A Comparison of Costs of Biodiesel Production from Transestericationn

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Abstract *- Nowadays, biodiesel is well accepted as a renewable energy. However, the high production cost of biodiesel is a remaining problem. The preliminary economic design in this work aimed to determine the optimal operating condition by using HYSYS 3.2 software. The transesterification of triglyceride (oil) and methanol to produce methyl ester (biodiesel) was the reaction used in the simulation. The study includes the recovery of the excessive methanol from all units in the process. The studied parameters affecting the purity of the production and the operating cost in this work were reaction times (2-60 minutes), reaction temperatures (55 °C-75 °C) and molars ratios of alcohol to oil (6:1-10:1). Moreover the work considered the size and number of the reactors that can improve the purity of the product. The study found that the optimal condition that minimizes the operating cost is the ratio of methanol to oil at 6:1 (or 0.238:1 by wt.), the reaction temperature at 70 °C, and the reaction time of 20 minutes. In addition, for the same production rate, the process with double size of the reactor improves the product purity (from 96.62 % to 98.21 %). For the number of reactors, it is found that two half-size reactors give better product purity and operating cost than the single reactor with the equivalent size.*

Keywords - **Biodiesel, Ester, Transesterification, HYSYS.**

1. INTRODUCTION

Nowadays, biodiesel is the hot topic as a renewable energy. It is a product of tranesterification of oil and alcohol. Biodiesel has physical properties similar to petroleum diesel, therefore, biodiesel can be used individually or mixed with diesel in diesel engines. Moreover, glycerin, a byproduct, can be used in food, medical or cosmetic industries.

However the cost of biodiesel is still higher than petroleum diesel. Therefore, this research was worked on a steady state design of the process in order to optimize the plant operations by using HYSIS 3.2 simulator software [1]. The software provides thermodynamic and fluid properties for basic chemical compound. Moreover it can be added some chemical reagents and their kinetics. Therefore the results of the simulation are more realistic.

2. ASSUMPTIONS

Since palm oil is an economic plant in the south of Thailand, the study then used palm oil as a raw material. Though in literatures, oils used in research are from soybean, palm oil, sunflower seed, etc., so some assumptions for this research are the following:

1. The palm oil used in this work consists of 3-palmatic acid only and contains fatty acid (FFA) less than 1% with gum removal. As the result, saponification of FFA and a base catalyst (NaOH) would not be much considered.

2. The different types of fatty acid do not affect the yield of biodiesel. Therefore the kinetic of soy bean can be used.

3. No effect of catalyst in the study.

4. Evaluate only for the variable costs from energy cost and raw material.

3. LITERATURE REVIEW

Transesterification Reaction

Vegetable oil (TG) can react with alcohol (ROH) in transesterification reaction to provide biodiesel or alcohol ester ($R'CO_2R$) and glycerin (GL). The by products from this reaction are diglyceride (DG) and monoglyceride (MG) [2], [3], [4].

Kinetic of transesterification reaction has at least 3 main reactions as shown in equations (1)-(3). And the kinetic data for methyl ester are shown in Table 1.

$$TG + ROH \underset{k_2}{\overset{k_1}{\longleftrightarrow}} DG + R'CO_2R \quad (1)$$

$$DG + ROH \underset{k_4}{\overset{k_3}{\longleftrightarrow}} MG + R'CO_2R \quad (2)$$

$$MG + ROH \underset{k_6}{\overset{k_5}{\longleftrightarrow}} GL + R'CO_2R \quad (3)$$

Table 1. Kinetic data for transesterification of methyl ester

Reaction		Ea (cal/mole)	K (litre/mole/min)
TG→DG	k1	13,145	3.89 E07
DG→TG	k2	9,932	5.74 E05
DG→MG	k3	19,860	5.82 E12
MG→DG	k4	14,639	9.78 E09
MG→GL	k5	-6,421	1.10 E-05
GL→MG	k6	-9,588	2.29 E-09

Modified ref. [4]

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Effects on Reaction

There are usually 3 parameters that have an effect on the transesterification, which are temperature (T), reaction time (t) and ratio of oil to alcohol.

