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Simulation Study of Reactive Distillation Column for the Production of Methyl Oleate

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Abstract - ***Reactive distillation (RD) technique combines the reaction and separation steps of the chemical process in a single unit. Thus it reduces the material and operating cost with reduction in energy requirement. The variety of successful applications of RD technique has been investigated and still research is going on to explore the new systems and to develop the more efficient mechanism of RD. In this study, the simulation of RD column was carried out using Aspen Plus process simulator for the laboratory scale RD column for the production of methyl oleate by varying process conditions to choose the best suitable condition for maximum yield and conversion.***

Key Words: *Biodiesel, Esterification, Free Fatty Acids (FFA's), Simulation, Reactive distillation (RD)*

1. INTRODUCTION

Many industrially important chemical processes may include the series of steps such as pretreatment of reactants, chemical reaction, separation and purification of product(s), recycle of unconverted reactant(s), recovery of solvent or catalyst etc. These steps are very essential in order to obtain better reactant conversion, product yield and purity. To carry out these steps different equipment units such as reactor, distillation column, evaporator etc. are required. In other words reaction and separation steps are carried out in separate units. Thus while process design, a separate material, energy and cost considerations are required for every individual equipment. With the increase in number of units required in the process, the overall fabrication, installation and operating cost increases due to the increase in material and energy needs.

To overcome some of these limitations of the conventional chemical process, an alternative technique known as 'Reactive Distillation (RD)' is available. In reactive distillation, reaction and separation steps of the process are carried out inside the single equipment called as reactive distillation column. Here reactants are converted to products with simultaneous removal of products either from top or bottom of RD column and recycle of unreacted or excess reactant(s) [1]. This technique is especially advantageous for reversible reactions, because for such reactions, generally the reactant conversion is less due to equilibrium limitations. But if these reactions are carried out in RD, then conversion can be increased far beyond expectations by shifting the equilibrium towards the product side due to the continuous removal of reaction products from the reactive zone. The suitability of RD for a particular reaction depends on various factors such as volatility of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of RD for every reaction may not be feasible [2].

Some important advantages of reactive distillation technique are as mentioned below [1], [3]-
1) Capital investment and operating cost are reduced because the amount of hardware would be reduced by use of RD as compared to conventional processes.
2) Improved conversion of reactant approaching close to 100%. This increase in conversion gives a benefit in reduced recycle costs.
3) Increased yield by shifting the chemical and thermodynamic equilibrium through continuous removal of reactants or products from the reaction mixture.
4) Improved selectivity- Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
5) Heat integration benefits- If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and hence reduce the reboiler duty.

1.1 Constructional features of RD column

A typical RD column consists of three sections; middle section is the reactive section, rectifying section is at the top and stripping section is at the bottom part of the column. Rectifying and stripping sections are filled with suitable packing material whereas the reactive section contains either the mixture of catalyst and packing material if heterogeneous catalyst is used or only packing material, if the homogeneous catalyst is used in the reaction system. The condenser is connected to this column at the top and a reboiler at the bottom. The

arrangement for reflux can also be provided as per the requirement. A schematic representation of RD column is shown in fig. 1. One of the reactant is fed just above and another reactant is fed just below the reactive section, so as to achieve the countercurrent contact between the reactants. Generally laboratory scale or pilot scale RD column consists of a glass column with the three sections as mentioned above. It is connected to a three neck round bottom flask at the bottom which can be used as reboiler. The heating mantle is used to provide the necessary heat energy to the reboiler. The glass column is connected at the top to the water condenser with the provision for reflux. The temperature measurements at the reboiler, reactive section and at top section can be done by using either thermometer or thermocouple or RTD. The liquid reactants can be fed by using dosing pumps or peristaltic pumps.

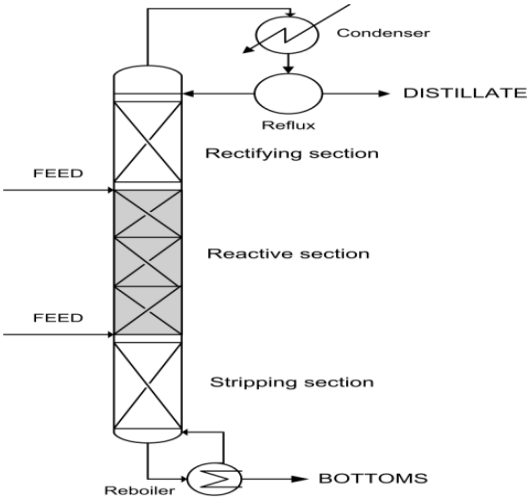

Fig -1: Schematic representation of Reactive distillation column

1.2 Applications of RD

Reactive distillation technique can be used for various unit processes such as-:

