Application of Process Analysis for Esterification and Two-step Transesterification in the Biodiesel Production Plant

Winardi Sani¹, Khalid Hasnan², Mohd Zainal Md Yusof³

Abstract—Esterification and transesterification reacting vessels are the core unit operations of typical industrial biodiesel production plants. Feedstock with a high free fatty acid is esterifie_d rst in an acid condition before continuing to the transesterification under presence of an alkaline catalyst. Process analysis is an important tool to a plant engineer in the biodiesel plant operation to estimate the conversion of the palm oil to biodiesel and the yield. This paper describes the process analysis for the methanolysis of crude palm oil through the esterification and the subsequent two-step transesterification in the biodiesel production plant with a capacity of 1000 kg per batch. Physical pretreatment of the crude palm oil (CPO) is necessary to remove the unsaponifiable and other undesired trace components to become bleached palm oil (BPO). Conversion at 85%(w/w) of free fatty acid (FFA) to biodiesel has been achieved in the esterification of BPO with methanol under acid catalyst reaction. The first transesterification is able to produce up to 88% (w/w) conversion of triglycerides (TG) to biodiesel. The remaining TG is carried out in the second step of the transesterification to complete the reaction toward achieving a high methyl ester content. Analytical method using gas chromatography is used for validation against the theoretical results. GC analysis results conforms the conversion estimated by the process analyses based on the material balance, especially in the esterification and rst-step transesterification, 81% and 88%, respectively. After one hour retention time of the second-step transesterification, 95% conversion of TG to biodiesel has been achieved. The process analysis applied at the equilibrium states shows consequently in accordance with the GC analysis results. Therefore it offers a useful compendium to a plant engineer for better understanding of the biodiesel processes.

Keywords—Biodiesel, Esterification, Two-step transesterification, Material balance

I. INTRODUCTION

Biodiesel has attracted the attention of many researchers and engineers more than two decades worldwide to prolong the lifetime of the fossil-based fuel. Issues in the environment, the limited reserves of petroleum, and the high cost of biodiesel as well as the oil price fluctuation in the market, among other things, are the major driving forces in conducting research and development in the renewable energy sector either in the lab scale or the industrial one. The pilot plant in UTHM with a capacity at one metric ton (MT) and operated in batch mode under a supervisory control and data acquisition (SCADA) system, has been constructed to strengthen a promising research in area of renewable energy. Crude palm oil (CPO) is chosen as the dominant feedstock due to the abundance of this crop in the State of Johor which is also the biggest producer of palm oil in the Peninsular of Malaysia with around 0.7 Mha of the plantation area for the palm trees. Owing to the grandness of the palm oil to the community and to sustain the inherently local strong, UTHM has taken a prudent initiative to explore the potential niche area in the refinery of the biodiesel production. The block flow diagram (BFD) of the biodiesel plant is depicted in Figure 1.

II. PROCESS DESCRIPTION

The CPO stored at a temperature 40 °celsius—is fed into the degumming and bleeding vessel of the pretreatment plant. Phosphoric acid is used to remove the phospholipids due to their strong emulsifying action [7]. The operating conditions are kept under vacuum at a temperature of 90 – 110 °C to make the CPO free of moisture. The dried oil is treated with bleaching earth or clay to absorb 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 [4,5,6] 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 triglycerides comprises of five different fatty acids. It follows 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 process hereby takes place in one hour with water as the by product. However, this process also yields the desired biodiesel at a certain extent of conversion and glycerol as the byproduct. Water and glycerol resulted from the reaction must be discharged after completion. The subsequent transesterification is done in two steps. Removal of glycerol by manually phase separation is done before proceeding to the second step. At the end of the transesterification, hot water 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. The operating conditions for both processes are at 65 °C and 2 bar to ascertain the reacting mixture being in liquid phase. This higher pressure is established by introducing nitrogen gas to the mechanical-agitated vessels.

III. PROCESS SPECIFICATION

It quantifies the amount of the reacting components necessary for the entire processes of producing biodiesel from palm oil. The process specification is indicated in Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ratio To Oil</th>
<th>MeOH [mol]</th>
<th>PTSA [wt %]</th>
<th>NaOMe [kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esterification</td>
<td>1.25</td>
<td>3</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>First</td>
<td>1.25</td>
<td>17.7</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

In the esterification of the bleached, degummed palm oil, para toluenesulfonate, C₇H₅O₃S, abbreviated with PTSA, is employed for the acid catalyst. Sodium methoxide (NaOCH₃) 30 % acts as the alkaline catalyst in the first and second transesterification. This specification makes the plant operator convenient in preparing the chemical materials. Each reaction occurs in nitrogen blanket which ensures the inherently safe condition.

