Esterification of Fatty Acids for Biodiesel in Thermally coupled Distillation- Steady State Simulation Study

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Abstract - *Biodiesel can be produced from a number of natural and renewable sources and the current manufacturing processes however, have several disadvantages: expensive separation of products from the reaction mixture and high costs due to relatively complex processes involving one or two reactors and several separation units. This study proposes an efficient process intensification method for its ternary separation namely the use of a reactive divided wall column that is able to separate all products at high purity, in only one unit. This research aimed to study the kinetic esterification of waste vegetable oil into biodiesel and find optimum conditions for this process. Aspen plus is used as computer aided process engineering tools to perform rigorous steady state simulation. Results shows that the proposed RDWC system requires less energy and lower investment cost thus having sufficient contribution towards inexpensive biodiesel production. In particular, the fully thermally coupled distillation sequence can handle the reaction and complete separation in accordance with process intensification principles.*

*Key Words***:** Biodiesel, RDWC, Aspen Plus, esterification process intensification.

1. INTRODUCTION

Biodiesel is a suitable substitute for petroleum-derived diesel. It is biodegradable, almost sulphur less and a renewable fuel, though still not produced by environmentally friendly routed. This alternative fuel consists of methyl or ethyl esters, a result of either transesterification of triglycerides (TG) or esterification of free fatty acids (FFAs)[1]. Biodiesel has become more attractive because the feedstock used is renewable biomass sources such as vegetable oil or animal fats. In case of biodiesel production reactive distillation and adsorption have been considered [2,3].

Reactive Distillation integrates reaction and separation in single unit consequently intensifying mass transfer and allowing in situ energy integration. This simplifies the process flowsheet operation. However combination of two operations is possible only if reaction corresponds to reasonable conversion and selectivity data at pressure and temperatures that are compatible with the distillation conditions. The reduction in the number of processing units and direct heat integration between reaction and separation can reduce capital investment as well as utility costs. Increased overall conversion can be achieved in reactive distillation by continuous removal of products from reactive zone of equilibrium limited reactions.

Process Intensification policies are accounted in designing of new chemical processes in chemical engineering [4]. Distillation is most used separation technique and requires large amounts of energy in order to achieve a given separation. A thermally coupled distillation sequence has been studied in both academia and industry that can present energy savings in contrast to conventional distillation for the separation of some mixtures [5-7]. Among thermally coupled distillation sequences the most important is the fully thermally coupled distillation sequence named as Petlyuk distillation column. Petlyuk column has been implemented by using single shell divided by wall [8, 9]. This configuration is also known as divided wall distillation column (DWDC) that can achieve reduction in energy and capital costs. Also, distillation column thermally coupled with side rectifier or side strippers have been used in petroleum industry to obtain several products with reduction in energy demands in the reboiler.

However to reduce the cost of biodiesel, in general, oil feeds containing high FFAs such as waste fats, or non edible type oils are much cheaper than vegetable oils such as soybean or rapeseed oils. The production of biodiesel from waste cooking oil is an approach to lower biodiesel production costs. WCO contains FFA in much extent and since FFA forms soap with alkali catalyst during transesterification, they must be removed prior to transesterification. Therefore, the FFA in WCO is often undergoes esterification using heterogeneous acid catalysts.

$$R_1{-}COOH + R_2{-}OH \overset{Catalyst}{\leftrightarrow} R1{-}COO{-}R_2 + H_2O \qquad (1)$$
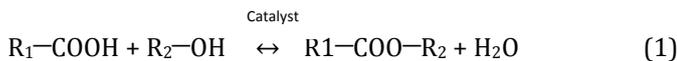
In this work the direct esterification reaction of FFA i.e., oleic acid which is present in higher percent in WCO was studied. Heterogeneous acid catalyst used was cationic ion exchange resins Amberlyst 15 wet. It is a strongly acidic, sulfonic acid, macro-reticular polymeric resin based on cross linked styrene divinylbenzene copolymers.

