Process for Fatty Acid Methyl Esters by Dual Reactive Distillation

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Abstract

Fatty acid methyl esters (FAME), valuable oleo-chemicals and main constituent of biodiesel, can be manufactured in a continuous process based on reactive distillation and solid catalyst. A central problem is the effective water removal. In this work we propose a novel approach, namely dual esterification with a mixture of methanol and long-chain alcohol, as 2-ethylhexanol, which plays the role of reactant and mass separation agent. The key benefits are multi-functional reactive distillation device, high flexibility in operation and reduced equipment costs due to the highly integrated design.

Keywords: Conceptual Design, Reactive Distillation, Biofuels.

1. Introduction

Fatty acid methyl esters (FAMEs) are high-value fine chemicals used in cosmetics, but today the main interest has shift to biodiesel. Recently, Omota & Dimian proposed a continuous process for producing fatty esters based on reactive distillation making use of super acid solid catalysts, more specifically sulphated zirconia, working at temperatures of 130-160 °C. [1] A central problem is the effective water removal necessary to shift the equilibrium to complete conversion and protect the catalyst. When using a heavy alcohol, as 2-ethylhexanol (2EH), the favorable LLE separates water as top product with

high yield and simultaneously ensures sufficient alcohol reflux. The problem can be solved when azeotropes with water form a suitable entrainer. [2] However, this technique does not work for methanol, which should be separated from both top and bottom products, and recycled back to the reaction zone.

The application of reactive distillation for fatty acid methyl esters manufacturing was the focus of few recent papers. Omota & Dimian analyzed the feasibility, and demonstrated that using reflux of acid instead of alcohol allows quantitative water removal with stoichiometric feed of methanol. [1] Consequently, no downstream methanol recovery is necessary. In this case the process is rather reactive absorption than reactive distillation. This viewpoint was confirmed independently by Steinigeweg & Ghmeling. [3] They used a resin-based Amberlyst-15 catalyst hosted in Katapak packing and laboratory column. Getting complete conversion was problematic since the reaction temperature with Amberlyst cannot exceed 120 °C. Excess of methanol with secondary distillation is necessary. On the contrary, using SZr catalyst allows much higher temperatures and pressures, at convenient values for the catalyst.

2. Conceptual Design

The feasibility of fatty acid esterification with the individual alcohols in a RD setup may be studied by means of a residue curve map as shown in Figure 1. Both diagrams show a large region of partial miscibility, but with fundamental differences. For 2EH the immiscibility gap regards both alcohol and fatty acid binary mixtures with water. Operating the column with either alcohol or acid reflux is possible, but for obvious reason the first is preferred. In the case of methanol the immiscibility gap embraces only the water/acid binary, but approaching closely the methanol/water edge.
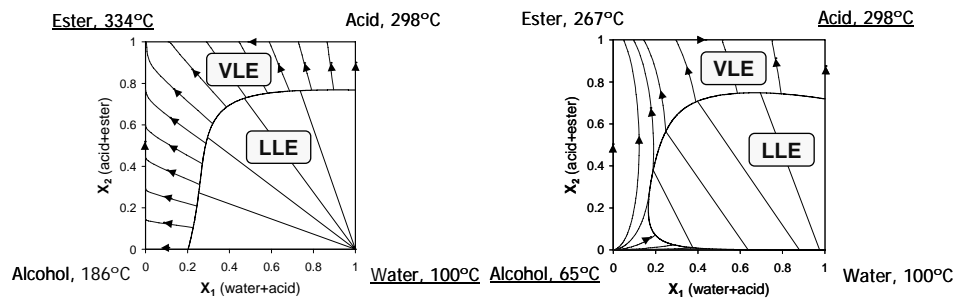

Figure 1. RCM for dodecanoic acid esterification with 2EH (left) and methanol (right).

The practical implication is that the top vapor should contain only water and acid. This condition is rather difficult to fulfill since extremely low volatility of fatty acids. Superposing the two diagrams it can be observed that adding a heavy alcohol in top could help to remove the water produced by the lighter alcohol. Thus 2EH plays both the role of reactant and mass separation agent.