3.2.1 The reaction time affects concentration of methyl ester, such that the concentration increases exponentially in 5 minutes then after 60 minutes, the concentrations of TG, DG and MG slightly decrease and start to reach the steady state [2].

3.2.2 The reaction temperature plays an important role on the quality of the products. Normally, The range of the temperature used in the process is between. 50 °C – 65 °C. The temperature which is higher than the normal boiling point of methanol (68 °C) causes more vaporization of methanol (loss). On the other hand, the temperature which is lower than 50 °C causes higher viscosity of biodiesel [2].

3.2.3 The ratio of methanol to oil also affects that, the higher molar ratio, the higher conversion of alcohol. The ratios, normally used, are between 5:1 to 10:1 [3]. However using too high excess methanol can obstruct glycerin separation [5].

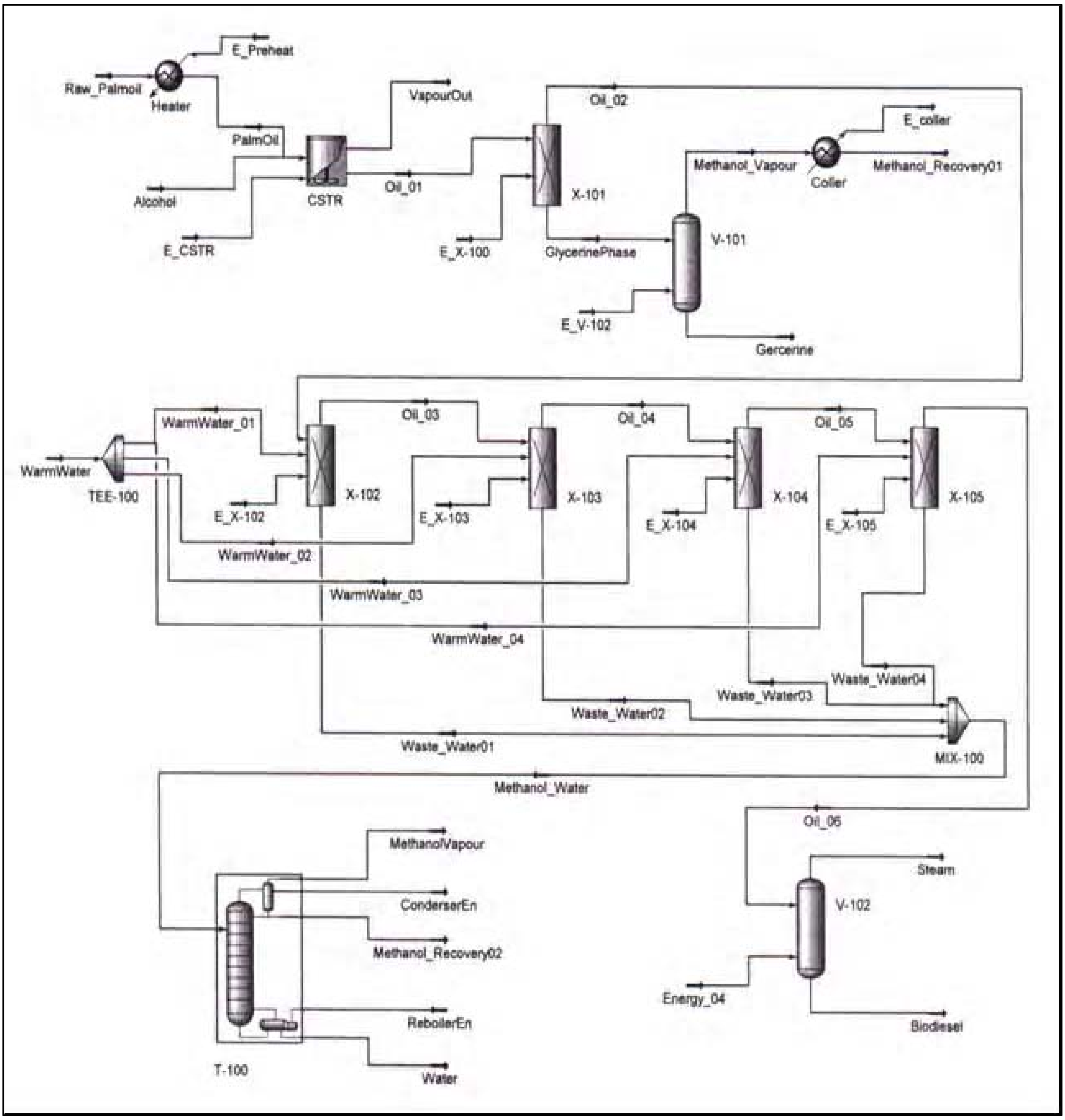

Fig. 1. Flow diagram of the preliminary biodiesel process, PFD_1.

4. METHODOLOGY

This work considered the steady state design for biodiesel plant by using HYSYS 3.2 [1] to design and simulate the biodiesel production [6]. The interested parameters used for designing the process are reaction times (t), reaction temperatures (T) and the ratios of methanol to oil (R).

These parameters have an effect on the production purity and the operating or total cost, which is defined as material and energy costs per unit weight of methyl ester production. The process flow diagram (PFD) of the biodiesel production in this work is shown in Fig. 1.

From Fig. 1, the PFD_1 consists of a continuous stirred tank reactor (CSTR), glycerin-oil separation tanks (X-101), an evaporator V-101 to evaporate methanol from glycerin and a distillation column to separate methanol from waste water.

