Application of Reactive Distillation for Biodiesel Production Enhancement: An alkyl process

W. Limniyakul¹, T. R. Srinophakun²*, and S. Wanganusorn³

¹Department of Chemical Engineering, Kasetsart University
Bangkok 10900, Thailand

²Department of Chemical Engineering, Kasetsart University
Bangkok 10900, Thailand

³School of Manufacturing Systems and Mechanical Engineering, Sirindhorn International Institute of Technology
Thammasat University, Pathum Thani 12120, Thailand

*Corresponding author’s email: fengtcs [AT] hotmail.com

ABSTRACT—This article presents a reactive distillation simulation model of biodiesel production from the feed of 1,000 kg/h Jatropha oil. Starting with the verification of the conventional process at the purification sections and improve transesterification calculation, the model gives a realistic solution. GaussViewW and GAUSSIAN 03W are used to generate the molecular structure for other key compositions including triglyceride, diglyceride, and monoglyceride of oleic and linoleic acid which are major components of Jatropha oil. The biodiesel conversion 1.14% and energy 1.36%; requirement by the reactive distillation process are higher than the conventional process which the conversion of conventional process and reactive distillation are 98.2 and 99.8 respectively. However, reactive distillation can almost consume the reactant completely. While there are some triolein and diolein in biodiesel from the conventional process, these residues impact on the quality of biodiesel. The recycling system can also reduce fresh methanol by about 81%. The optimum conditions of reactive distillation are 2 stages of the reaction zone, no rectifying section, no stripping section, 5 reflux ratio, and 1 atm. The controllability of the process is studied by varying the feed oil ± 2%. The control structure of the process can handle these disturbances and keep the product at the desired specification.

Keywords—biodiesel, reactive distillation, homogeneous catalyst

1. INTRODUCTION

The reactive distillation is an operation of which reaction and separation perform in a single unit. There are several advantages such as: (1) it can reduce capital and production costs by combining two sections into one. (2) Removal products can increase the reaction conversion, (3) the heat duty can be reduced by utilizing the heat of reaction, (4) the limitations of azeotropic mixture can be overcome by reaction (Doherty and Buzad, 1992), (5) the recycling costs for excess reactant, which is necessary for a conventional reactor to prevent side reactions and chemical equilibrium limitation, can be reduced. Due to all these reasons, many publications dealing with the simulation and experimental evaluation of reactive distillation have rapidly increased. The biodiesel productions have two main processes; reaction and purifications. Therefore, this project aims to develop the reactive distillation model for biodiesel production instead of the conventional process. Using the reactive distillation can reduce capital investment such as the production of methyl acetate (Siirola, 1995). For the acid catalyst reaction between iso-buten and methanol to form methyl tert-butyl ether, the traditional reactor followed by distillation concept has a complexity inherently because the mixture leaving the reactor forms three boiling azeotropes. (Sundmacher et al., 1995; Doherty and Buzad, 1992) The development and application of the equilibrium stage model for reactive distillation has been described in several types of research (Taylor et al., 1999; Jhon & Lee, 2002; Chen et al., 2003; Pyhalathi, 2005; Alfradique and Castier, 2005; Cheng and Yu, 2005; Katora et al., 2005; Dalaoui and Seferlis, 2006; Venkateswarlu and Kumar, 2006.). The equilibrium stage models (Taylor et al., 1999) are demonstrated for calculates the material balances, vapor-liquid equilibrium equations, mole fraction summations and enthalpy balances (MESH). Cheng and Yu (2005) studied the optimal feed locations of reactive distillation and presented 3 heuristics. The operation pressure in the distillation is carried out at the atmospheric pressure. However, some cases operate at low or high pressure (Doherty and Malone, 2001). The production of biodiesel by reactive distillation was base on alkali catalyst transesterification by Zhang (Zhang et al., 2003). The kinetic models of transesterification reaction available (Freedman et al., 1986; Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000; Foon et al., 2004; Karmee et al., 2004; Vicente et al., 2005; Vicente et al., 2006). Because of the same catalyst selected
and a similar component of oil, the kinetic model of Noureddini and Zhu (1997) is selected to describe the transesterification reaction of jatropha oil. After complete reaction, there are two layers between biodiesel and glycerol (Zhou et al., 2006). The water washing unit was used to separate the biodiesel and glycerol, but it is easy to separate by gravity unit introduced by (Krawcyk, 1996). Therefore, the experimental and simulation studies for the production of biodiesel in the alkali-catalyzed reactive distillation column have been reported the present work.