The remaining problem is the operating pressure. It is worthy to note that vacuum and large dilution of the bottom product is needed in the case of 2EH, while high pressures of 6-12 bars is required when working with methanol. By the present approach nor vacuum neither high pressure is necessary. The pressure will be determined by the maximum temperature maximizing the catalyst performance in terms of activity and selectivity.

3. Simulation

Figure 2 presents the flowsheet simulated rigorously with AspenPlus™. The key equipment is the RD column and the two-phase flash vessel. Additional recovery columns for alcohols are considered for closing the material balance, although even simpler flowsheet will emerge at the end. The RD column consists of 20 stages, with 3 non-reactive in top and 16 reactive of Katapak-S filled with sulphated zirconia catalyst for each kinetic data were available from previous works. [1,4,5] A holdup of 100 l was assumed, and later validated as realistically by hydraulic calculations. Molten lauric acid (100 kmol/h) is fed at 140 °C, while 2-ethylhexanol (20 kmol/h) is fed as liquid at 130 °C on top stage and methanol (120 kmol/h in base case) as vapor on the first and below the last reactive stage, respectively. The column pressure is 1.5 bar. UNIQUAC was used as thermodynamic option with distinct activity coefficients for VLE and LLE. Equilibrium stage model was employed as reliable at conceptual stage.
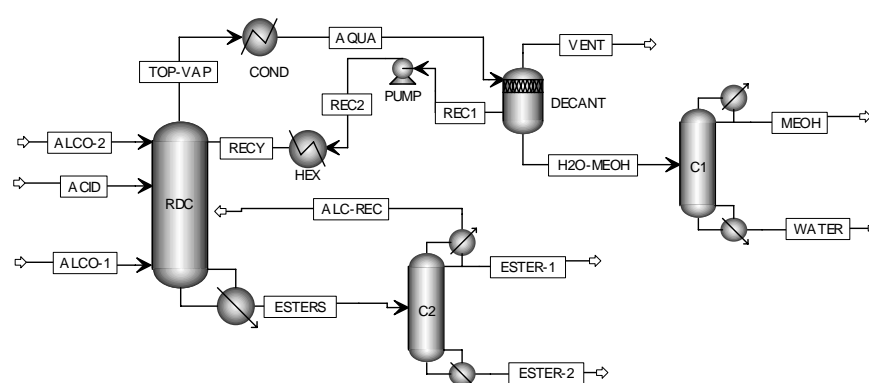

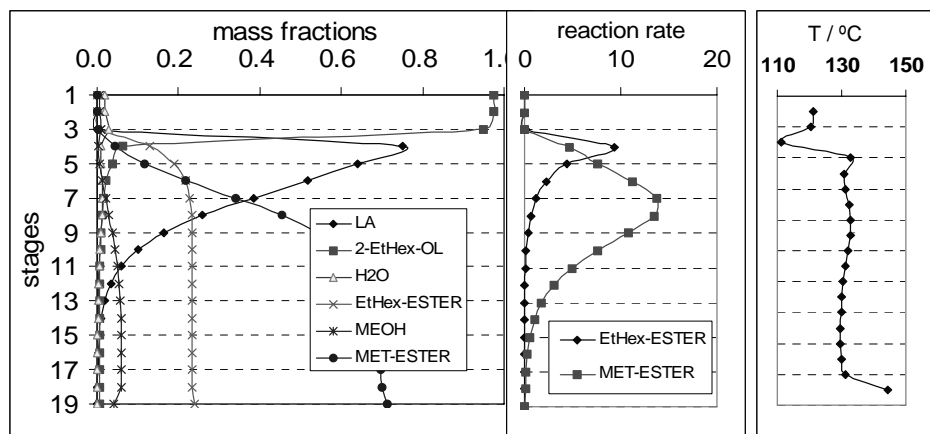Figure 2. Process simulation diagram for dual fatty acid esterification

Figure 3. Column profiles: concentration, temperature and reaction rate

As illustration of a base case Figure 3 presents profiles of liquid mass fractions, reaction rate and temperature. The results confirm the analysis. The mass fraction of lauric acid falls from top to bottom, the fatty acid being consumed mostly in the upper part of the reaction zone, but additional stages are necessary to push the conversion to completion. The heavy ester forms on the first three reactive stages, while the light ester mostly in the middle part. Accordingly, the reaction rate profiles show two distinct zones. Water is entrained by 2EH on the first three non-reactive stages, further condensed and then removed in decanter. Indeed, in the reaction zone there is very low water concentration in liquid.

