

A COMPARATIVE STUDY FOR BIODIESEL PRODUCTION BY REACTIVE DISTILLATION: SIMULATION PROCESS

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ABSTRACT

Biodiesel is an excellent substitute for conventional diesel fuel because of being renewable, nontoxic, biodegradable and low emissions. This study concerns with production of methyl oleate-ester (biodiesel) using glyceryl trioleate and methanol with NaOH as a catalyst employing both traditional process and reactive distillation process. Aspen-Hysys v 8.0 is used for this simulation. The phase equilibrium was predicted by the Wilson thermodynamic model and the reactants are fed, methanol to olein oil (molar feed ratio = 6:1). Results reveal to that integrated design of (RD) ensures the removal of glycerol by-product that shifts the chemical equilibrium to completion. Thus RD process are more efficient than traditional process for biodiesel production due to less units and lower energy consumption.

Keywords: Biodeisel, Aspen Hysys, Olein, Reactive Distillation, Transesterification

1. INTRODUCTION

The growing demand of the world on fuel and energy sources for daily activities are increasing recently due to the huge development of industries, agriculture, cities, and transportation. As a result of the rising world fuel price, the current limited reservoirs will soon be depleted at the current rate of consumption and due to concerns about global warming are the key factors driving renewed interest in renewable energy sources and in bioenergy [1, 2]. The research in energy from all over the world focuses on finding an alternative source of energy replacing petrol fuel. Nowadays,

fatty acid esters (Biodiesel) are clean burning fuel produced from a renewable feedstock such as vegetable oils or animal fats. An important alternative for making the biodiesel production process more attractive is to take advantage of the process intensification characteristics. Process intensification is defined as any chemical engineering development that leads to a substantially smaller, cleaner, and more energy- and production-efficient technology [3].

Biodiesel, among these kind of fuels, as being an environment-friendly fuel in definition, is derived from the seeds of such plants as rapeseed, sunflower, soybean, safflower, from various waste oils, and from other oils of animal based, by way of reacting them with a short-chain alcohol via certain chemicals [4].

Generally, the total of 108 million tons of vegetable oils are being produced worldwide, 6 million tons thereof are being used in producing biodiesel. Many biofuels could be obtained from biomass, as a source of clean energy source, by using various transformation processes in Europe; and this fuel, having also been defined by the EU and US standards, is a very important alternative fuel [4]. There is a significant increase in the studies being conducted in our country on the issue of alternative energy sources.

In recent years, many studies about production of biodiesel fuels can be found by using the major traditional process (fatty acid esterification or triglycerides transesterification) all these attempts proposed technically optimized processes for the production of biodiesel fuel from vegetable oils (soybean oil, castor oil, palmitic fatty acid, decanoic fatty acid, and canola

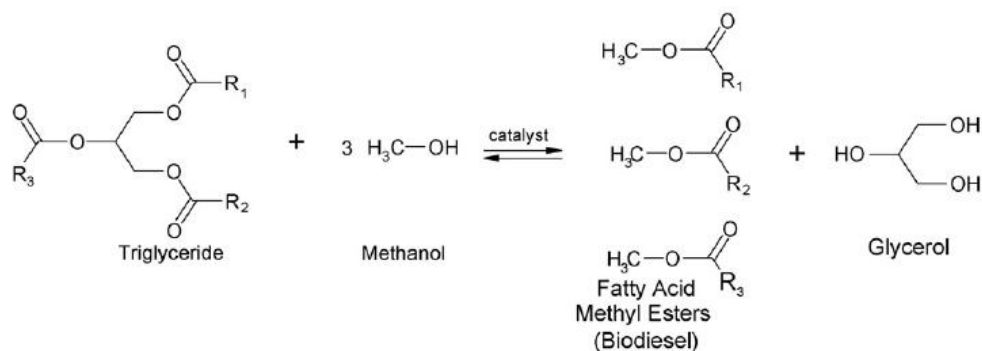
oil) to achieve the maximum percentage of conversion by using suitable alcohol and basic catalysts[1, 5~10].

In the present study, the Aspen Hysys (version 8.0) were used for simulating the methyl oleate biodiesel production by traditional process and reactive distillation process with the aim of obtaining a deep understanding about the processes, finding the best conditions for producing the largest amount of fatty acid methyl esters and assess its viability.

2.MATERIAL AND METHODS

2.1.Transesterification (Alcoholysis)

Transesterification (also called alcoholysis) is the reaction of a fat or oil (triglycerides) with an alcohol to form esters and glycerol according to Eqn.(1). A catalyst is usually used to improve the reaction rate and yield.



