



Use of Reactive Distillation for Biodiesel Production: A Literature Survey

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Abstract. Biodiesel has been shown to be the best substitute for fossil-based fuels to its environmental advantages and renewable resource availability. There is a great demand for the commercialization of biodiesel production, which in turn calls for a technically and economically reactor technology. The production of biodiesel in existing batch and continuous-flow processes requires excess alcohol, typically 100%, over the stoichiometric molar requirement in order to drive the chemical reaction to completion. In this study, a novel reactor system using a reactive distillation (RD) technique was discussed for biodiesel production. RD is a chemical unit operation in which chemical reactions and separations occur simultaneously in one unit. It is an effective alternative to the classical combination of reactor and separation units especially when involving reversible or consecutive chemical reactions such as transesterification process in biodiesel production. Copyright © 2006 Teknik Kimia UNSYIAH

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INTRODUCTION

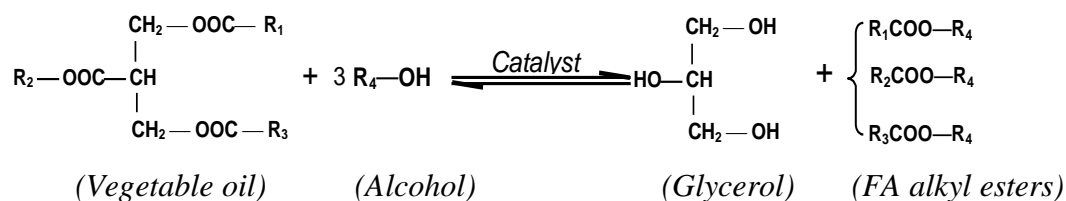
The idea of using vegetable oil as a substitute for diesel fuel was demonstrated by the inventor of the diesel engine, Rudolph Diesel, around the year 1900, when vegetable oil was proposed as fuel for engines. Vegetable oils have good heating power and provide exhaust gas with almost no sulfur and aromatic polycyclic compounds. Due to the fact that vegetable oils are produced from plants, their burning leads to a complete recyclable CO₂. The oil use as diesel fuel was limited due to its high viscosity (near 10 times of the gas oil). In order to adapt the fuel to the existing engines the vegetable oils had to be modified (Stavarache et al, 2005).

Various derivatives such as microemulsions or blends of various vegetable oils with conventional fuel have been proposed as alternative fuels for diesel engines. The esters of vegetable oils or animal fats appear to be the most promising

alternative. Today, methyl or ethyl esters of fatty acids are used as substitute to petroleum-based diesel fuels under the name of 'biodiesel'.

Bio-diesel fuels have many advantages over petroleum diesel fuel: produce less smoke and particles, have higher cetane number, produce lower carbon monoxide and hydrocarbon emissions, are renewable, biodegradable and non-toxic. When ethyl esters are used as fuel the advantage of totally recyclable CO₂ cycle is obtained since ethyl alcohol could be of vegetal origin. Transesterification is not a new process. The scientists Duffy and Patrick conducted it as early as 1853. Transesterification involves the reaction between an alcohol and a vegetable oil or animal fat that are mixtures of triglyceride (esters of glycerin with long chain fatty acids).

Biodiesel from vegetable oils has attracted increasing interests among the governments, industry sectors, and the



With the step-wise reactions of



Figure 1. Transesterification of seed oils to produce fatty acid esters. Where the TG, DG, MG, and GL stand for tri-, di-, mono-glycerides, and glycerol, respectively. R₁, R₂, and R₃ are the same or different alkyl groups of typically C₁₄-C₂₂ chains. R₄ is the methyl or ethyl groups depending on the alcohol used.

general public. It has been shown to be the best supplement to fossil-based fuels due to various advantages. Additionally, it is well suited for immediate uptake into the system utilizing existing diesel engines and fuel distribution infrastructure. Technically, biodiesel is a better fuel than fossil-based diesel in terms of engine performance, emissions reduction, lubricity, and environmental benefits (Van Gerpen, 2005). Research and development activities on biodiesel research, production and utilization have advanced to such a stage that its application as a diesel supplement is feasible and practical. Biodiesel consumption has dramatically increased in the past 5 years. As more and more commercial biodiesel production facilities come under consideration, the demand for technically and economically sound reactor technologies increases.