2. PROCESS SYSTEM

Esterification reaction was carried using oleic acid and methanol as reactants to produce methyl oleate or biodiesel under specific process conditions.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + CH_3OH \leftrightarrow$$
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 + H_2O \qquad (2)$$
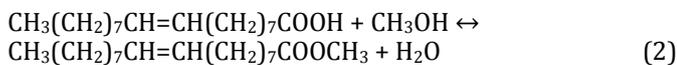
The mechanism for cation exchange resins in esterification of FFA with methanol (A) to give methyl ester (ME) is presented through equation. Adsorption of FFA to IER functional group takes place. Then alcohol is adsorbed on the resins resulting into an intermediate. Last step is desorption of methyl ester and IER gets accumulated in water formed.

$$FFA + I (H^+) \leftrightarrow FFA. I (H^+) \qquad (2.1)$$

$$FFA. I (H^+) + A \leftrightarrow FFA. I (H^+).A \qquad (2.2)$$

$$FFA. I (H^+).A \leftrightarrow I (H^+) + ME + H_2O \qquad (2.3)$$
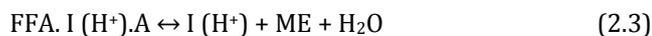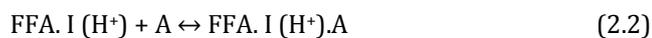
Chemicals: Oleic acid which is present in WCO more than 50% was used with methanol of high purity.

According to equation (2), it is necessary stoichiometric amount of organic acid and methanol but in practice it is difficult to maintain that ratio because fluctuations in raw materials can occur, for that reason methanol is used in excess. It is important to note that excess methanol favors the production of esters. This also gives rise to the requirement of recovering methanol.

The other objective of this work is to recover methanol as a product stream using Petlyuk column.

3. PROCESS SIMUALTION

Aspen Plus has been used in many works considering reactive distillation [10-12]. For that reason it is suitable for the study of complex reactive distillation columns.

As mentioned in previous studies, the stages of distillation column are modeled using MESH equation which is solved using bubble point method [13] with tolerance error of 0.001 in thermally coupled distillation column sequence, he recycle stream are converged via Wegstein method with same tolerance error.

Regarding thermodynamic aspects, the reaction mixture may form homogenous or heterogeneous azeotropes. As a result, appropriate thermodynamic models like NRTL, UNIFAC, UNIQUAC were needed to represent the correct thermodynamic behavior when reactive system was analyzed using process simulator. The study was carried out using Aspen Plus simulation tool.
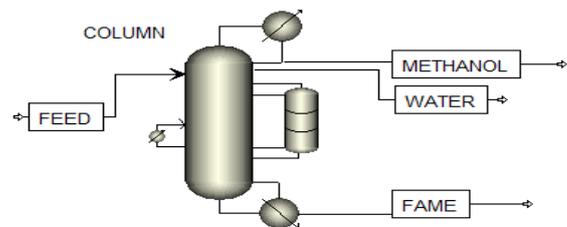
Figure 1. Reactive Petlyuk Distillation Column

In this study UNIQUAC model was considered.

Table 1 presents the design characteristics of the complex distillation sequence used for the simulation study.

The mixed feed of FFA and methanol was fed into stage above the reactive section of column in vapor-liquid phase (100°C at 1.5 bar). The equilibrium reactions were considered in each stages of the distillation column. In the reactive Petlyuk distillation column, reaction occurs in all stages and methanol was recovered in the top product of the main column.