Alkyl groups for a chemical reaction are;
 R_1, R_2 and R_3 are $\text{C}_{17}\text{H}_{33}$ (oleic)

Due to the chemical reaction is reversible, excess alcohol is used to shift the equilibrium to the products side. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and

amyl alcohol [2, 11]. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and the shortest chain alcohol). To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed [9]. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. The reaction can be catalyzed by alkali, acid, or enzyme. The alkalis include $NaOH$, KOH , carbonates and corresponding sodium and potassium alkoxides. Sulfuric acid, sulfonic acid and hydrochloric acid are usually used as acid catalysts. Lipases also can be used as biocatalysts. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially [2].

2.2. Reactive Distillation (RD)

Reactive distillation is a chemical unit operation in which chemical reaction and product separation occurs simultaneously in one unit. Reactive distillation column consists of a reactive section in the middle, with non-reactive rectifying and stripping sections at the top and bottom as illustrated in Figure (1) [2].

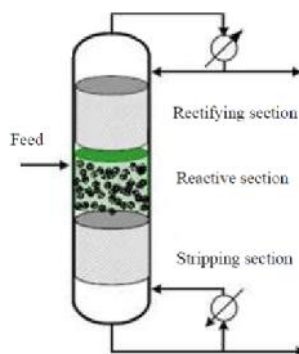


Figure 1. The general configuration of Reactive distillation

The reactive distillation technology offers many benefits as well as restrictions over the conventional process of reaction followed by distillation or other separation approaches. Reducing capital cost, higher conversion, improving selectivity, lower energy consumption, the reduction or elimination of solvents in the process and avoidance of azeotropes are a few of the potential advantages offered by reactive distillation. Conversion can be increased far beyond what is expected by the equilibrium due to the continuous removal of reaction products from the reactive zone. This helps to reduce capital and investment costs and may be important for sustainable development due to a lower consumption of resources [2, 4].

2.3. Simulation Procedure

The system studied here is composed of olein oil (oleic acid ester also called glyceryl trioleate or triolein), methanol, olein biodiesel (oleic acid methyl ester or methyl oleate or methyl oleate ester) and glycerol. For the simulation, Aspen Hysys v. 8.0 will be used. The transesterification reaction requires three moles of methanol and one mole of triolein to give three moles of methyl oleate ester (biodiesel) and one mole of glycerol. However, this reaction is reversible, therefore an excess of alcohol is required to drive the reaction toward the product side to increase conversion. The kinetic model proposed by Song *et al.* [12] was employed, and the temperature of the reactive stages was maintained between 30 and 50°C for meeting the model limits. The phase equilibrium was predicted by the Wilson thermodynamic model.

3. RESULTS & DISCUSSION

3.1. Traditional Process

Wilson-Ideal property model was used in simulation as shown in Figure (2). Reactants are fed, methanol to glyceryl trioleate molar feed ratio = 6:1. The conversion of reaction reach up to maximum value 95% according to the kinetic data that given by Song *et al.*[12].

The mixture effluent outlet from reactor is send to alcohol recovery unit is generally carried out by distillation column (5 plates and feed pressure =400 kPa) to recovery the excess methanol then recycle it to reactor. The bottom effluent of distillation column pump to purification unit that consists of washing column by using pure water (4 stages and operating at 110 kPa and 60°C) to separate a basic and glycerol components of the product mixture, then the upper effluent of washing column send to splitter then three phase separator respectively to concentrate the biodiesel product (operating at 110 kPa and 60°C). Conversion of the reactor is 95%, with a purity of biodiesel product from the process reaches to $\approx 95\%$ vol. (depend on the operating conditions of distillation column).

3.2. RD Column

The RD column has 20 stages and reflux ratio ($R = 0.7$). The glycerol trioleate is fed above and methanol below the reactive zone (mid 9 stages), respectively. In order to reduce the amount of glycerol trioleate in the final product which is heavier than the alcohol, it must be fed in the top of the reactive zone. Figure (3) presents the flow-diagram of transesterification of the triolein with methanol for RD process. High purity final products are

feasible. By allowing 2% mol of methanol in the bottom stream, the reboiler temperature in the RD column can be kept below 195°C.