1.1 Methodology

Also, three steps of reversible transesterification reaction which are triglyceride to diglyceride, diglyceride to monoglyceride and monoglyceride to glycerin were added for improving the calculation result. The structure of unsupplied components triglyceride, diglyceride, monoglyceride, and fatty acid methyl ester can be generated by GaussViewW or in the ASPEN PLUS. Because of the less complicated and more accuracy of Gauss ViewW, this program was used to draw unsupplied components. These structures were then optimized by GAUSSIAN 03W and were used in the property estimation step. Set of simulations which were defining chemical elements, property estimating, selecting a thermodynamic property, determining plant capacity, choosing proper operating units and setting up input conditions were performed by ASPEN PLUS 2004.1.

2. PROCESS SIMULATION

The simulation procedures involve defining chemical components, selecting a thermodynamic property, determining plant capacity, choosing proper operating units and setting up input conditions (±flow rate, temperature, pressure and other conditions). Many components such as methanol, sodium hydroxide, and glycerol are available from the library of ASPEN PLUS. The trioleic and trilinoleic acid are a major component of Jatropha oil (Chatakanonda et al., 2005) while methyl oleate and methyl linoleate are biodiesel. All of this structure cannot obtain from the ASPEN PLUS library. Therefore, the unavailable components such as mono, di, and methyl oleate of oleic acid and linoleic acid defined by GaussViewW. The proposed structures were optimized by GAUSSIAN 03W for the most stable structure. These structures were imported to ASPEN PLUS in the mol format to fulfill the simulation data. Due to the methanol and glycerol are highly polar components, the Non-Random Two-Liquid (NRTL) thermodynamic/activity models were recommended to predict the activity coefficients of the components in the liquid phase and unit operating condition shown in Table.1.

<table>
<thead>
<tr>
<th>Table.1 summary of unit operating condition for each process</th>
<th>Conventional</th>
<th>Transesterification</th>
<th>Integration transesterification with methanol recovery</th>
</tr>
</thead>
<tbody>
<tr>
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<td>CSTR</td>
<td></td>
</tr>
<tr>
<td>temperature (°C)</td>
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<td></td>
</tr>
<tr>
<td>pressure (atm)</td>
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<td>-</td>
<td></td>
</tr>
<tr>
<td>methanol to oil ratio (mol/mol)</td>
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<tr>
<td>methanol recovery column type</td>
<td>Radfac</td>
<td>Radfac</td>
<td></td>
</tr>
<tr>
<td>reaction zone at</td>
<td>-</td>
<td>tray three</td>
<td></td>
</tr>
<tr>
<td>reflux ratio</td>
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<td>1</td>
<td></td>
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<tr>
<td>Boil up ratio</td>
<td>0.6</td>
<td>0.6</td>
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<tr>
<td>number of stages</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>top/buttom pressure (atm)</td>
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<td>1</td>
<td></td>
</tr>
<tr>
<td>glycerol removal equipment</td>
<td>decanter</td>
<td>decanter</td>
<td></td>
</tr>
<tr>
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<td>25</td>
<td></td>
</tr>
<tr>
<td>alkali removal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>900</td>
<td></td>
</tr>
<tr>
<td>% conversion</td>
<td>98.2</td>
<td>99.8</td>
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</tr>
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</table>
3. RESULTS AND DISCUSSION