Biodiesel can be made from transesterification of vegetables oils or animal fats with methanol or ethanol in the presence of a catalyst. Studies of the mechanism and kinetics have shown that this process consists of a number of consecutive, reversible reactions (Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000). Triglycerides are first reduced to di-glycerides, and then to mono-glycerides. Lastly, the mono-glycerides are

reduced to fatty acid esters and glycerol, as shown in Figure 1. Each mole of triglycerides reacts stoichiometrically with 3 moles of a primary alcohol and yields 3 moles of alkyl esters (biodiesel) and 1 mole of glycerol. The order of the reaction changes with the reaction conditions. The completion of the reaction depends on multiple parameters including the alcohol-to-oil molar ratio, catalysts, temperature, reaction time, and the quality of the feedstock. As an effective means of conversion rate enhancement, excess alcohol is used to drive the equilibrium towards the product side.

The excess alcohol remaining in the fuel and glycerol after reaction must be recovered and purified through rectification and distillation for reuse. Such a batch process is labor and energy intensive and low in productivity. Continuous transesterification processes are preferred over batch processes in commercial production due to the consideration of product quality control, labor and operating costs. The basic advantages of the continuous-flow process include greater productivity, lower operating and labor costs, and a more consistent product quality. Most of the existing processes still utilize 100% or more excess alcohol which is then recovered from the product mixture after the

reaction. The operating parameters, such as reaction time of 60 ~ 120 minutes and operating temperatures of 20~70°C, were directly adopted from batch operation processes.

Application of the reactive distillation (RD) technique to biodiesel production could be led to a more effective and efficient reactor system. Application of reactive distillation in chemical engineering is not a new practice. Extensive research has been conducted on its applications in the chemical industry and is increasingly being used in various chemical systems (Tuchlenski et al., 2001; Malone and Doherty, 2000; Solokhin and Blagov, 1996). In some applications, particularly when reversible reaction equilibrium prevents high conversions, the RD technique can be employed to remove the reaction products from the reaction zone to improve overall conversion rate and selectivity. The significant advantages of RD over the conventional sequential process include the high chemical conversion rates and low capital and operating costs. Examples of RD application include esterification, ester hydrolysis, and ether synthesis (Omota et al., 2003; Po1pken et al., 2001).

The objective of this study was to discuss a feasible technique for commercial biodiesel production by utilizing the reactive distillation. The hypotheses were: (1) by employing the RD technique, biodiesel preparation and product concentration could be accomplished in one unit; (2) the use of excess alcohol would be greatly reduced, but the high alcohol to oil ratio could still be achieved locally in the reaction zone by recycling a small quantity of alcohol; (3) the recovery of alcohol in down-stream operations would be greatly reduced, and (4) the elevated operating temperature would shorten the reaction time considerably and increase the productivity per unit reactor volume. Combination of the above-mentioned advantages would eventually reduce the capital and operating costs, thus

providing an economical biodiesel production technology.

WHAT IS REACTIVE DISTILLATION?

Reactive distillation (RD) has received increasing attention over the past several years as a promising alternative to conventional processes. Although invented in 1921, the industrial application of RD did not take place before the 1980s. Distillation column can be used advantageously as reactor for systems in which chemical reactions occur at temperatures and pressures suitable to the distillation of components. Especially for equilibrium-limited and consecutive reactions, RD offers distinct advantages through the direct removal of the reaction products by distillation. By continuous separation of products from reactants while the reaction is in progress, the reaction can proceed to a much higher level of conversion than without separation. Therefore, conversions far beyond equilibrium conversions and higher selectivities can be obtained, leading to significantly lower investment and operating costs (Sundmacher and Kienle, 2003).

There are three main cases in the chemical industry, in which combined distillation and chemical reaction occur:

- a) use of a distillation column as a chemical reaction in order to increase conversion of reactants
- b) improvement of separation in a distillation column by using a chemical reaction in order to change unfavorable relations between component volatilities
- c) course of parasitic reactions during distillation, decreasing yield of process

Especially interesting equilibrium reactions suitable for RD are esterifications, ester hydrolysis reactions, etherifications, and transesterifications. In recent years,