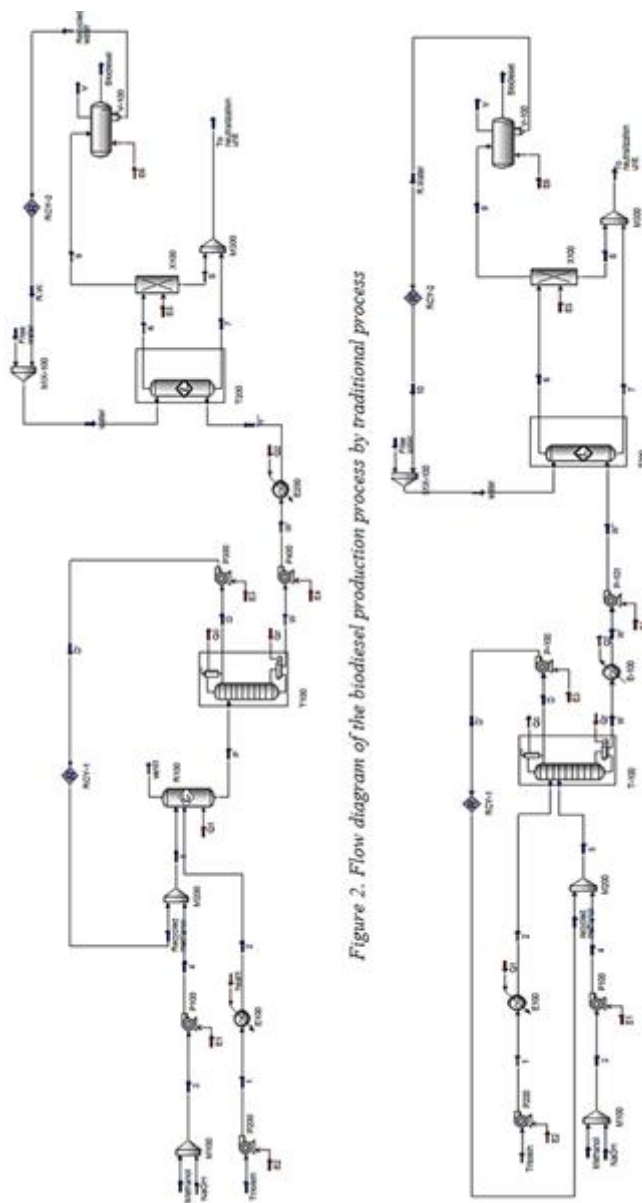


Figure 2. Flow diagram of the biodiesel production process by traditional process

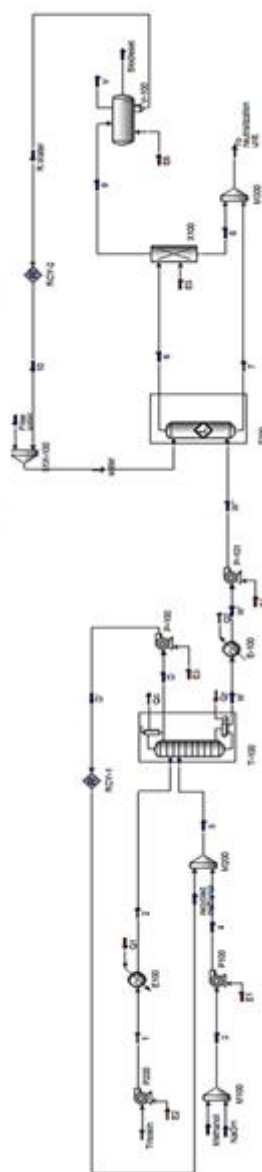


Figure 3. Flow diagram of the biodiesel production process by reactive distillation (RD) column

When an excess of alcohol is used, the maximum reaction rate is located at the top of the column, with total acid conversion in the bottom but partial conversion of alcohol in the top. For the optimal reflux ratio the maximum reaction rate is located in the center (reacting zone) of the column, providing complete conversion of both reactants at the ends of the column. This behavior is shown through the composition and temperature profiles in the reactive distillation column in Figures(4 and 5) respectively. Then, the mixture effluent outlet from reactor being sent to alcohol recovery unit is generally carried out by distillation column (5 plates and feed pressure =400 kPa) to recovery the excess methanol then recycle it to reactor. The bottom effluent of distillation column is pumped to a purification unit, this unit consists of washing column by using a pure water (4 plates and operating at 110 kPa and 60°C) to separate a *NaOH* and glycerol components of the product mixture, in which the upper effluent of the washing column send to splitter then a three phase separator respectively to concentrate the biodiesel (methyl oleate) (operating at 110 kPa and 60°C). Conversion of the RD is 100% with a purity of biodiesel product of the process reaches to $\approx 100\%$ vol. (depending on the operating conditions of RD).

A comparison between both processes show the transesterification with reactive distillation (RD), both the reaction and separation steps take place simultaneously in one single process unit, enhancing process conditions for both unit operations, resulting in high-yield conversions at small time frames. Other benefits shown for RD are: less recycle streams, less need for pumping equipment and piping, less production of waste streams, which implicates into lower investment and operating costs as mentioned by

Shinde *et al.* [2]. A study by Miranda-Galindo *et al.* [13] stated that in all cases where reactive distillation is used, variable cost and energy requirements are reduced by 20% or more when compared to the classic setup of a reactor followed by distillation (describing in section 3.1).