The unreacted methanol from this unit is then recycled to the reactor. Oil from X-101 contains soap from saponification of free fatty acid and NaOH catalyst, so tanks X-102 to X-105 are washing tanks used to remove soap from methyl ester by warm water. Waste water from this washing still contains a large amount of methanol and then is sent to distillation column (T-101).

(i) Process Design

1. Oil used in this work containing of FFA of less than 1% is heated to 120°C for 20 minutes to evaporate water in oil [7] (cost of oil is about 20-25 Baht /kg).

2. In the CSTR, the reaction temperature, the reaction time and the ratio of methanol to oil were varied in order to determine the optimum condition. First, the molar ratio is fixed at 6:1 [7], so the reaction time and temperature are varied to get the optimum. The optimum ratio was later determined.

3. Process flow diagram was improved as shown in Table 2. The input flow rate of each case is set constant.

4. The data from simulations of 1-3 were collected and evaluated based on economic design in order to obtain optimum operating condition.

Table 2. Details of 3 PFDs studied in this work

Process	Details
PFD_1	1 CSTR 50 litters. (shown in Figure 1)
PFD_2	1 CSTR 1 100 litters
PFD_3	2 CSTRs 50 litters in series with removed glycerin

5. RESULTS AND DISCUSSIONS

Effects of Reaction Temperature

The simulation in Figure 2 shows that at the same reaction time, increasing reaction temperature increased product purity.

Figure 3 shows the effect of reactor temperature on the product purity or % purity (percent by weight of methyl ester to all products) and a total cost. The % purity increased when the reaction temperature increased. Increasing reaction temperature from 55°C to 65°C caused the lower varied costs because from Arhenious, high temperature would push the process move forward, resulted in more products. Therefore cost per unit of product could be reduced. However, after 65 °C, the reaction stayed in equilibrium, increasing temperature did not bring more products but that consumed more energy, as a result, the total cost per unit of biodiesel increases.

