Reducing Costs and CO2 Emissions on the Production of Biodiesel by the Supercritical Methanol Method

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Over the past decade, significant research efforts have focused on finding alternative non-fossil energy sources as an attempt to reduce the effects of global warming and the dependence on petroleum fuels. Biodiesel has emerged as an interesting alternative. Biodiesel is generally produced by a catalytic reaction, which may lead to high energy consumptions to separate the catalyst and to undesirable side reactions. A recently proposed process involves the use of short-chain alcohols (methanol) at supercritical conditions, avoiding the use of a catalyst and the occurrence of side reactions. Such a process, known as the Saka-Dadan process, allows the use of low-quality oils as reactants and requires fewer pieces of equipment than conventional catalytic processes; however, its high energy requirements and the reaction conditions make the main product, biodiesel fuel, still more expensive than petroleum diesel. This paper proposes an intensification-based alternative to the Saka-Dadan process for biodiesel production. As an attempt to reduce equipment costs, a reactive distillation system is proposed to achieve the tasks of esterification reaction and the biodiesel purification in a single shell. Then, to reduce energy consumptions, two thermally coupled reactive distillation systems are analyzed. In particular, a reactive Petlyuk system and a reactive thermally coupled direct sequence have been studied. Simulations have been carried out by using the AspenOne[TM] process simulator to demonstrate the feasibility of such alternatives to produce biodiesel with methanol at high pressure and temperature. Results indicate that thermally coupled reactive systems present favorable energy performance and higher thermodynamic efficiency when compared to the conventional scheme, allowing high conversions of the fatty acid. CO_2 emissions and costs calculations were also computed, finding an important reduction on both parameters by using the thermally coupled reactive systems when compared to both the conventional process and the reactive distillation process (without thermal coupling).

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1. Introduction

Biofuels are fuels obtained from natural sources; they have been developed as an attempt to reduce the impact of human activity on the greenhouse gases concentration in the atmosphere. Biofuels are renewable and clean fuels; bioethanol and biodiesel are among the most important biofuels. In particular, biodiesel has been largely studied because of its direct application to existing engines. Biodiesel is a mixture of methyl or ethyl esters derived from fatty acids used as fuel in diesel engines and heating systems. It has many advantages over petroleum diesel; for instance, it is non-toxic, biodegradable and free from sulfur and carcinogenic compounds. Its main disadvantages, however, are its high viscosity, low energy content and high nitrogen oxide emissions.

Conventional biodiesel production processes involve the use of a catalyst, such as sodium hydroxide or sulfuric acid; this generally implies high energy consumptions for the separation of the catalyst and, in the case of basic catalysis, the formation of undesirable products due to the saponification reaction. Biodiesel can also be produced by using alcohols at supercritical conditions, avoiding the use of catalyst and significantly reducing the number of separation units. A two-step production process has been already proposed by Minami and Saka (2006). This process is known as the Saka-Dadan method. The tryglicerides are first treated with water (hydrolysis) to get fatty acids and glycerol, which is immediately removed. As the hydrolysis reaction advances, tryglicerides are converted to di and mono-glycerides, then producing the fatty acids. Later, the fatty acids react with methanol at 270°C and 7 MPa to get methyl esters (biodiesel) and water (esterification). It has been shown (Kusdiana and Saka, 2004) that the presence of water on the raw material does not affect the yield of methyl esters. Hence, the process can deal with animal fats and waste oils, which contain high amounts of free fatty acids and water. Nevertheless, because of the temperature and pressure conditions, the process remains as an energy-demanding process which (besides the cost of the raw material) impacts directly on the final cost of biodiesel.

This paper suggests applying process intensification to biodiesel production. The most common intensification alternative is to carry out the reaction and the separation tasks simultaneously in one shell using reactive distillation column. The main advantage of reactive distillation is that it requires a single piece of equipment, instead of a reactor and a separation column. As an improvement to reactive distillation, our approach also proposes the use of thermally coupled reactive distillation for biodiesel production. Such system has the potential of reducing energy consumptions on the process where chemical reaction occurs. That configuration has been previously studied by Barroso-Muñoz et al. (2007) which combined reactive distillation and thermally coupling in a reactive Petlyuk column.

This work intends to demonstrate the feasibility of using thermally coupled reactive distillation to produce biodiesel with methanol at high pressure and temperature. We assume first order kinetics to represent the esterification reaction. The accuracy of our kinetic model is compared to experimental data provided by Minami and Saka (2006). Simulations were performed on the Aspen One^{TM} process simulator. CO_2 emissions have also been computed for the esterification step. Finally, thermodynamic efficiencies of the reactive distillation systems and their costs were also obtained.

