Aspen HYSYS Simulation for Biodiesel Production from Waste Cooking Oil using Membrane Reactor

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Abstract. Biodiesel is a promising energy alternative solution to cater the demand of clean sustainable energy sources. Conventional biodiesel production is done by transesterification method using stirred tank reactor and homogeneous base catalyst, then followed by purification process. However, there are some drawbacks associated with this method. They include soap formation, sensitivity to free fatty acid (FFA) content and purification difficulties. Due to these downsides, biodiesel production using heterogeneous acid catalyst in membrane reactor is proposed. This project is aimed to study the effect of FFA content and membrane separation effectiveness on FAME yield. Waste cooking oil, inorganic pressure-driven membrane and WAI is used as raw material, membrane and heterogeneous acid catalyst, respectively. Biodiesel yield formulation is derived from literature data and then used in an Aspen HYSYS process simulation. Early phase cost estimation shows that FFA content does not affect the estimated capital investment, while the membrane separation effectiveness does significantly. Future work will include its comparison with the conventional biodiesel production process.

1. Introduction
The dramatic growth of global population leads to high demand of sustainable energy supply and great attention on waste treatment. Biodiesel appears to be one of the most promising and feasible energy sources and clean fuel as it emits less toxic pollutants and greenhouse gases than petroleum diesel. It can be used as a stand-alone or blended with conventional diesel. It is also proven to be compatible for diesel engines without any required special modifications and will result no negative impacts to operating performance of the engines.

Apart from the demand of sustainable energy, pollution issue is also important to be recognized. One of the key approach to minimize pollution is by recycling the waste into valuable products. Waste cooking oil is one of polluting materials which increases with human population. Hence, due to its abundance and low cost, waste cooking oil is going to be used as the raw material of biodiesel production.

The current technologies of biodiesel production are based on micro-emulsion [1], pyrolysis [2] and transesterification [3]. Out of these methods, transesterification is the most commonly applied method in the industry with feedstocks varying from virgin oil (e.g.: canola oil, vegetable oil, olive oil, etc), used oil, animal fats and micro-algal oil. Conventional biodiesel production is done by transesterification method using stirred tank reactor and homogeneous catalyst, then followed by purification process. Homogeneous base catalysts are commonly used in biodiesel production due to
its fast reaction rate and availability. However, the drawback of using this type of catalyst is its sensitivity to FFA content in the oil. This will lead to soap formation, hence decrease the biodiesel yield and cause purification difficulties [4]. On the other hand, conventional acid catalyst for producing biodiesel has been known to have a very long residence time. Therefore, biodiesel production from waste cooking oil using heterogeneous acid catalyst in membrane reactor is proposed. This option is considered to intensify the reaction and separation processes into a single reactor. The produced biodiesel or fatty acid methyl ester (FAME) can be drawn from the reactor simultaneously while retaining the unreacted oil. This situation then shifts the equilibrium reaction to the biodiesel side. This method will also remove the need of water to wash off the product from any impurities as required by the conventional production process. Thus, the purpose of this study is analysis the techno-economic feasibility of biodiesel production by using a heterogeneous acid catalyst membrane reactor. In the current study, the FFA content and the membrane separation effectiveness are evaluated. Their impacts are then evaluated by using an in-house capital cost estimation tool.

2. Process description

2.1. Membrane reactor selection

Transesterification process of biodiesel production can be carried out in various reactors such as batch, plug flow, fixed bed or continuous stirred-tank reactors. Batch reactor for commercial biodiesel production is not recommended because of its tedious mode of operations [5]. Thus, plug flow reactors, CSTR and fixed bed reactors are more viable to be used in commercial biodiesel production. However, some challenges ranging from poor biodiesel yield [5] to mass transfer limitation [6] are associated with these reactors. Membrane reactor is proven to be more environmentally friendly because it minimizes the waste water production [7].

Furthermore, membrane reactors are able to intensify the process and selectively remove the products throughout the process. Hence, it improves the product purity [5]. Membranes are generally classified into three groups; inorganic, organic and combination of both. Among those groups, inorganic membranes, such as metallic, ceramic or zeolitic membranes, are the most preferred due to their ability to withstand high temperatures, high acidic or basic environments [5]. Similarly, Barredo-Damas et al. [8] noted that beside of its high chemical, thermal and mechanical resistance, the cost of ceramic membranes has decreased.

2.2. Catalyst selection

Catalyst is one of the most important factors in biodiesel production which will affect the reaction rate, operating conditions and yield. Lam et al. [4] stated that heterogeneous and enzymatic catalyst are the most suitable catalyst for transesterification of low quality feedstocks. It is due to their insensitivity to FFA and the downstream separation are relatively easy. However, enzyme catalyst is less preferable because of its sensitivity to methanol, very slow reaction rate and high cost [4]. In addition, heterogeneous base catalyst is also sensitive to FFA and will form soap if the FFA content is greater than 2 wt% [4]. Therefore, heterogeneous acid catalyst is the most preferable catalyst for waste cooking oil transesterification process. Among variety options of heterogeneous acid catalyst, synthesized tungsten on alumina supported catalyst (WAl) appears to be the most effective catalyst. Komintarachat and Chuepeng [9] shows that 1 wt% WAl loading and 0.3 methanol/WCO weight ratio give 97.5 wt% FAME yield at 383 K in 2 hours from WCO containing 15 wt% FFA.

2.3. Reaction data

Esterification and transesterification processes is widely used to produce biodiesel. The general reaction is represented in Figure 1.
The desired product of this reaction is the methyl esters (biodiesel), while the by-product is glycerol. Impurities include leaching of heterogeneous acid catalyst or soap if basic catalyst is used [4]. The waste produced by biodiesel production is mainly water from the purification process.

