THE EFFECT OF REACTION CONDITIONS ON THE ESTERIFIED PROCESS OF FATTY ACID WITH METHANOL TO PRODUCE BIODIESEL BY LIQUID ENZYME CATALYST AND SUPER ABSORBENT POLYMER

ẢNH HƯỞNG CỦA ĐIỀU KIỆN PHẢN ỨNG ĐẾN QUÁ TRÌNH ESTE HÓA CỦA AXIT BÉO VỚI METHANOL ĐỂ SẢN XUẤT DẦU SINH HỌC BẰNG XÚC TÁC ENZYME LỎNG VÀ CHẤT SIÊU HẤP THỤ

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Abstract - Biodiesel is a source of renewable energy produced through the transesterification of vegetable oils, animal fats, or the esterification of fatty acids with short chain alcohols such as methanol, ethanol, propanol and butanol in presence of acid catalysts (H_2SO_4, HCl...), basic catalysts (KOH, NaOH) or biocatalysts (lipase enzymes). The purpose of study on the effect of operating conditions on the esterification of fatty acid with methanol to produce biodiesel by using liquid enzyme and super absorbent polymer (SAP) is to determine the optimized value of impact factors included the reaction temperature, molar ratio, catalyst and SAP amount. Results showed that the conversion of reaction achieved approximately 90 % at the reaction temperature of 45ºC, the molar ratio fatty acid to methanol of 1:3, the liquid enzyme catalyst and SAP content of 10wt% (based on the fatty acid mass) for 6 hours of reaction time.

Key words - biodiesel; liquid enzyme; super absorbent polymer (SAP); Oleic acid; Methanol

Tóm tắt - Nhiên liệu sinh học là một nguồn nhiên liệu tái tạo, được sản xuất thông qua quá trình chuyển ester hóa dầu thực vật, mỡ động vật, hay quá trình este hóa axit béo và ancol mạch ngắn (metanol, etanol, propanol and butanol) với sự có mặt của các loại xúc tác axit, bazo vô cơ hoặc enzyme. Nghiên cứu ảnh hưởng của các điều kiện tiến hành quá trình este hóa axit béo với methanol để sản xuất dầu sinh học bằng chất xúc tác là enzyme lỏng với chất siêu hấp thụ (SAP) nhằm mục đích xác định các giá trị tối ưu của các yếu tố ảnh hưởng đến quá trình phản ứng bao gồm nhiệt độ, tỉ lệ mol chất phản ứng, hàm lượng chất xúc tác và SAP. Kết quả nghiên cứu cho thấy rằng ở nhiệt độ 45ºC, tỉ lệ mol giữa axit béo và methanol là 1:3, hàm lượng xúc tác và SAP đã sử dụng là 10% khối lượng acid thì hiệu suất phản ứng đạt giá trị cao nhất gần 90% sau 6 giờ phản ứng.

Từ khóa - dầu sinh học; enzyme lỏng; chất siêu hấp thụ; axit oleic; methanol

1. Introduction

In the world, annually, the consumption of the fuel is highly rising due to the living and industrial demands, so the amount of natural fuel energy becomes exhausted. On the other hand, using the natural fuel releases a large amount of carbon dioxide (CO_2) into the atmosphere that causes the environmental pollution as well as greenhouse emissions [1, 2]. In order to solve these problems, the seeking a renewable and friendly environmental energy is essential. Fortunately, biodiesel, the fuel that satisfies those requirements was discovered. This fuel has properties similar to those of a diesel, however, it is not made from fossil sources but biological sources such as plants, animals or microorganisms. These feedstocks are part of the above-ground carbon cycle. This means that when biodiesel is burned, the carbon is simply released back into the atmosphere, and does not change the balance of atmospheric CO_2 levels [3-5].

