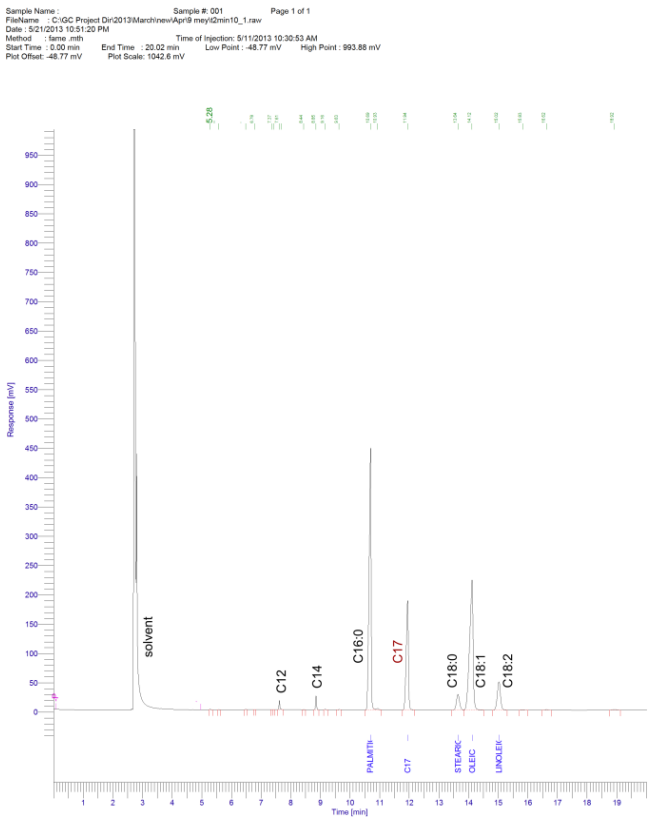

Fig. 5 A Chromatogram of Palm Methyl Ester

carbon. For biodiesel from palm oil, the biggest component (approx. 45%) is the saturated methyl palmitate ($C_{16:0}$). The higher the methanol to oil ratio, the conversion to methyl ester is correspondingly higher. This step is stopped after 60 minutes reaction time because the conversion reaches to an equilibrium. Its value tends to asymptotic and the rate of reaction becomes slower due to the formation of water and inefficiency of the catalyst. Moreover, this reaction is reversible, and an excess reaction time favors to backward (hydrolysis) of the ester which results in the reduction of the production yield. Figure 6 shows the ester content profile of the two different samples specified in Table 1. In the stage 1, process of the esterification of FFA and the acid-catalyzed transesterification occur simultaneously. Higher ester content, in w/w %, is achieved for the sample #1 due to higher methanol to oil ratio compared to that of the sample #2. The graph of the sample #2 in this stage tends to equilibrium after 60 minutes of the reaction time. After discharge of the water and glycerol residue, the process proceeds with the first transesterification. Hereby, the methanol to oil for the two sample are different. Sample #2 uses more methanol but the amount of catalyst as the sample #1. The significant difference appears in the slop of the curve at the beginning of the reaction. Fresh methanol and the efficiency of the base catalyst results in the better curve compared to that of the sample #1. At the end of this stage, because of the glycerol and soap formation, the reaction progress becomes slower and the curve tends consequently to a new equilibrium. In stage 3, the ester content profiles of the two samples show the obvious results. The sample #2 gives the better conversion than of the sample #1. The methanol to oil ratio determines the ultimate conversion to biodiesel.

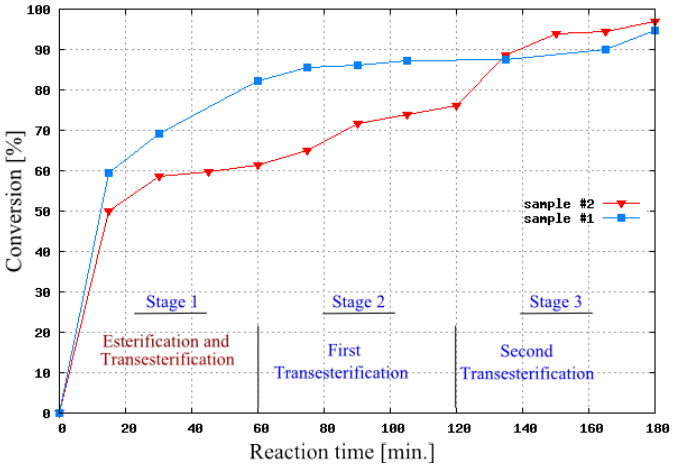

Fig. 6 Ester Content Profiles

In stage 1, the methanol to oil ratio is lower for sample #2 with the reason that the main purpose of this stage is to lower the FFA content. The total methanol consumption for the sample #2 is at the same amount of the sample #1. It means the same energy consumption is required for the purification step for the two samples.

VIII. Conclusion

The multi stage transesterification of a bleached palm oil to biodiesel has been applied in the pilot plant scale. The conversion of the triglycerides to biodiesel yields the highest value (above 98 %) if the methanol to oil ratio set at 2.5, 1.5, and 1.5 for each stage 1, stage 2, stage 3, respectively. In stage 1, the molar ratio of the methanol to FFA (palmitic acid) is 25:1 indicating an excess of methanol. The remaining methanol must be utilized for the acid-catalyzed transesterification that takes places in a slow reaction rate during the reaction progress. However, the ultimate target in every biodiesel plant is to obtain the highest conversion and the maximum yield. With these process variables implemented

in stages, the overall methanol consumption is lower compared to 6:1 ratio without stages as many researchers suggest [5,9]. With the high value of FFA, the esterification step is necessary before the based-catalyst transesterification. However, producing biodiesel in stages is favorable because the highest quality of the product can be achieved and the separation of biodiesel from the residues, water, glycerol, and soap is easier. Additionally, the proven transesterification theory has been applied with a technical modification in the implementation and results in better conversion as per verified using GC analysis method. The objective of a batch-mode production pilot plant has been achieved in term of a higher conversion of the raw material to biodiesel at a minimum amount in the energy consumption for steam, labor and methanol recovery.

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