Table 1. Feed and Petlyuk column specification

Parameters	Values	
Property Method	UIQUAC	
Feed Flow rate (l/min)	Oil-0.09	Methanol-4.5
Feed Temperature (°C)	100	
Molar ratio	1:50	
Feed Pressure (Bar)	1.5	
Column Specification		
Number of stages	10	
Condenser Type	Total	
Reboiler Type	Kettle	
Feed Type	Mixed	
Feed Stage	4	
Reboiler Duty (KW)	1.5	
Bottom rate (l/min)	0.05	
Heat duty of Connect stream	0.75 KW	
Flow of Connect stream	0.05 l/min	

2. RESULT & DISCUSSION

The composition profile for the liquid phase in the reactive Petlyuk distillation column is shown in fig. 2. According to this figure, the top product was methanol and the bottom product was methyl ester of mol fraction 0.99. The most of the reaction takes place below stage 4 where the feed was introduced to the reactive distillation column. The side product is water. The temperature profile in fig. 3 depicts the increase in temperature in reactive section.
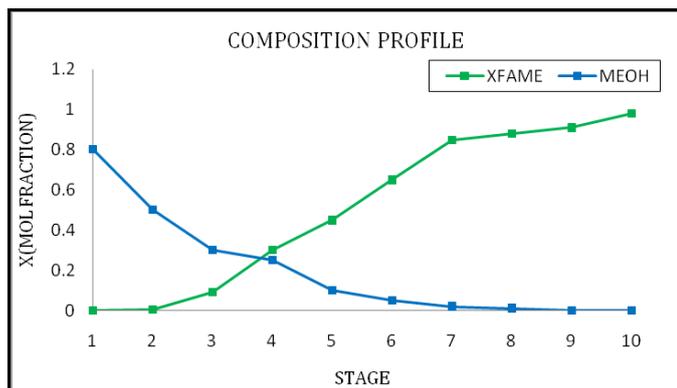
Figure 2. Composition profile for liquid phase of the column
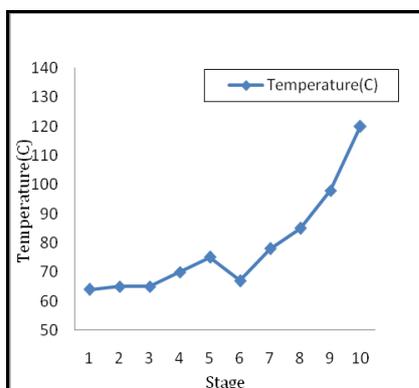
Figure 3. Temperature profile of the petlyuk column

To ensure the high yield of biodiesel production, different processes use a wide range of methanol to oil ratio. The reboiler duty required for different % methanol recovery for the methanol: oil ratio of 50:1 is analyzed by sentivity analysis keeping the operating conditions of distillation column fixed. It is depicted by figure 4 that with increase in methanol recovery, reboiler duty increases exponenially.

As it can be seen from the results that highest purity of 99% can be achieved and an acceptable methanol recovery can be achieved by using this sequence of divided wall distillation column. the recovered methanol can be recycled to the feed stream and the need toexcess methanol can be mnimized.
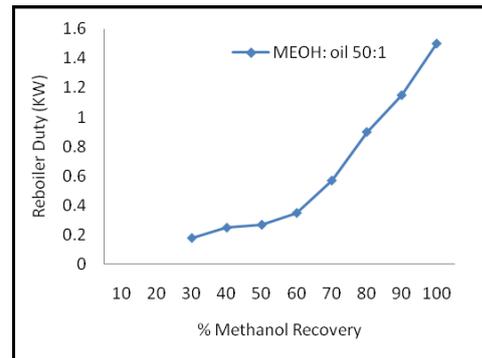
Figure 4. Required reboiler heat duty for different different level of methanol recovery.

3. CONCLUSIONS

The esterification of oleic acid with methanol catalyzed by cation exchange resins was studied. A complex thermally coupled distillation column was simulated considering the reaction inside the column, and the results indicate the production of the ester as bottom product. It is important to mention that reactive Petlyuk distillation column can handle the reaction and separation and also recover methanol. These results are incentive for the implementation of a process with low operating cost that makes biodiesel production economically viable.

NOMENCLATURE

Abbreviations

IER	Ion Exchange Resin
NRTL	Non-Random Two Liquid
UNIFAC	Universal Functional Activity Coefficient
UNIQUAC	Universal Quasi Chemical
MESH	Material, Energy, summation constraints, and Heat equations

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