2. Methodology

To be able to analyze the biodiesel production process, the first step involves obtaining a kinetic model and defining a thermodynamic model. A first-order kinetic model was tested to represent the esterification reaction; the rate equation is given by Equation (1).

$$\frac{dC_{MEOL}}{dt} = kC_{OLAC} \tag{1}$$

Using the values of the rate constant proposed by Saka (2007), the activation energy was calculated. This kinetic model was tested by simulation of a batch reactor. The reaction under study is represented by Equation (2).

$$AAC + MEOH \leftrightarrow MEAC + H_2O \tag{2}$$

where AAC stands for acetic acid, MEOH is methanol, MEAC represents methyl acetate and H_2O is water. The reaction was assumed to occur at 7 MPa and 270°C, using a volumetric ratio of 0.9/1 (methanol/oleic acid).

The thermodynamic model selected was the NRTL equation to model the liquid phase and the Redlich-Kwong equation for the gas phase. Accuracy of the results was proved by comparing the equilibrium data calculated with the data provided by Minami and Saka (2006).

Next step consisted of performing simulations of the conventional biodiesel production process using the Aspen One™ process simulator. The oil was simulated as triolein, a triglyceride contained in high concentrations on many vegetable oils, such as rapeseed oil, sesame seed oil, peanut oil and palm oil. The hydrolysis reactor was simulated as an equilibrium reactor with the RGibbs module. A decanter was used to separate the two phases formed with the reaction. Then, the product stream containing the fatty acid as well as the methanol stream (at 7 MPa and 270°C) go to an esterification reactor. This esterification reactor was simulated as a plug flow reactor using the kinetic model previously discussed. The stream leaving the reactor is introduced in a distillation column to eliminate the water. The bottoms stream is sent to a second esterification reactor, where the remaining acetic acid is converted into methyl acetate. The stream leaving this second reactor passes through an expansion valve, and then it is sent to a low-pressure flash drum; the methanol is vaporized and the biodiesel fuel is obtained in the liquid stream. TA diagram of the simulation is shown on Figure 1.

Once the conventional process was simulated, a reactive distillation column (RD) is incorporated into the process. Its goal is eliminating the esterification reactors and performing the reaction and the separation in the same shell. The reactive distillation column was designed as having 15 stages; it separates all the water as the top product, part of the methanol as a side-stream product and a mixture of methanol and methyl oleate at the bottom. Temperature in the reactive distillation column must remain lower than 300°C to avoid methyl oleate isomerization.

As a final step, a process using a reactive Petlyuk column (TCRD) was proposed. The design of the thermally coupled process was developed based on the structure of the

reactive distillation column. The process including the reactive Petlyuk column is presented in Figure 2. Once the three processes (conventional, RD and TCRD) were successfully simulated, thermodynamic efficiencies were computed as described by Henley and Seader (2006); CO_2 emissions were also calculated as proposed by Gadalla et al. (2005); and the total costs for the systems were estimated following the Guthrie method as presented by Turton et al. (2004).

3. Results

Activation energy was computed as 75372.23 J/mol K. The value of the reaction rate constant was then calculated as 2.90×10^{-3} s^{-1} at 270°C. To simulate the process, a 46 kmol/h stream was assumed to feed the hydrolysis reactor, reacting with an excess of 2476 kmol/h of water to shift the reaction equilibrium to the products, obtaining 138 kmol/h of oleic acid and 46 kmol/h of glycerol. In the decanter, a water-rich stream is obtained, containing 2209 kmol/h of water and 99 kmol/h of glycerol. The oil phase is sent to the first esterification reactor. To simulate the reactive distillation column (RD) and the reactive Petlyuk column (TCRD), a retention time of 0.3 h was taken, since this value was found to be enough to obtain conversion higher than 95%.
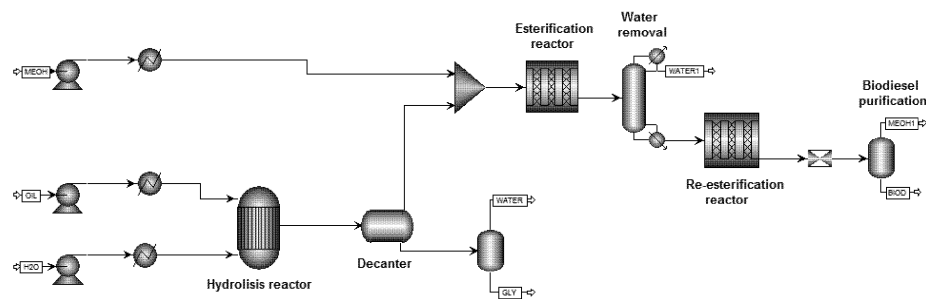