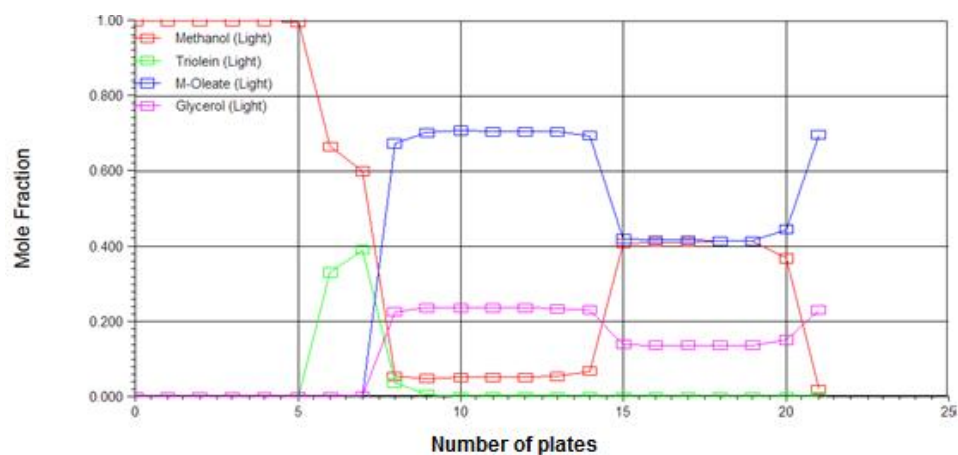


Figure 4. Reactive distillation column (RD) profiles for liquid composition

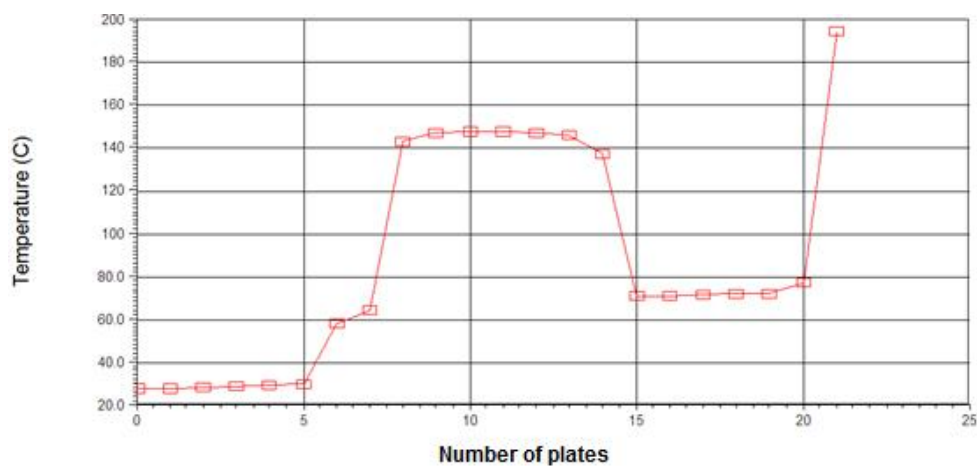


Figure 5. Reactive distillation column (RD) profile for column temperature

The performance of a reactive distillation column is affected by several process parameters including the sizes and location of the reaction and separation zones in the equipment, reflux ratio, feed flow rate and feed tray location. The reactive distillation unit can be a tray or packed column, tray columns are recommended for homogeneous systems because the greater holdup and the associated longer residence time as presented by Singh *et al.*[14]. A study presented by Nguyen and Demirel [15] showed that further reduction of energy and equipment costs is possible by thermally coupled distillation sequences, as they allow interconnecting vapor and liquid flows between the two columns to eliminate the reboiler or condenser or both in one of the columns, the thermally coupled sequence reduced the energy consumption by 13 % in the reactive distillation column and 50 % in the subsequent methanol recovery column.

4. CONCLUSIONS

Biodiesel fuel can be produced by a sustainable continuous process based on catalytic reactive distillation with more efficient than traditional process. The integrated design ensures the removal of glycerol by-product that shifts the chemical equilibrium to completion. Manufacturing of biodiesel (methyl oleate ester) by reactive distillation can be applied to a variety of alcohols and triglycerides, as a multifunctional reactor, the actual applications depends on the feedstock at hand. It is concluded that reduced capital and operating costs, due to less units and lower energy consumption, biodiesel is produced by using RD column. The process proposed here can dramatically improve the economics of current biodiesel synthesis and reduce the number

of downstream steps. The key benefits are high unit productivity, up to 5-10% times higher than of the traditional process and there is no waste streams because no salts are produced (neutralization step not required).

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