Simulation and optimization of Camelina oil fatty acids reaction to produce fatty acid methyl esters in a reactive distillation reactor

Ibtisam M. Kamal, Firas H. Albadran, Fanar M. Bamerni, Danar H. Aziz, and Mustafa Alfaize

a Chemical Engineering Department, Faculty of Engineering, Soran University, Kurdistan Region Iraq.
b Chemical and Petroleum Refining Engineering, College of Oil and Gas Engineering, Basrah University for Oil and Gas, Iraq.
c Chemistry Department, Faculty of Science, Zakho University, Kurdistan Region Iraq.
d College of Petroleum Engineering, University of Alayen, Thi-Qar, Iraq.

*corresponding: ibtisam.kamal@soran.edu.iq

Abstract

Reactive distillation (RD) is a chemical unit operation in which chemical reaction and product separation occurs simultaneously in one unit resulted in reduce the number of downstream steps, energy savings, and greenhouse gases. In the current work, process flow sheets for industrial routes for conversion of camelina oil fatty acids to fatty acid methyl esters (biodiesel) in presence of acid catalyst is modelled in Aspen HYSYS for the purpose to scale up the esters production. The effect of the operating and design parameters is optimized in addition to design the production plant. The simulation results showed that optimum ester yield is obtained for linoleic acid and palmatic components using 6:1 alcohol to oil ratio, reaction temperature 60°C and feeding the oil and the alcohol at stage number 3 and 5 respectively.

Keywords: Camelina oil, fatty acids, esterification, simulation, optimization

1. Introduction

Biofuels are fuels produced from biomass Sindhu et al., 2019 [1]. The two principal biofuels are ethanol and biodiesel. Biodiesel is a clean burning fuel that has become increasingly attractive due
to its environmental benefits and to the fact that it is made from renewable resources. Vegetable oil or animal fat are extracted from the seeds or fats using the conventional extraction processes are reacted in the presence of a catalyst with an alcohol (usually methanol) to produce biodiesel Keera et al., 2018 [2]. Alternatively, biodiesel can be produced via in situ transesterification by which the oil-bearing seeds are reacted directly with the alcohol and catalyst Chemical or biological catalysts are employed to activate the transesterification process. The selection of the catalyst depends on the properties of the raw materials, especially the free fatty acid content Kasim et al., 2010 [3]. Huge efforts have been dedicated to develop and design of new chemical processes which are more selective and energy efficient, among is the reactive distillation process. The potential advantages offered by RD are reducing capital cost, higher conversion, improving selectivity, lower energy consumption, reduction or elimination of solvents in the process and voidance of azeotropes Gaurav et al., 2016 [4]. On another hand, for scale-up, simulations are often preferred over experimental trial-and-error approach to reduce the involved time and material cost of prototyping Giwa et al., 2018 [5]. The success of reactive distillation and its application for large scale industrial processes including biofuels production has been widely signified Da Silva et al 2010 [6]. Also, Aspen HYSYS was used to simulate biodiesel production Firas Albadran et al 2019 [7], Neelharika et al 2017 [8], Wu and Leung, 2011[9]. The aim of the current work is concentrated on the analysis of a RD process for methyl esters production from camelina oil and to identify the relationship between the operating and design variables and % conversion.

2. Simulation study

In this research work, Aspen HYSYS Ver.9 was employed to develop a model for carrying out the esterification process of camelina oil using RD column. The composition of the major fatty acids of camelina oil were based on the findings of previous study Bamerni, 2018 [10]. The column consisted of 15 stage, camelina oil is charged into the column at the third stage, whereas the stage for charging a mixture of (%97 methanol and %3 H₂SO₄) is the fifth stage. All the reaction components are charged at 60°C. The section covered by the 3rd and the 5th stage is considered as the reaction section, while the section at the top of the reaction section is the rectification section and the one down is the stripping section. Both the condenser pressure and reboiler pressure are set to the atmospheric pressure 101.3 kPa. Sparse Continuation Solver was used as the algorithm for the simulation of the RD column.

Two feed streams are Camelina oil (the upper stream) which composed of the four fatty acids with mole fraction as the following (oleic acid: 0.4091, stearic acid: 0.1312, linoleic acid: 0.2137, and palmitic acid: 0.2460). The oil is fed to the RD column at a temperature of 60 °C and a pressure of
101.3 kPa, at stage No.3 with a proposed mass flow 25 kg/h. The lower stream is a mixture of (methanol, recycled methanol from the top product of the RD and catalyst which is H₂SO₄). The mixture is fed firstly into a mixer at a temperature and a pressure of 60 °C and 101.3 kPa respectively, then to the RD column at stage No. 5 with a proposed mass flow 150 kg/h. The RD unit consists of the column itself, a reboiler, and a condenser. In order to simulate the operation of the distillation column, two design variables have set; they are the distillate rate and the reflux ratio. Initial values of 135 kg/h for the distillate rate and 2.00 for the reflux ratio were chosen. The temperature is decreased to 60 °C by the air cooler. Figure 1 shows the HYSYS model simulated for fatty acids methyl esters production using the RD reactor.