3.1 Conventional process

3.1.1 Transesterification

The conventional process started with the 1000 kg/hr of Jatropha oil feedstock. It was heated to 60 °C before sent to the reactor. At the same time, the sodium hydroxide, 1% wt of Jatropha oil was mixed with methanol of 1:5 mass ratio or 6:1 molar ratio alcohol to oil in static mixer M101 to produce 0.5% sodium methoxide which used as a catalyst. After that, sodium methoxide was sent to the reactor for transesterification processing. The kinetic model of Noureddini and Zhu (1997) is selected to describe the transesterification reaction of Jatropha oils, a simple conversion of biodiesel is assumed to be 95%. The excess of methanol is sent to the recovery section to recycle the methanol as shown in Figure 1. According to simulation results, 130 kg/h of fresh methanol and 38.4 kg/h of recycling methanol were mixed with the 12 kg/hr of sodium hydroxide in the static mixer M101. The 180 kg/hr of the mixture, called sodium methoxide, was preheated to 60 °C by the heat exchanger. The 1,000 kg/h of fresh Jatropha oil, which was assumed to trioleic, and trilinoleic, a major composition, were pumped and preheated by heat exchanger H101 to reach 60 °C before sent to the reactor. In the reactor R101, the temperature was controlled at 60 °C, 1 atm pressure and 1 hour operated. The final product is approximate 1,180 kg/h that contain biodiesel (methyl Oleic and methyl linoleic), glycerol, unreacted methanol, catalyst and some of the intermediate.

3.1.2 Methanol recovery

From transesterification section, the product and unreacted reactant are sent to distillation to remove and recycle unreacted methanol to reduce fresh feed of methanol. The range of column operating pressure is 0.2 - 0.3 atm to keep the bottom temperature below 150 °C because of declining of biodiesel. The distillation design parameter is the number of distillation stages, reflux ratio, and boiler ratio to separate methanol from another component. The value of parameters was shown in Table 1. The 1,180 kg/h of product from reactor R101 is sent to distillation. The top and bottom pressures of distillation are fixed at 1 atm., and the bottom temperature is lower than 150 °C. Therefore, the operation at the atmospheric pressure is better because higher capital cost comes with high operating pressure (Stitt, 2002). In the recycle stream, 38.4 kg/hr of methanol is recycled and mixed with fresh methanol, then charged back into the reactor. The 1,142 kg/hr of the bottom stream is sent to glycerin removing.

3.1.3 Glycerin removal

Since the mass fraction of glycerol in biodiesel should not be over 0.24 %, the removal glycerin unit is significant. After the methanol recovering section, the water washing column was used to separate the biodiesel from the glycerin. But it is an easy way to remove the glycerin from another component instead of using water washing column because glycerin does not dissolve in the biodiesel. There are two layers between biodiesel and glycerin. Therefore, the gravity unit is enough to be used for this separation. The bottom stream from distillation is sent to the decanter unit to separate the first and second liquid. Glycerin identified as a key component of second liquid was removed in the second liquid stream. In the second liquid stream, there are 80.4 % glycerin and only 7 % biodiesel. Therefore, glycerin can be sold as a low grade because of its quality.

3.1.4 Alkali removal

The amount of sodium hydroxide should not be higher than 0.8 %. Therefore, the alkali removal section is used to decrease the amount of sodium hydroxide in the biodiesel product. The first step, 900 kg/h of hot water (50 °C) is mixed with the first liquid stream coming from the glycerol removal in the static mixer. Next, the mixing component is sent to decant which was operated at 50 °C and 1 atm. The water set as a key component is removed in the second liquid stream. The efficiency of decanting is set 100 % because biodiesel and water are not dissolved together. The biodiesel leaving from glycerin removal is sent to the alkali removal. The 900 kg/h of water which is a minimum requirement is used to dissolve sodium hydroxide in the product. In the static mixer, the alkali catalyst is then dissolved into water. The mixtures are sent to decanter used for removing between biodiesel and water. The biodiesel 97.7 % at a rate of 982 kg/h is obtained. The quality of biodiesel meets the standard (EN 12142).

3.2 The Biodiesel production by reactive distillation

In conventional biodiesel productivity, it consists of a reactor following by distillation. Transesterification is a reversible reaction which the equilibrium limits conversion. The advantage reactive distillation was said, previously. The most detail of the process is similar to the conventional one. Figure 2 shows the biodiesel process using reactive distillation. There are 3 (three) - steps process which is reactive distillation, separation glycerin, and alkali removing.