- Acetylation
- Alkylation
- Amination
- Dehydration
- Esterification
- Etherification
- Trans-esterification

The RD technique can also be successfully applied to the esterification of long chain fatty acids. One example is the work carried out by Omota et al. (2003) [4]. They have studied the feasibility of a single column process using a heterogeneous catalyst for the esterification of lauric acid with 2-ethyl-hexanol and methanol. They found that it is possible to obtain pure fatty acid ester in a single column process. Both esters can be produced in the same setup, but under different operating conditions. However, problems may occur because the product purity is highly sensitive to changes in the reflux ratio. The optimal reflux ratio is very low, which could give control problems.

Bhatia et al. (2006) [5] reported that reactive distillation can be successfully applied for the esterification of palmitic acid with isopropanol through reactive distillation with zinc acetate catalyst supported on silica gel. The process parameters such as total feed flow rate, reboiler duty, feed temperature, reflux ratio etc. were varied during the experimental study to obtain the optimum values of these parameters. The experimental data were used to validate the theoretical predictions obtained from steady state model and rate based model. Finally they have concluded that the predictions from the rate based model matched with experimental results.

The esterification of acetic acid and butanol to produce butyl acetate was carried out by E. Sert and F. S. Atalay (2011) [6] in a packed bed RD column. For this purpose a RD column with a height of 2 m., filled with a mixture of catalyst (Amberlyst- 15) and packing material (raschig rings) in reactive section and only raschig rings in non reactive section was used. During experiments several operating conditions such as total feed flow rate, molar ratio of butanol to acetic acid, amount of catalyst, reboiler temperature and three different column configurations were varied and their effect on reactant conversion was observed. Finally they have suggested the optimum process conditions at which butyl acetate purity of 82% and acetic acid conversion of 80.5% was obtained. In addition to that, the thermodynamic aspects of this system such as equilibrium constant, vapour pressure and UNIQUAC parameters were investigated.

2. PRODUCTION OF METHYL OLEATE USING RD

Methyl oleate which is commonly known as biodiesel has variety of other applications, such as it can be used as plasticizer, solvents or co-solvents, oil carrier in agricultural industry etc. [7]. It can be produced by the esterification reaction between oleic acid and methanol in presence of some suitable acid catalyst.

The reaction is reversible in nature and can be represented as reaction (1)-

$$\underset{\text{(Oleic acid)}}{C_{18}H_{34}O_2} + \underset{\text{(Methanol)}}{CH_3OH} \longleftrightarrow \underset{\text{(Methyl oleate)}}{C_{19}H_{36}O_2} + \underset{\text{(Water)}}{H_2O} \quad \ldots\ldots (1)$$

As this reaction is reversible and equilibrium limited, it is an excellent candidate for RD. The boiling points of the components of this reaction are given in table (1) below.

Table -1: Boiling points of the components

Sr. No.	Name of the component	Boiling point (°C)
1.	Oleic acid	358
2.	Methanol	64
3.	Methyl oleate	352
4.	Water	100

So while carrying out this reaction in RD, then the heavy product (methyl oleate) is obtained from the bottom along with traces of unreacted oleic acid, whereas water is collected from the top along with unreacted or excess methanol due to their lower boiling points. Thus while charging the reactants inside RD, high boiling reactant (oleic acid) is fed just above and low boiling reactant (methanol) is fed just below the reactive section.

2.1 Kinetics of oleic acid esterification with methanol

Chengcai Song et. al. (2009) [8] have developed kinetic model for the esterification of oleic acid with subcritical methanol in presence of zinc acetate catalyst in a batch reactor. They have also studied the effect of different process conditions by varying pressure, temperature, molar ratio of methanol to oleic acid etc. on the esterification reaction.

The conversion of oleic acid, i.e.- the amount of unreacted oleic acid in the product mixture was obtained from its acid value using titration method.