IV. MATERIAL AND MODEL

The crude palm oil (CPO) with a food grade is purchased from the local palm oil refinery. The FFA level as palmitic is at 3.4 % (w/w), and the moisture content of 0.2 % (w/w) by measurement. It means the oil contains 94.6 % (w/w) of triglycerides and other trace components. [1] reported that the triglycerides comprises of five different fatty acids. It follows consequently, the average molecular mass, $M=848.24$–kg/kmol. To enable analysing the mass balance in the chemical reactions, the palm oil is modeled as tripalmitic due to the major contribution in the composition. Methyl palmitate or palmitic acid methyl ester is therefore the biodiesel under this study. The transesterification of triglycerides under this assumption therefore, the general chemical reaction is accordingly modeled as follows:

V. ANALYSIS AND RESULTS

For the theoretical analysis purpose, the fatty acid attached in the glycerol backbone are modeled solely as the tripalmitic acid. Additionally, GC analysis for methyl ester content determination of samples during the plant operation is also applicable for validation. The material balance will be applied following the operating stage performed in the esterification and transesterification vessels of the actual plant. The process calculations of this balance is performed based on the mole unit, and it is however tabulated for convenient in the mass unit.

A. Esterification

The FFA level of 3.4% (w/w) needs to be reduced to 0.5% maximum to avoid saponification problem in the transesterification. Esterification itself is a chemical reaction similar to the Figure 1(a), with the difference in the catalyst used. Instead of an alkaline condition, esterification employs an acid catalyst. Converting the FFA into the biodiesel governs the stoichiometric as shown in Figure 2.
Referring to Figure 3, R stands for palmitic acid, CH₃(CH₂)₁₄COOH. Lowering the FFA level to 0.5% yields 85.3% conversion to the desired product, or it is equivalent to 30.6 kg of biodiesel.

The conversion of FFA to biodiesel is 85.3%, or in other words, 5 kg of FFA remains in the oil after esterification. The conversion of the FFA to biodiesel stops at this level due to water accumulation that hinders the completion of the reaction process.

PTSA acts as the acid catalyst. It does not react with the reactants. The amount before and after the reaction is therefore constant. Its function is to accelerate the reaction process without getting involved in the reaction. During the esterification of FFA to biodiesel, an acid transesterification of triglyceride takes place as well. FAME is the desired product in the esterification along with reducing the FFA content. The first crude biodiesel produced through the esterification comes from the FFA conversion and the TG reaction. The theoretical yield, referring to the definition in [9] 80.7%. The yield is defined as the weight percentage of the final product relative to the CPO weight at the initial stage. Water and glycerol are discharged to the glycerol neutralization vessel by separation. The main product is then transferred to the next vessel for transesterification reaction.

B. First Transesterification
The acid catalyst resulted from the previous esterification must be first neutralized. However, the conversion of the TG to biodiesel takes place at a moderate level. The reaction shall therefore be completed in the second reaction to the desired conversion up to 96.5% minimum.

C. Neutralization
The acid condition of the oil mixture in the previous process must be neutralized before proceeding to the alkaline transesterification. The alkaline catalyst is employed to neutralize the existing PTSA (CH₃C₆H₅SO₃H). This process is described in the following stoichiometric equation:

\[ CH₃C₆H₅SO₃H + CH₂ONa \rightarrow CH₃C₂H₃OH + CH₂NaSO₃ \]  \( Eq. (1) \)

Methylsulfuric acid sodium salt (M = 134.09 kg/kmol) formed in the Eq. (1) is soluble in water. Toluene (normal boiling point at 110.6 °C) is also produced during this reaction and it will be removed in the vacuum flashing.

PTSA acts as the limiting reactant and it therefore reacts with the sodium methoxide completely at the end of the process. Based on the stoichiometric equation, 1 mole of sodium ion is required to form the soap. Since the methoxide exists in the form of sodium methoxide at a concentration of 30%, 1.336 kg of the alkaline chemical (or 0.85 kg of NaOCH₃) is required to thoroughly neutralize 3 kg of the acid catalyst (PTSA). 2.34 kg of salt is formed after the neutralization stage, and it must be removed after the first-step transesterification.

D. Soap Formation by FFA
The dissolution of the sodium methoxide in the methanol leads to the formation of the methoxide ion and methanol. The remaining free fatty acid (FFA) results from the previous esterification and is then converted by the sodium methoxide to soap (sodium palmitate, M = 278.41 kg/kmol) according to the following reaction:

\[ CH₃(CH₂)₁₄COOH + CH₂ONa \rightarrow CH₃(CH₂)₁₄COONa + CH₂OH \]  \( Eq. (2) \)

For the material balance calculation, the FFA is used as the limiting reactant since it must be totally removed and converted into soap. The neutralization process produces also methanol. 5 kg of FFA produces 5.43 sodium salt that must be removed after transesterification.