Results and Discussion

3.1 Effect of Molar Ratio of Alcohol to Free Fatty Acid (FFA)

Various molar ratios of methanol/fatty acid (3:1, 4:1, 5:1 and 6:1) were investigated. Practically because the reaction is reversible, excess methanol is required to drive the reaction to completion at faster rate Ghayyib, 2012 [11], Musa, 2016 [12]. It is obvious to observe that as the molar ratio of methanol/fatty acid increases % conversion increase as shown in (Figure 2). The highest %conversion is obtained for linoleic and palmatic acid using methanol to alcohol ratio 6:1, reaction temperature 60°C and feeding the oil and the alcohol at stage number 3 and 5 respectively. This increase is explained by the shift in the equilibrium which is caused by the excess methanol Bilgina, 2015 [13].
3.2 Effect of a Number of Stages on percentage conversion

The results indicated that adding more stages improves the system performance. It can be observed from (Figure 3) that % conversion for oleic acid reached 58.6% when the number of stages are 15. When the number of stages increase to 20 and 25, the percentage conversion of oleic acid become 67% and 67.8%, respectively. Increasing the stages causes the separation of product from the unreacted reactant more efficiently, thereby enhancing the biodiesel purity Hidayat and Sutrisno, 2018 [14], Sakhre, 2019 [15]. However, it is noted that the performance of the RD reactor is slightly improved when number of stages are higher than 15 Boon-anuwat et al 2015 [16]. Our results in Figure 3 show similar findings.

3.3 Effect of reaction temperature

The effect of temperature on esterification of fatty acids of camelina oil was studied at temperature ranged from 25 °C to 70 °C by maintaining other reaction parameters constant (alcohol to oil ratio = 6:1, H₂SO₄ 3% v/v, no. of the RD column stages =15 stage). It is well noted that the lower % conversion is obtained at 25 °C, by increasing the temperature up to 70 °C better % conversion is achieved as listed in table 3. However 60 °C is chosen as the optimum reaction temperature because at higher temperatures more energy consumption is required. The high temperature cause increase in activity of molecules which mean more molecules have more energy, therefore the probability of molecules to react increased Sugiharto and Kusmiyati, 2010 [17], Istiningrum et al., 2017 [18].

3.4 Effect of the length of the alcohol’s carbon chain

The esterification of fatty acids is usually carried out by short chain anhydrous alcohols having low boiling points. Three different alcohols have been examined using similar conditions. It seems that the yield of esterification reactions is strongly dependent on the physical properties of the alcohol
used as shown in Table 3. The higher reactivity associated with alcohols having lower carbon chains are behind the increase of % conversion to the corresponding esters.

**Table 3.** Effect of temperature and length of the alcohol’s carbon chain on % conversion

| Component       | Temperature °C | % Conversion | Short chain alcohols |
|-----------------|----------------|--------------|----------------------|
|                 | 25  | 45  | 60  | 65  | 70  | Methanol | Ethanol | Isopropanol |
| Palmatic acid   | 99.6 | 99.8 | 100 | 100 | 100 | 100      | 0.42    | 0           |
| Stearic acid    | 98   | 58.6 | 0  | 0   | 99.5 | 99.5    | 0       | 0           |
| Oleic acid      | 21.5 | 100 | 15.7 | 0.34 | 61  | 58.6    | 0       | 0           |
| Linoleic acid   | 100  | 100 | 100 | 100 | 100 | 100      | 15.73   | 0.34        |

Methanol (b.p. = 64.7 °C), Ethanol ((b.p. = 78.5 °C), Isopropanol ((b.p. = 82.5 °C).

3.5 Effect of Feed Location of Methanol

In general, a lighter reactant should be fed on the bottom stage of the reactive zone, whereas a heavier reactant is fed on the top stage of the reactive zone. When changing the feed stage of methanol, the number of reactive zone would be changed. Due to large differences in the boiling temperatures between methanol and other components of the reaction mixture therefore small rectifying stage is required in order to obtain pure methanol as distillate Hidayat, and Sutrisno, 2018 [14]. From the simulation results, moving the feed stage of methanol down to the bottom of the reactive distillation column decreases the conversion of fatty acids as shown in Figure 4.

4.6 Effect of fatty acid structure on ester percentage recovery

Camelina oil composed mainly of saturated fatty acids including Palmatic and Stearic and unsaturated fatty acids including Oleic and Linoleic acids. The chemical structure of those fatty acids is illustrated in Figure 5. It is well established that viscosity increases with chain length of the fatty acids (stearic > palimitic). This holds also for the alcohol moiety. The degree of molecules crowding increases with increasing the chain length and consequently the viscosity. The effect becomes more evident at lower temperatures, where the molecular movements are even more restricted Rodrigues et al. 2006 [19]. The increase in viscosity resulted in decreasing the alcohol and the fatty acids reactivity leading to decreasing % conversion to the corresponding esters. On another hand, factors such as double-bond configuration influence the fatty acids viscosity. Rodrigues et al., 2006 reported that one double bond was shown to increase viscosity, whereas two or three double bonds caused a decrease in the viscosity. Refaat, 2009 [20] demonstrated that the double bonds in Oleic acid allowing a close packing between the molecules. These effects should
account for the differences in viscosity of oleic and linoleic that give rise to higher percentage conversion of linoleic acid compared to oleic acid.

4. Conclusions

The use of reactive distillation along with H₂SO₄ catalyst for biodiesel production from esterification of Camelina oil with methanol was found beneficial over the conventional process of sequential esterification and separation. The optimum condition for producing biodiesel by reactive distillation using H₂SO₄ catalyst was found as follows: 6:1 of methanol to fatty acids molar feed ratio, reflux ratio of 2, and 3 reactive stages. The simulation results showed that optimum biodiesel yield is obtained for linoleic acid and palmitic acid components using methanol, reaction temperature 60°C and feeding the oil and the alcohol at stage number 3 and 5 respectively. This condition provided a conversion of (oleic acid 58.6%, stearic acid 99.5%, linoleic acid100%, and Palmitic acid 100%).

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