In the chemical aspect, biodiesel is the mono alkyl esters of long chain fatty acids produced through the esterification progress of fatty acids (Oleic acid, Palmitic acid, Linoleic acid) with short-chain alcohols (Methanol, Ethanol, Propanol, and Butanol) or the transesterification of natural oils (vegetable oil or animal fat) in the presence of the catalyst. Nowadays, the homogeneous chemical catalysts are being used widely in industrial production of biodiesel based on their low cost and high yield. Nevertheless, utilizing these chemical agents also causes several negative effects on the performance of biodiesel process. For example, the homogeneous acid catalyst is mostly used in the esterification of fatty acid with alcohol. However, this process creates corrosion by presence of sulfuric acid as well as consumes the high amount of alcohol and energy. Moreover, it also generates a lot of toxic wastewater. Either using the homogeneous alkaline in transesterification (sodium hydroxides and methoxide) consumes a large amount of catalyst and produces the soap (saponification of triglycerides) that lead to reducing the yield of biodiesel production**.** Recently, studying on using enzyme biocatalysts such as Novozyme 435, lipase enzyme to replace chemical catalysts in biodiesel production is attractively considered due to their advantages. Mulalee, S. et. al. [6], demonstrate that biocatalyst is not only easily recovered and reused, but also consumes low energy and make more friendly environmental. The enzyme used in biodiesel production process is usually immobilized to improve enzyme recovery as well as increase stability, allowed for reusing. Nevertheless, one of the main limits of using immobilized lipases is the high price because of the high expense of enzyme as well as equipment and the immobilization itself. In order to reduce the cost, the liquid enzyme is used to replace the immobilized enzyme. The liquid lipase has not only price 30-50 times lower than immobilized enzyme [7, 8] but also can be reused for several times after recovering from the water phase**.**

Therefore, in this study the effect of variable factors as temperature, molar ratio of reagents and liquid enzyme content on the esterifying oleic acid with methanol has been investigated. This progress uses SAP as water absorbent to increase the efficiency of reaction.

2. Materials and methods

2.1. Material properties

Eversa Transform Lipase is a kind of liquid enzyme studied in this research. It is 100 kLU/g (kLU= 1000LU. 1LU is the amount of enzyme that releases 1µmol of titratable butyric acid per min at pH=7.00 and 35^0C). Eversa Transform Lipase is a generous gift from Novo Industries (Denmark). Oleic acid (99%) is purchased from Showa Company (Japan). Methanol is obtained from Echo Chemical Company LTD (Taiwan). Super absorbent polymer (SAP) is donated by Formosa Plastic Corporation (Taiwan), the white and smooth powder with a particle size of 0.2-0.9mm.

2.2. Experimental design

The esterification is carried out in a 100 mL bottle flask equipped with a stirrer and thermal system. All of materials are weighted and heated up to the reaction temperature in the incubator machine. Water has been reported to improve the activity properties of enzyme [9]. So 10wt% water by substrate (oleic acid) is added to assist the process. The study on the effect of catalyst content is carried out with the mass proportion of enzyme to oleic acid varying in the range of 5% to 15%. Moreover, study on the influence of the mole ratio of methanol to oleic acid is performed with values of this factor 1:1, 5:1 and 10:1, while the total volume of methanol and oleic acid kept constant. The effect of temperature is investigated by carrying out esterification at four different temperatures: 35, 40, 45, 50(^{0}C). Finally, in order to investigate the effect of SAP amount on the yield, SAP content is varied from 0 to 15wt% by oleic acid. The reactions are performed for 6h.

2.3. Biodiesel conversion analysis

The percentage of converted oleic acid is determined by the titration method with 0.1 mol.L^{-1} KOH solution and phenolphthalein is used as an indicator. According to the change of acid value before and after reaction, conversion of oleic acid is calculated. The acid value (AV) and percentage of conversion are determined by following formulas:

$$\text{Acid value (AV)} = 56.1\ CV/m\ (\text{mg/g}) \quad (1)$$

Where C is the concentration of KOH, V is the consumption volume of KOH, and m is the weight of sample.