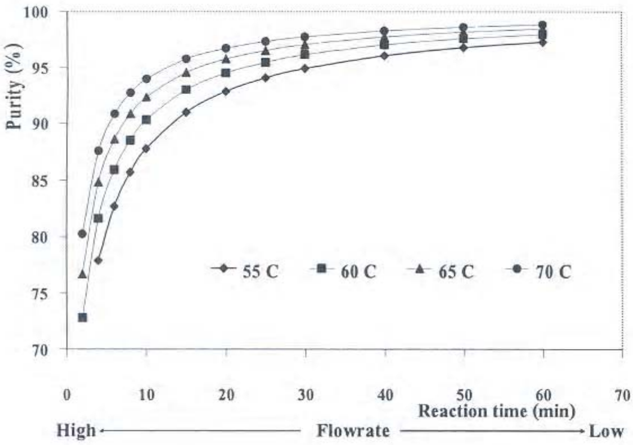

Fig. 2. Effect of reaction times and temperatures on product purity at the ratio of 6:1.

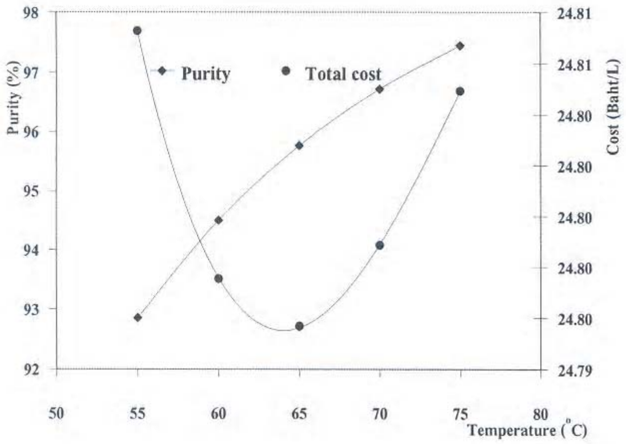

Fig. 3. Effect of reaction temperature on % purity at the constant time of 20 minutes and the ratio of 6:1.

Effects of Reaction Time

Figure 2 also shows that increasing reaction time by decreasing feed flow rate, increased the product purity. Additional, the percent purity increased exponentially from 0 to 20 minutes. After 20 minutes, the purity slightly increased and almost reached a steady state after 60 minutes. This can be concluded that the process operation using the reaction time higher than 20 minutes is waste of energy.

Therefore increasing either the reaction temperature or the reaction time, increased the product purity. Additional, in order to get the accepted product purity (96.5%, [2]), the operating reaction temperature and the reaction time found to be in the range of 55 °C, 50 minutes to 70 °C, 20 minutes.

Figure 4 shows the effect of the reaction time on costs of methanol, oil, energy and operating cost. The ratio of energy cost and palm oil to methyl ester tended to increase in the first 20 minutes because the reaction moved forward quickly. One mole of the controlled reactants (oil) converted to 3 moles of methyl ester or biodiesel. The reaction stayed constant after 20 minutes caused the total cost to be constant. One interesting contrast was increasing cost of methanol for the first 20 minutes due to more methanol used in the reaction. The overall total cost decreased insignificantly in the first 20 minutes and became constants after that or when the reaction reached its equilibrium.

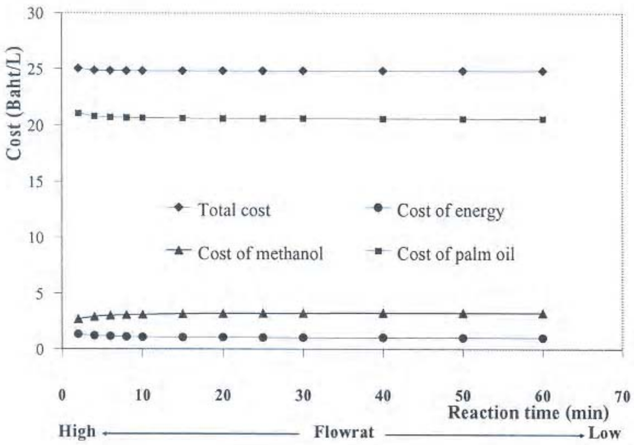

Fig. 4. Effect of reaction time on costs at the reaction temperature 70 °C and ratio of methanol to oil at 6:1.