Komintarachat and Chuepeng [9] has studied the effects of WAI catalyst loading, methanol to oil weight ratio, temperature and time on ester yield. Based on their study, it is found that FAME yield is represented by Equation 1, obtained via developing statistical model:

\[
\text{FAME Yield (wt\%) = 7.1609 } T - 1326.6326 t - 12.5697 C^2 - 0.0186 T^2 - 3.9446 t^2 - 321.9353 R^2 + 0.0712 CT + 3.5161 Tt + 0.5940 TR
\]

(1)

Where T, t, C and R represent reaction temperature (K), reaction time (hour), WAI catalyst amount (wt\%) and methanol/WCO weight ratio, respectively.

3. Process simulation

3.1. Fluid package and components

The flowsheet for biodiesel production using membrane reactor is developed in Aspen HYSYS version 8.8 using NRTL fluid package. The composition of free fatty acids is taken from Wen et al. [10] while composition of triglycerides is assumed. FFA content of 15 wt\% is assumed in the base case. Table 1 shows the composition of waste cooking oil as per base case design.

Table 1. Typical composition of waste cooking oil as basecase design

| Components    | Mass Fraction |
|---------------|---------------|
| Tripalmitin   | 0.074         |
| Tristearin    | 0.027         |
| Triolein      | 0.184         |
| Trilinolein   | 0.478         |
| Trilinolenin  | 0.051         |
| Other TG      | 0.036         |
| Palmitic Acid | 0.013         |
| Stearic Acid  | 0.005         |
| Oleic Acid    | 0.032         |
Linoleic Acid 0.083
Linolenic Acid 0.009
Other FFA 0.006
H₂O 0.003

3.2. Simulation environment
Early phase process evaluation method is followed in this study to design the process and its evaluation [11]. Waste cooking oil and methanol are pumped and heated to 383.1 K and 11.51 bar before being fed to the reactor. Membrane reactor is simulated using a series of conversion reactor and component splitter with recycle retentate stream. Conversion reactor is run with 96.54% triglycerides conversion and 92.34% FFA conversion. The conversions are calculated from FAME yield assuming the reaction temperature of 383 K, 1 wt% WAI catalyst loading, 0.3 MeOH/WCO weight ratio and reaction time of 2 hours. Membrane separation factor is assumed to represent inorganic pressure-driven membrane which separate the feed based on the molecular weight. Table 2 displays membrane separation factor as per base case design.

| Components                  | Permeate | Retentate |
|-----------------------------|----------|-----------|
| Triglycerides               | 0        | 1         |
| Free fatty acids            | 0.30     | 0.70      |
| Fatty acid methyl esters    | 0.35     | 0.65      |
| Glycerol                    | 0.90     | 0.10      |
| Methanol                    | 1        | 0         |
| Water                       | 1        | 0         |

Permeate stream, containing the biodiesel, is drawn from the membrane reactor while retentate is recycled back to the reactor. Permeate is then cooled to room temperature and immediately formed FAME-Rich phase and Glycerol-Rich phase [6]. Methanol in FAME-Rich phase is separated using distillation column, then recycled back to methanol storage tank. The bottom product of this distillation column is fed to second distillation column to separate FAME and FFA. FAME (biodiesel) is recovered in distillate stream of the second distillation column. Figure 2 shows the HYSYS model for biodiesel production using membrane reactor.

Figure 2. HYSYS model for biodiesel production using membrane reactor
From this developed basecase, capital cost is estimated by using in-house capital cost estimation tool. Then, two uncertainties are varied in this study to see the significances of their effects. These are the FFA content and the membrane effectiveness separation. The FFA content is varied from 10 wt%, 15 wt% to 20 wt%. The membrane effectiveness separation is varied as shown in Table 3.

| Components                  | Feed Fraction in Permeate |
|-----------------------------|---------------------------|
|                             | Case 3 | Base Case | Case 4 |
| Triglycerides               | 0      | 0         | 0      |
| Free fatty acids            | 0.20   | 0.30      | 0.40   |
| Fatty acid methyl esters    | 0.25   | 0.35      | 0.45   |
| Glycerol                    | 0.80   | 0.90      | 1      |
| Methanol                    | 1      | 1         | 1      |
| Water                       | 1      | 1         | 1      |

4. Results and discussion

The effects of the abovementioned uncertainties to the estimated capital cost or capital expenditures (CAPEX) are shown in Figure 3. It is shown that the FFA content does not affect the estimated CAPEX. On the other hand, the membrane effectiveness separation does significantly influence the estimated CAPEX. The better the product separation via the membrane reactor will simplify the size of the recycle stream and the downstream equipment. Hence, the estimated CAPEX is reduced by 10% compared to the basecase. And vice versa, the estimated CAPEX is increased by almost 20% with the worse product separation via the membrane reactor.

![Figure 3. CAPEX changes due to variations of FFA in WCO and membrane effectiveness separation](image)

5. Conclusion and Future Works
The present study has shown techno-economic evaluation of early phase process design for biodiesel production from waste cooking oil with membrane reactor. Based on the developed reaction yield model from literature, a process production has been designed and simulated in Aspen HYSYS environment. An estimation of the required capital expenditure has been made with an in-house cost estimation tool. The effect of two uncertainties, namely the FFA content in the oil and the effectiveness of the membrane separation. The result shows that the FFA content does not significantly change the estimated capital cost, while the membrane separation does change the cost significantly.

This study is an on-going project which will include more uncertainties to cover and its comparison with conventional biodiesel process from waste cooking oil. Uncertainties for the capital cost estimate, among others, and the comparison will be evaluated in the future study by using Monte Carlo simulation.

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