$$\text{Conversion} = (AV1-AV2) \times 100/AV1\ (\%) \quad (2)$$

Where: AV1=acid value of pre-reaction, AV2=acid value of post-reaction

3. Results and discussion

3.1. Effect of the methanol to oleic acid ratio

The molar ratio of alcohol to fatty acid is the most important factor affecting the efficiency of the esterification. Figure 1 shows the effect of molar ratio on the conversion of oleic acid to methyl oleate with three different molar ratios of oleic acid to methanol: 1.0, 5.0 and 10.0. In order to keep forward reaction of producing methyl ester, the molar ratio of methanol to oleic acid should be higher than stoichiometric ratio. Excess of alcohol in esterification reactions increases the reaction rate. However, for enzymatic reactions, a high methanol concentration can cause enzyme deactivation, which decreases the methyl ester production. In our study, the maximum yield (87.74%) is obtained at a 5:1-ratio of methanol to oleic acid. At higher molar ratios, methanol starts to inhibit the enzyme activity, so the conversion is decreased to approximately 28% at the molar ratio of 10:1. So we have chosen 5:1 as the optimum molar ratio of methanol to oleic acid.

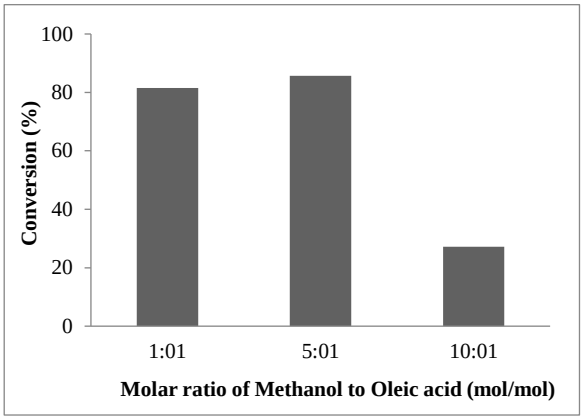

Figure 1. *Effect of Methanol to Oleic acid molar ratios on efficiency of reaction*

3.2. Effect of the reaction temperature

In general, every Enzyme has its own optimum temperature range, high temperature may denature the lipase contrariwise low temperatures cannot activate the lipase. The influences of temperature on the reaction performance are tested in the range of 35-55^{0}C. The factors as methanol/Oleic acid molar ratio 5:1, catalyst load 10%, and SAP load 10% are fixed.

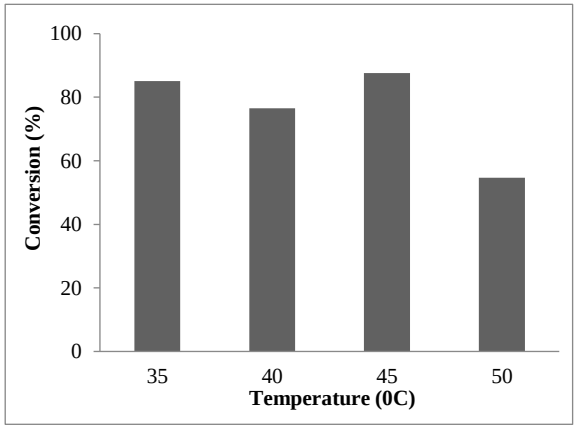

Figure 2. *Effect of temperatures on efficiency of reaction*

As can be seen from Figure2, the conversion percentage increases with increasing the temperature from 35 to 45 ^{0}C and then decreases with the temperature higher than 45 ^{0}C. The highest of the conversion is 88% at 45^{0}C. This result is contributed by the high activation of Eversa Transform Lipase at 45^{0}C as well as the optimum reaction temperature when using this Enzyme for the esterification of fatty acid.

3.3. Effect of the enzyme content

Due to playing the catalyzed role, the amount of enzyme is an attended factor on the operating condition. Esterification is carried out at different catalyst loads ranging

from 2.5% to 15% to evaluate its effect on the conversion. On the other hand, other factors are kept unchanged. The methanol/oleic acid molar ratio is 5:1, reaction temperature is 45^0C, initial water content is 10% and SAP load is 10%. The detail result is shown in Figure3. Liquid enzyme improves the yield of reaction. The higher enzyme content increases the percentage of conversion of oleic acid. The yield reaches the peak of 89% at 10% enzyme content. However, there is a slight decrease with catalyst dosage exceeding 12.5%. The excess of enzyme content may prevent the interaction of reactant molecules, which causes the reduction in the yield.