The general rate expression for the reaction (1) can be written as equation (2)-

$$-[dC_A/dt] = k_1 . C_A^{\alpha} . C_B^{\beta} - k_2 . C_C^{\gamma} . C_D^{\lambda} \quad \ldots\ldots (2)$$

Where, C_A, C_B, C_C and C_D denotes the concentrations of oleic acid, methanol, methyl oleate and water respectively with their reaction orders α, β, γ and λ. K1 and k2 are the rate constants for the forward and backward reaction respectively.

In this work Song et. al. [8] has maintained the high concentration of methanol than that of other component. Hence the above equation (2) was simplified as-

$$-[dC_A/dt] = k_1 . C_A^{\alpha} \quad \ldots\ldots (3)$$

By using integral method of analysis and from Arrhenius equation, the following results were obtained which are summarized in the following table (2)-

Table -2: Values of the parameters from kinetic study

Sr. No.	Parameter	Value
1	Reaction order, n	2.2
2	Pre- exponential factor, k_0	120.0
3	Activation energy, E	32.62 KJ / mol

3. SIMULATION OF RD COLUMN BY USING ASPEN PLUS

Model development and simulation of RD column for the esterification of oleic acid with methanol was done using Aspen Plus process simulator 11.1 [9]. The purpose of this simulation is to study the effect of important process parameters such as temperature, molar ratio of oleic acid to methanol, reflux ratio etc. on the conversion and yield and to decide the optimum process conditions. The RD column dimensions such as total height of the column, sectional height and diameter, types of packing material, reactant flowrates etc. are also finalized from the simulation results.

From the model library of Aspen Plus, the 'Radfrac' unit is selected as RD column model. The two reactant and two product streams are connected to the column as shown in figure (2).

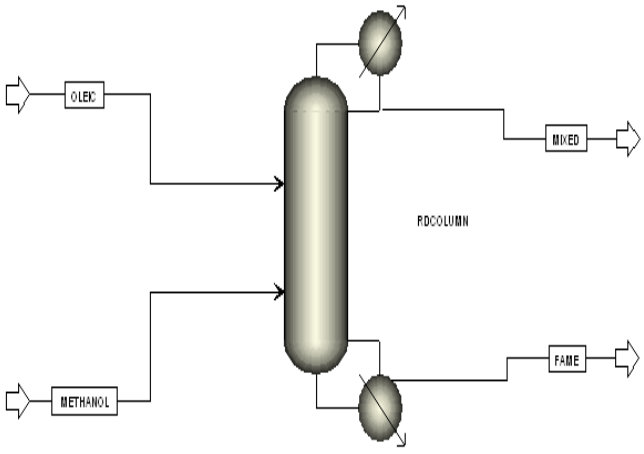

Fig -1: Flowsheet for RD column using Radfrac unit

After satisfactorily joining the input and output streams with the RD column block, the necessary input data was added. The molar ratio of oleic acid to methanol was fixed to 1:8, thus the flowrates of the inlet streams for oleic acid and methanol was set accordingly.

For the simulation, equilibrium stage model incorporated with kinetic reaction model is selected. The thermodynamic property method UNIQUAC is used with the estimation of all missing parameters to represent the concentration coefficient in the rate expression.

Thus trial and error method was followed, for finalizing the values of parameters such as reflux ratio, reboiler duty, bottoms rate, sectional height and types of packing etc. which provides satisfactory results.

Thus, finally the optimum values of the process parameters were obtained which gives the maximum conversion of oleic acid. The main product methyl oleate is having mole fraction in the bottoms stream equal to 98.2%. The result of this simulation is summarized in the following table (3)-

Table -3: Operating conditions of RD column

Sr. No.	Parameter	Value
1.	Molar feed flow rates- Oleic acid Methanol	2.0 mol/ hr 16 mol/ hr
2.	Molar ratio of oleic acid and methanol	1:8
3.	Reboiler duty	0.9 kW
4.	Reflux ratio	4.05
5.	Distillate rate	15.96 mol/ hr (483.95 gm/ hr)
6	Bottoms rate	2.037 mol/ hr (593.66 gm/ hr)
7	Reflux rate	64.65 mol/ hr (1960.01 gm/ hr)
8.	Purity of Bottom product (Methyl oleate)	98.2 %

4. CONCLUSIONS

Reactive distillation technique becomes an emerging and promising alternative to the conventional process methods. The concept of reactive distillation technique to produce methyl oleate by the esterification reaction between oleic acid and methanol was studied. The simulation work carried out using Aspen Plus process simulator shows the satisfactory result with optimum process conditions. Still there is scope available to compare these results with the results obtained from the actual experimental work.

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