Effects of Molar Ratio

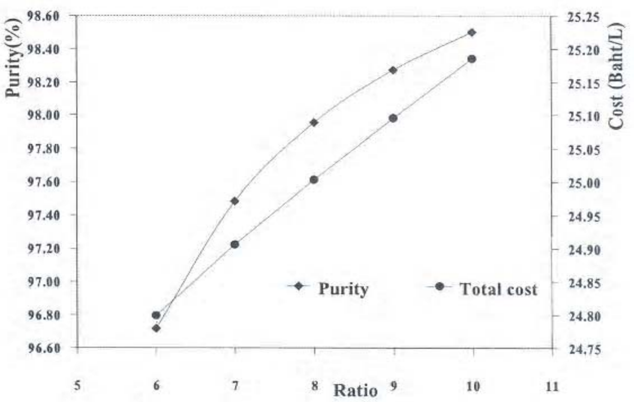

Fig. 5. Effect of molar ratio in % purity and varied cost at reaction temperature of 70 °C for 20 minutes.

From figure 5 shows effect of molar ratio of methanol to oil at reaction temperature of 70 °C for 20 minutes. Increasing molar ratio increased the product purity. Every ratio higher than 6:1 gave the % purity reached the specification. However, it was not a good design to operate process at higher ratio because increasing ratio would increase mount of methanol and it would be difficult to recover all unreacted methanol, also, consumed more energy. Moreover, some methanol might be lost from its vaporization.

Overall Cost and Energy Consumption

Figure 6 classifies the average operating costs for the biodiesel process. It is shows that the energy cost did not play an import role on the total cost as much as the cost of the reactants, methanol and palm oil. The sharing of the energy cost is only 5% while the cost of palm oil and methanol had the sharing of 80% and 15 %, respectively. One possible reason is that the reactions are exothermic reactions, which increase the temperature of the reactor by itself, so the heat for the reactors is not as much as required. The other reason is that if compare prices per unit, the price of energy (3 Baht /unit) is about 7-8 times lower than price of palm oil (20-25 Baht /kg). Therefore, if the price of oil is lower, the operating cost of methyl ester also decreases.

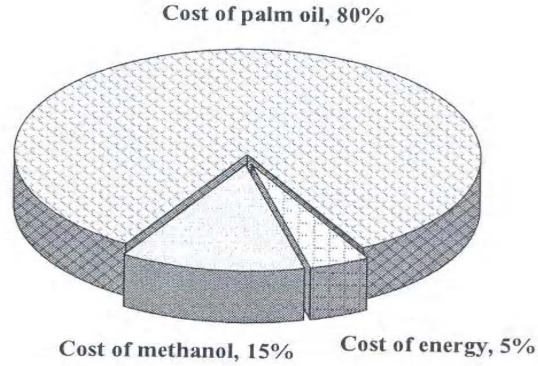

Fig. 6. Average percentage of varied costs in the process.

Figure 7 shows the average percentage of energy distribution in each unit operation of the process. It is seem that most energy was consumed by the methanol recovery unit (66%) such as from the distillation column and the rest was used by the reactor (17%), evaporator (to evaporate water from methyl ester (11%) and preheating the reactants before feeding to the process (6%).