3.2.1 Reactive distillation

The reactive distillation is an integrated reaction and separation in one unit. The transesterification and methanol recovery section was replaced by reactive distillation. This column has used both reaction and separation. The 120 kg/hr
of Methanol was mixed with sodium hydroxide to produce sodium methoxide which is a catalyst. After that, the catalyst was heated to 60 °C that is an optimal condition for producing biodiesel and was sent to the reactive distillation. Jatropha oil 1,000 kg/h was heated to 60 °C and was charged to reactive distillation. The methanol and oil were fed at the third tray (Upside to downside). The transesterification reaction and methanol recovery occurred in reactive distillation which the operating conditions are 1 reflux ratio, 0.6 boilers, 1 atm, and 5 stages. The reaction zones were set at tray three. Methanol which was a product in the distillate stream was recycled and combined with fresh methanol. Biodiesel and other component were removed in the bottom stream and sent it to the purification section.

3.2.2 Glycerin removal

The amount of glycerin can affect the quality of biodiesel. The gravity unit (decanter) was introduced to separate for this propose. The glycerin phase which is lower than biodiesel was set as a second liquid and removed by the second liquid stream. The conditions in the decanter were set 25 °C and 1 atm. Biodiesel and other component were removed by the first liquid stream and was sent to the alkali removing. The amount of glycerin in the biodiesel is 0.001% that was in standard (ASTM6751).

3.2.3 Alkali removal

After removing glycerol, there is a lot of base catalyst dissolving in biodiesel. Therefore, the catalyst was should removed by using hot water. After adding water, the catalyst was dissolved into the water phase. There are two layers which are biodiesel and water layer. The hot water 900 kg/h at 50 °C was used to dissolve catalyst. After the alkali removing section, the amount of catalyst in the biodiesel was less than 0.0005 % which meets the standard (ASTM6751).

3.3 Optimum parameters of reactive distillation

Due to the limitations and constraints in the experimental, some of the important design parameters such as column pressure, reflux ratio, number of rectifying, number of stripping and number of reaction zones could not be studied experimentally. Therefore, the effect of the parameter on the conversion of biodiesel needs to be evaluated by simulation. The simulations were based on the base case of reactive distillation.

![Figure 1](image-url) The conventional biodiesel production of this work

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>MEOH</th>
<th>NAOH</th>
<th>OIL</th>
<th>1A</th>
<th>2A</th>
<th>3A</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>RECYCLE MEOH</th>
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<td>100</td>
<td>100</td>
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<td>Mass Flow kg/hr</td>
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<td>1000</td>
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<td>-</td>
<td>405.2342</td>
</tr>
</tbody>
</table>
3.3.1 Height of reaction zone

In the homogeneous catalyst, it depends on the contacting between reactant in the column. For homogeneous catalyst which is sodium hydroxide was used to increase the biodiesel conversion. Therefore, the height of the reaction zone was depended on the contacting between oil and methanol. The arrangements of two feed reactants were analyzed to find the optimum reaction zone. The methanol is light reactant should be fed at the lower and oil should be fed at the top of the column. The column conditions were based on the base case. An only number of reaction zone was varied. The number of reaction zone increases from one to six. The effect of the reaction zone on the biodiesel conversion was illustrated in Figure 3. The conversion increases as the reaction zone increase because the residence time in one stage is not sufficient. The increasing reaction zone after 2 stages does not effect on the conversion. Therefore, the optimum reaction zone is 2 stages.

Figure 2 The biodiesel production by using reactive distillation
The effect of the number of rectifying zone on the biodiesel conversion was investigated. The parameters in the column were fixed as a base case. Only the number of rectifying is varied from one to four. The effect of the rectifying number was shown in Figure 4. In this case, methanol which is a light component compared with other was separated by the top of the column. The increasing rectifying zone can increase the amount of methanol in the distillate stream. The biodiesel decreased by this action because the methanol was removed from the column. The yield of biodiesel is no difference as increasing rectifying zone, while the amount of methanol increases. This methanol affects on the power requirement of the pump. The increase of methanol requires power consumption. Therefore, the best number of rectifying zone is 0.