Figure 1. Diagram of the simulation of biodiesel production by the Saka-Dadan method.
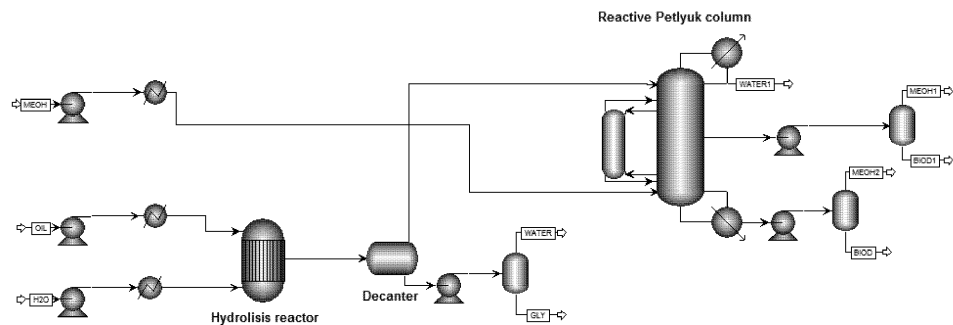

Figure 2. Diagram of the simulation of biodiesel production by the Saka-Dadan method using a reactive Petlyuk column.

Table 1 shows a comparison of the total energy requirements for the esterification step of the three alternative configurations. Values of CO_2 emissions are presented on Table 2. For the esterification step, in the case of the conventional process, the CO_2 emissions correspond to the production of steam to satisfy the energy requirements of the two esterification reactors and the distillation column. In the case of the RD and TCRD processes, the CO_2 emissions correspond to the production of steam for the RD column and the flash unit linked to the bottoms of the column. Steam is produced at temperatures of 480 and 580 K. Table 3 shows the results of the thermodynamic efficiency calculations. It can be observed that, when using a thermally coupled system to perform the separation, the lost work is reduced, then increasing the thermodynamic efficiency of the system. Table 4 provides the costs of utilities used, whereas Table 5 presents the results for the costs calculations for both the whole process and the esterification reaction.

Table 1. Thermal energy consumption for the esterification step.

Process	Q_T (kJ/h)	Energy savings
Conventional	30709555.1	0%
RD	25124307.4	18.19%
TCRD	21551773.5	29.82%

Table 2. Carbon dioxide emissions.

Process	Whole process			Esterification		
	Q_{Fuel} (kJ/h)	CO_2 (kg/s)		Q_{Fuel} (kJ/h)	CO_2 (kg/s)	
		Fuel Oil	Natural gas		Fuel oil	Natural gas
Conventional	318796886.0	25446.6	17096.3	73949326.2	5902.7	3965.7
RD	309653405.4	24716.7	16605.9	64805845.2	5172.8	3475.4
TCRD	303335678.3	24212.5	16267.1	58488118.1	4668.56	3136.6

Table 3. Thermodynamic efficiencies.

Process	η (%)
RD	40.13
TCRD	45.95

Table 4. Utilities costs and cost indexes.

Steam cost @ 580 K (U$/lb)	Steam cost @ 480 K (U$/lb)	Water cost (U$/lb)	Electricity cost (U$/kWh)	Cost index (1996)	Cost index (2009)
0.0056	0.0046	0.0005	0.057	382	539.7

Table 5.Costs calculations.

Process	Whole Process			Esterification		
	Utilities costs (U$/year)	Equipment costs (U$/year)	Total costs (U$/year)	Utilities costs (U$/year)	Equipment costs (U$/year)	Total costs (U$/year)
Conventional	33165744	3163726	36329470	23077579	2135350	25212929
RD	30336016	1803605	32139621	13911349	720606	14631955
TCRD	29246936	1668856	30915792	12822269	585857	13408126

4. Conclusions

Intensification alternatives for the production of biodiesel fuel by the Saka-Dadan method have been proposed. A first-order kinetic model has been proven to accurately represent the experimental data. The proposed process involves the use of reactive distillation and thermally coupled reactive distillation to carry out the esterification reaction and the purification of the product in the same shell. These alternatives have presented lower energy consumptions when compared to those corresponding to the conventional process. The purity of the biodiesel fuel in the reactive distillation systems was fixed at 90% (mass) to avoid isomerization of methyl ester, which occurs when the temperature is higher than 300°C. In terms of CO_2 emissions and total annual cost, the TCRD system shows the lowest values of the three analyzed systems. The thermodynamic efficiency (η) calculations show that the reactive Petlyuk column has higher values of η, then achieving a better use of thermal energy. In summary, the use of a thermally coupled reactive system has shown to be an interesting alternative to reduce production costs of biodiesel at high pressure and temperature.

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