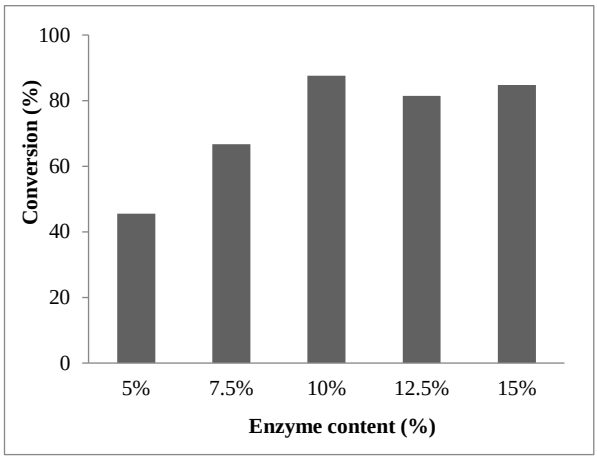

Figure 3. *Effect of Enzyme content on efficiency of reaction*

3.4. Effect of the SAP content

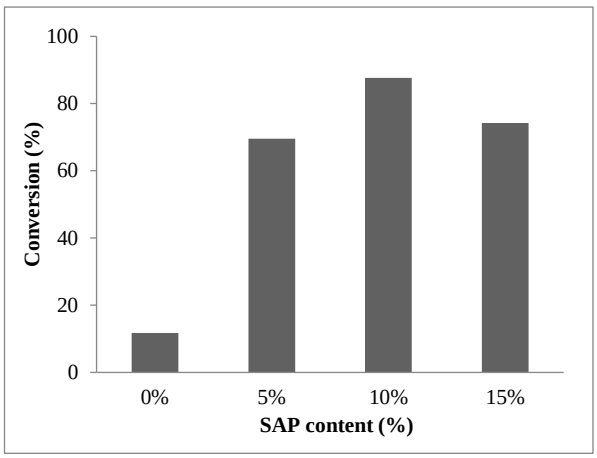

Figure 4. *Effect of SAP content on efficiency of reaction*

As an excellent absorbent with high water removal capacity, SAP plays an important role in absorbing the water produced by the esterification of methanol and oleic acid. Figure4 describes the effect of SAP amount (0%, 5%, 10% and 15% mass ratio of oleic acid) on the conversion of oleic acid to methyl oleate. It is found that the biodiesel yield increases with the increase of the amount of SAP content and reaches at 11.78%, 69.6%, 87.74% and 74.23% with 0%, 5%, 10% and 15% SAP content, respectively. With high SAP content (15%), the yield of reaction decreased the excessive SAP may suppress the dispersion of lipase, thus reduce the mass transfer of the reaction. Therefore, the 10% of SAP amount should be the suitable dosage in the experiment.

4. Conclusions

In this study, liquid enzyme Eversa Transform is successfully investigated to esterify fatty acid and oleic acid by using supper absorbent polymer. Reaction conditions as molar ratio of the two substrates, reaction temperature, lipase and SAP amount have been studied and the following conclusions are drawn:

- The Methanol to Oleic acid molar ratio affects the reaction efficiency. The best performance comes with 5:01 molar ratio.
- The conversion of Oleic acid increases with increasing the temperature. The peak of yield is obtained at 45 ^{0}C.
- Eversa Transform Lipase content up to 10% is useful for esterification.
- SAP has a positive effect on the reaction performance.

In this study, the maximum Oleic acid conversion of 87.74% is obtained under the following conditions: 10% liquid enzyme and 10% SAP content at 45 ^{0}C and the Methanol to Oleic acid molar ratio of 5:01 during reaction time of 6 hours.

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