The stripping zone can start from one to four. The effect of the number of stripping on the conversion was illustrated in Figure 5.
As seen in Figure 5, the amount of biodiesel and glycerol increases when the stripping zone increases from one to two. Because increasing the stripping zone, the products were removed higher. Therefore, if the reaction shifted to the right-hand side; the product is higher. After two strippings, the product is still the same because of the limit of the separation. The yield of biodiesel does not change as an increasing number of stripping zone. Therefore, optimum stripping should be zero.

3.3.4 Column pressure

Normally, the pressure of the column is operated at the economical ratio of heat-transfer costs and the improving separate (via increasing relative volatility with reducing pressure). However, in the reactive distillation, the selection operating pressure affects the reaction rate and the reaction equilibrium. The operation at maximum possible pressure is beneficial from the chemical equilibrium and rate of reaction consideration (Subawalla and Fair 1999, Bhatia et al. 2006). The parameters of the column were fixed as the base case. Only column pressure was varied. Figure 6 demonstrates the effect of column pressure on the biodiesel conversion and reboiler duty. The increasing operating pressure led to the reactive zone temperature and usually increased the reaction rate. According to Figure 6, the biodiesel conversion is increased by about 0.03 % when pressure increases from 1 to 4 atm while the reboiler duty increases about 33.35 %. From the results, the biodiesel slightly increases when pressure column is increased, but the cost of the column is considerable higher (Stitt, 2002). Therefore, operating at atmospheric pressure is satisfactory.
3.3.5 Reflux ratio

The reflux rate and reflux ratio are important parameters and affect both reaction and separation performance in a reactive distillation column. The conditions of reactive distillation were fixed as the base case. Only the reflux ratio was varied from 0.1 to 60. Figure 7 demonstrates the effect of reflux ratio on the biodiesel conversion. An increase in the reflux ratio caused the product to dropped. The biodiesel conversion increased by 0.011 % as the reflux ratio increased from 0.1 to 5. The biodiesel conversion did not change after 5 reflux ratio. Moreover, the reflux ratio not only affects conversion but also affects the quantity of methanol in the distillate stream. When the reflux ratio was increased, the methanol in the distillate stream was decreased. The amount of recycles methanol effect to the auxiliary equipment such as a pump. If the amount of recycling is high, more power should be required to carry the methanol. Figure 8 displays the effect of reflux ratio on the amount of methanol in the overhead. The methanol recycle reduced 90 % when increased reflux ratio from 0.1 to 5. The methanol doesn’t change after ten reflux ratio. An increase in reflux ratio will also increase the vapor rate within the tower, thus increasing expenses the cost of the condenser (Douglas, 1988). Figure 9 shows the effect of reflux ratio on the condenser duty. As the reflux ratio increased, the condenser increased too. After 5 reflux ratio, the condenser duty slightly increased. Consider the effects (the biodiesel conversion, the methanol recovery, and condenser duty); the suitable reflux ratio should be 10.

![Figure 7](image1.png)  
**Figure 7** The effect of reflux ratio on the biodiesel

![Figure 8](image2.png)  
**Figure 8** The effect of reflux ratio on the methanol recycle
4. CONCLUSION

In this work, the reactive distillation was studied to model and to simulate the biodiesel production from Jatropha oil. Molecular modeling is used to formulate the fundamental properties of specific components. The biodiesel processing was based on and compared to the conventional process of Zhang et al. (2003). The optimum conditions of reactive distillation are 2 stages of the reaction zone, no rectifying section, no stripping section, 5 reflux ratio, and 1 atm. The controllability of the process is studied under possible fluctuation. The proposed control structure can handle these disturbances and produce the product at the desired specification.

5. ACKNOWLEDGMENT

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6. REFERENCES

Chemical Engineering Science. 57: 1537 – 1543.