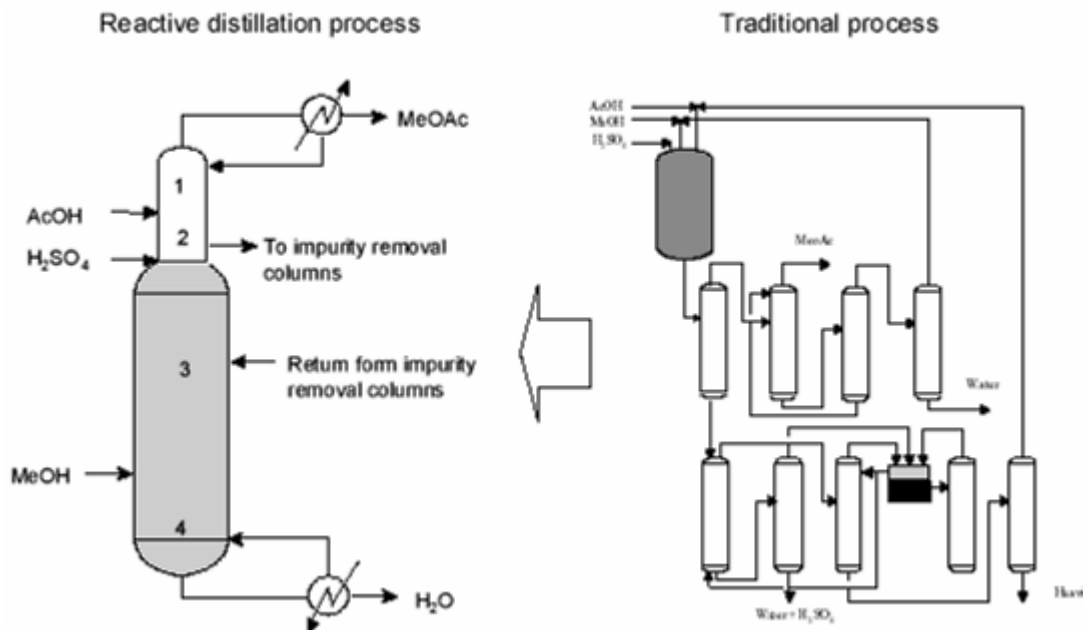


Figure 2. RD and traditional process for methyl acetate (Sundmacher and Kienle, 2003)

attention has been paid to ethyl *tert*-butyl ether and methyl *tert*-butyl ether synthesis and also alkyl ester synthesis and hydrolysis such as ethyl acetate and methyl acetate, which serves as a model system for RD processes. Eastman Kodak developed an RD process for the manufacture of high-purity methyl acetate (Agreda et al., 1990) and the flowsheet comparison between the traditional process and the RD process are shown in Figure 2.

Reactive distillation (RD) is a chemical unit operation in which chemical reactions and product separations occur simultaneously in one unit. It is an effective alternative tool to the classical combination of reactor and separation units, especially when reversible or consecutive chemical reactions are involved. Both packed and tray columns can be used for the RD applications, however, tray columns are recommended for homogenous systems because of the greater liquid holdup and the associated longer retention time. The operation of an RD process can be very complicated and the performance of a RD column is influenced by several parameters,

such as size of reactive and separation zones, reflux ratio, feed rate and location, etc.

BIODIESEL PRODUCTION BY REACTIVE DISTILLATION

The most commonly used method for biodiesel production is via transesterification of vegetable oil using various catalysts, such as acidic, alkaline and enzyme. The extent of transesterification and side reactions depends upon the types of feedstock, catalyst formulation, catalyst concentration, reaction temperature and alcohol-to-oil ratio. Free fatty acid and moisture content in the reactant mixture also play important roles in biodiesel production (Ma and Hanna, 1999). The actual mechanism of the transesterification reaction consists of sets of equilibrium reactions in series and all of the reactions are reversible (Darnoko and Cheryan, 2000). Due to the characteristic of transesterification reaction of biodiesel production, the application of RD technique could be led to a more effective and efficient reactor system (He et al, 2005).

Presently, studies on biodiesel production by RD have been conducting by several researches: Millers and co-workers

fitted to a 500 mL three-neck round-bottom flask as the reboiler. A water-cooled condenser was fitted to the top of the