E. Alkaline catalyst and methanol
Sodium methoxide 30% by weight required to neutralize the acid catalyst and the FFA has been determined previously. The methanol content of the alkaline catalyst must be included when calculating the required methanol needed for the right mixing of the reactants. With 1.25 molar ratio methanol to the initial TG, the actual molar ratio is above 80% in methanol excess. With 187.4251 kg as the remaining triglycerides or it is equivalent to 0.2322 mol (M = 807.3 kmo1/kg). The total sodium methoxide necessary is 13.225 kg. That is the sum of the catalyst for neutralization and the actual catalyst in the base condition. The total methanol in the first transesterification is actually the sum of the methanol and methanol inherently at 70% in the sodium methoxide. It corresponds to 57.4823 kg or 1.8 mol. The mole ratio of methanol to the oil is then 7.74:1, that means, the methanol excess is 4.34 mole relative to the theoretical stoichiometries.

The neutralization of the acid catalyst and the remaining FFA contribute to the low conversion of the oil to biodiesel. The sodium methoxide becomes less reactive as alkaline catalyst for the biodiesel production. It acts first as the neutralizing reactant before as the catalyst. It prevents the transesterification from completion. The conversion of the oil to biodiesel therefore reduces significantly. With the total conversion of 88.3%, the mass balance for the reactants can be determined. After the first transesterification, the crude biodiesel undergoes a phase separation based on a difference in density. The reacting vessel contains solely the crude biodiesel and the remaining triglycerides.

F. Second Transesterification
In the same vessel, the second transesterification is accomplished to complete thoroughly the reaction to a higher
conversion of oil to the biodiesel product. With the desired remaining triglycerides of 0.2 w/w % maximum, conversion of the biomass is then: the unconverted oil is 1.92 kg and the desirable remaining triglycerides of 0.2 w/w % maximum, as required in the EN 14214 standard, the remaining oil after the second transesterification is then: the unconverted oil is 1.92 kg and the remaining triglycerides becomes the limiting reactant. The amount of the alkaline catalyst being added reduces to 1.5 w/w %, which is also specified in Table 1. The second step is accordingly the ultimate transesterification, where the TG conversion to crude biodiesel must be at the highest point for the complete reaction. This is accomplished by the high excess of methanol. The theoretical conversion at 96.5 % minimum shall accordingly be achieved in the real plant operation.

VI. GC ANALYSIS

GC analysis to determine the methyl ester content (between C14 and C21) in biodiesel follows EN14103:2003 method [3]. The FAME analysis is conveyed in a split injection into an analytical column with a polar stationary phase and a flame ionization detector (FID). The GC configuration used here is the PerkinElmer Clarus 500, fitted with a capillary split/splitless injector and FID. In order to determine the retention times of the fatty acid methyl esters, methyl heptadecanoate (C17) acting as the internal FAME standard needs to be run.

![Fig. 4 Ester Content Profile](image)

The samples have been taken at a certain time intervals, 10 or 15 minutes after each process which retention time of each process during the plant operation is set at one hour. Three hours are needed for the entire production. The samples are measured first using the TLC method for ester content determination. The appropriate samples are hence selectively prepared for the GC analysis. The results of this analysis is shown graphically in Fig. 4. The values of the ester content after esterification, first-step transesterification, and second-step transesterification are 81%, 88%, and 95%, respectively. Referring to the graph, the chemical equilibrium is achieved both at the end of the esterification and the end of the first transesterification. The time dependency of the rate of the concentration change of the reactants is therefore negligible. The conversion of TG to biodiesel after one hour operation of the second-step transesterification is 95% can be understood that the reaction is actually complete. The curve in the last region indicates that the tendency to the higher conversion is probably still possible. By slightly increasing the retention time, the reaction becomes definitely completed and the ultimate target of the minimum conversion at 96.5% can be accordingly achieved.

VII. CONCLUSION

The process analysis is the significant tool for a plant engineer for proper running biodiesel production plant to estimate the product quality and yield. Starting from the pretreatment of the CPO to bleached palm oil (BPO), and the subsequent processes such as esterification, transesterification, and purification as well as the methanol recovery have been described to illustrate the important unit operations in the biodiesel production plants. The conversion of 81% after esterification and 88% after first-transesterification measured in the GC analysis confirms the estimated value resulted from process analyses based-on material balance. Palmitic acid is used for TG model since it is the major component in the fatty acid profile for palm oil. The ultimate target of 96.5% conversion of TG to biodiesel, can be achieved by a slightly increasing the retention time of the second-step transesterification in the actual plant operation. The process analysis for the last step can be done when the reaction comes chemically to an equilibrium in which the conversion of 96.5% minimum shall definitely be achieved.

ACKNOWLEDGMENT

This research study has been funded by the "Fundamental Research Grand Scheme" from the Higher Education Ministry of Malaysia (FRGS Vot 1063).

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