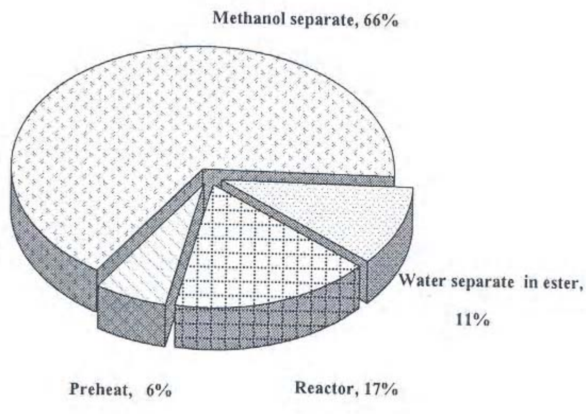

Fig. 7. Average percentage of energy consumption in each unit operation.

If the process applies heat exchanges between each unit, it can reduce the energy consumed in the process. For example if the methyl ester from the evaporator exchanges heat to the preheating unit, we can save the energy about 3% (for 50 % efficiency heat exchanger). However, having more heat exchangers has a fixed cost of that. Trades off between increase fixed cost and decrease operating cost is required.

Process Improve

Table 3 compares the results of improving the process for the three cases at the same input flow rates. PFD_1 had the smallest reactor volume. So it took the smallest amount of the reactants and energy. As the results, it provided the lowest operating cost. However, it gave the least amount of product purity because of the shortest process time. That is the shorter reaction time, the lower product conversion.

To improve product purity from PFD_1, PFD_2 had the reactor size twice of the one in PFD_1. This provided product purity and total cost greater than in PFD_1 because of the larger amount of the reactant and longer time in the reactor. However only the energy cost was the same as in PFD_1 since more time in PFD_2, more methyl ester products, so the total operating cost per unit of methyl ester production in both PFD are the same.

PFD_3 used 2 half-size reactors of the reactor in PFD_2. The amounts of the reactants are the same as in the PFD_2 but greater than in PFD_1, so the reactants cost was the same as in PFD_2. The product purity from PFD_3 was normally higher than PFD_1. In addition, the work found that the purity from this case was also higher than in PFD_2 due to removal of glycerin in this case pushed the reaction move more forward. Since glycerin is a one of the reaction product, withdraw the products makes the reaction is not in its equilibrium, consequently, the reactions tried to move to its equilibrium by moving forward to get more products. Therefore the purity of the product is the highest one. However, the total cost per unit of methyl ester was higher than in PFD_1 but less than in PFD_2 since the amount the reactants are higher than that in PFD_1. Moreover, the energy cost is the highest because having 2 reactors requires more energy for the extra reactor l. Therefore if the product purity is the first factor to consider and second consider is the total cost, PFD_3 should be applied to the process.

Table 3. Comparing % purity and Costs among 3 process structures

Process (For 20 min)	% Purity	Energy Cost (Baht/L)	Total Cost (Baht/L)
PFD_1	96.62	1.03	21.04
PFD_2	98.21	1.03	21.08
PFD_3	99.71	1.18	21.07

6. CONCLUSION

This study is to compare the cost of biodiesel with petroleum diesel, the price of biodiesel is higher than the other. However, it is the way to use renewable energy. The optimal operating condition which minimizes the varied cost is using the ration of methanol to oil at 6:1 (or 0.238:1 by wt.), reaction temperature of 70 ^{o}C for 20 minutes by recovering methanol from each unit.

In addition, for the same production rate, the process with double size of the reactor improves the product purity (from 96.62 % to 98.21 %). For the number of reactors, it is found that two half-size reactors give better product purity and operating cost than the single reactor with the equivalent size. Therefore, if the process requires high percent of the product purity, the plant should have 2 reactors in series which the effluent stream from the first reactor should be removed glycerin before feeding to the second reactor. Moreover even using 2 reactors costs more 1 reactor, reaction or operating time can be largely reduced from using 1 reactor.

Since the main cost of biodiesel production is from (palm) oil cost, therefore reducing this cost can reduce the cost of biodiesel. Using used oil can reduce this cost though used oil have more free fatty acid which need to be reduced before transesterification process. Also, recovering heat from each unit can reduce the operating cost.

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