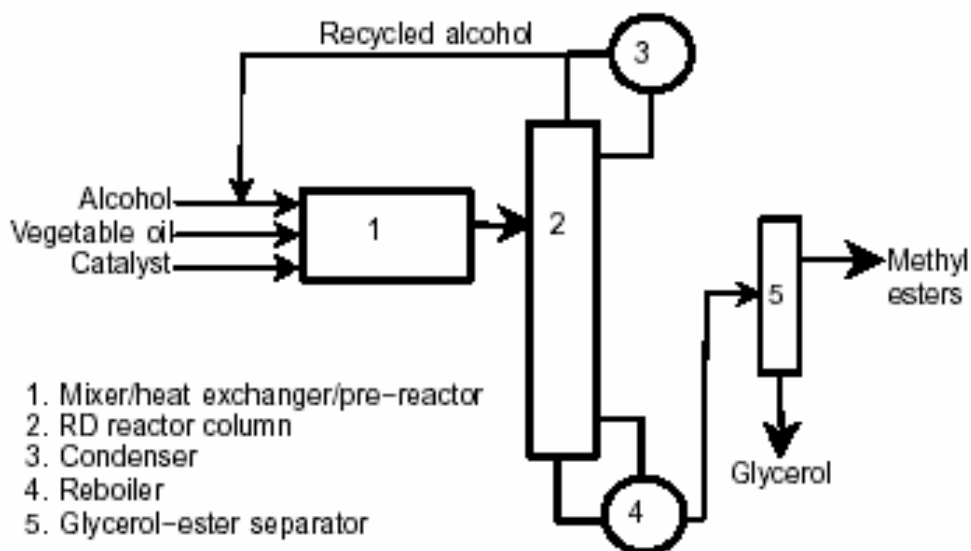


Figure 3. Schematic of RD system for biodiesel production (He et al, 2006)

(Michigan State University, US), Brian He and co-workers (University of Idaho, US), Kiss and co-workers (University of Amsterdam), etc. Their preliminary result shows that RD can be applied for biodiesel production. Many studies still must be conducted to further know the performance of RD for biodiesel production.

Figure 3 shows a schematic laboratory-scale continuous-flow RD system for biodiesel production from He et al. (2006). The central component was a glass distilling column with perforated Oldershaw plates. This 10-plate column had an inner diameter of 28 mm, a weir height of 1.7 mm, and a distance of 25 mm between plates. The nominal liquid hold-up on each plate was 1 mL, totaling 10 mL for the column. The column had a vacuum jacket around it as a means of thermal insulation to prevent heat loss from the column during operations. A short 150 mm (5 mL capacity) in-line static mixer was used as a feed mixer, heat exchanger, and pre-reactor prior to the RD column. The lower end of the column was

column to recover alcohol. The feed entered the column near the top. The condensed methanol was combined with the feed methanol and refluxed back to the column. The product mixture was withdrawn from the reboiler to a glycerol-ester separator, where the glycerol and esters were separated by gravity in a continuous mode. The separator was 70 mm in diameter \times 300 mm long with an adjustable entry point. The input and output streams of methanol/KOH solution, canola oil, and product mixture were handled simultaneously with peristaltic pumps, which were calibrated and adjusted to achieve the desired flow rates. Temperatures of the pre-reactor, condenser, column, and reboiler were measured and monitored. The heating rate of the reboiler was controlled as a constant in order to maintain a constant methanol recycling rate. The heating load and feedback control were accomplished with a feedback controller.

Generally speaking, the operation of an RD reactor is complicated because its performance is affected by several

parameters, including the reaction kinetics, size of the reaction and separation zones, reflux ratio, feed rate, and feeding tray location, etc. (Solokhin and Blagov, 1996; Tuchlenski et al., 2001). The optimum operating conditions are determined as the result of systematic investigations of all operating parameters. However, the complexity of the RD reactor system is minimized when applied to the biodiesel production for four reasons. First, the difference between the boiling temperatures of methanol and fatty acid esters is so large that the separation of the excess alcohol from the product mixture becomes easy (Table 2). The rectification zone of the RD column can be easily determined, which requires one or two theoretical separating stages. Second, as a result of the low rectification requirement, the feeding position is then determined to be at the upper section of the RD column, one or two theoretical separating stages below the top plate. Third, the transesterification reaction occurs in the liquid phase only. The plates below the feeding point determine the reaction zone. The reaction time is then established by the total liquid hold-up and the feeding rate of the reactants. Finally, the operating temperature is easily determined by the boiling temperature of the alcohol used when the operating pressure of the column has been determined.

CONCLUSION

RD has been found feasible for biodiesel production. RD reactor bears three major advantages over traditional processes: (1) shorter reaction time and higher unit productivity, which is highly desirable in commercial production units; (2) much lower excess alcohol requirement, which greatly reduces the effort of downstream alcohol recovery and operating costs; and (3) lower capital costs due to its smaller size and the reduced need for alcohol recovery equipment. Further

investigations are necessary on the process efficiency, energy utilization, and economic analysis in order to fully establish its impact on large-scale commercial biodiesel production. Economic analysis of the RD reactor system will be performed in a scaled-up facility.

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