The reflux consisting mainly 2EH, generates a top external recycle loop. On the contrary, the excess of methanol passes preferentially in the bottom product. In this way the reboiler temperature may be varied on a large interval.

The temperature profile is directly correlated with the pressure. A flat profile is preferred from engineering viewpoint. At 1.5 bar the temperature is almost constant at 130 °C. At atmospheric pressure the reaction temperature would be 105 °C, which would be suitable for Amberlyst or Nafion catalysts. Hence, the pressure becomes an operation variable that can be adapted to performance characteristics of the catalyst, as well as when this declines in time.

4. Optimisation

The design can be optimised with respect to product specifications. Product purity is the most important issue, particularly for pharmaceutical applications.

As shown in Figure 4, the purity of both products strongly depends on the distillate flow rate. This was selected as independent variable because it can be easily controlled by the material and heat input. A minimum of 110 kmol/h is required for operation, but the purity of the bottoms is only 96.5%.
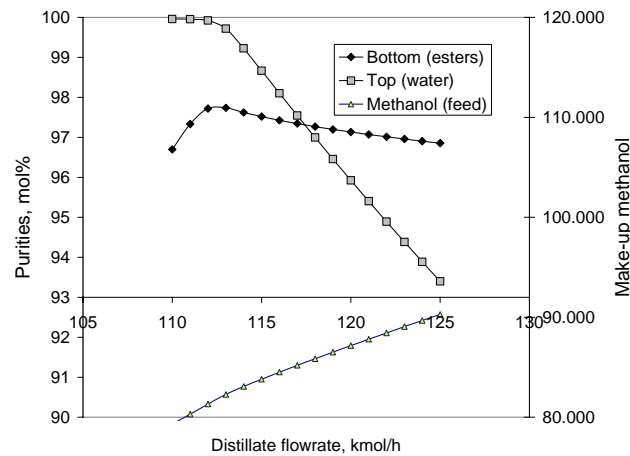
Figure 4. Purity of RDC products and methanol make-up as function of distillate rate.

Raising the distillate rate leads to an increase of the bottom purity up to a maximum of 98%, while the purity of water is only slightly affected. Further increase leads to both purities degradation. The diagram shows the make-up policy of methanol, which starts from the stoichiometric value of 80 kmol/h. The optimum vapour distillate is achieved at 113-114 kmol/h corresponding to a methanol consumption of 82.3 kmol/h, only slightly above stoichiometry.

The distribution of impurities in top and bottom products is particularly significant (Figure 5). Increasing the distillate rate drops to zero all impurities in bottoms except methanol. This remains constant at 2% above 114 kmol/h. On the contrary, further excess methanol in feed will go only in the top product.
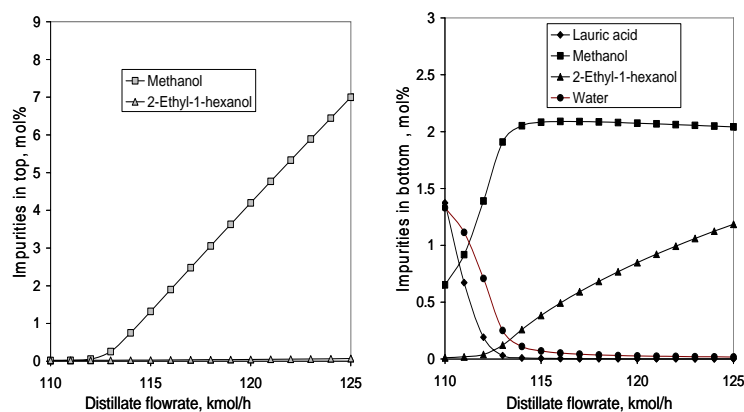

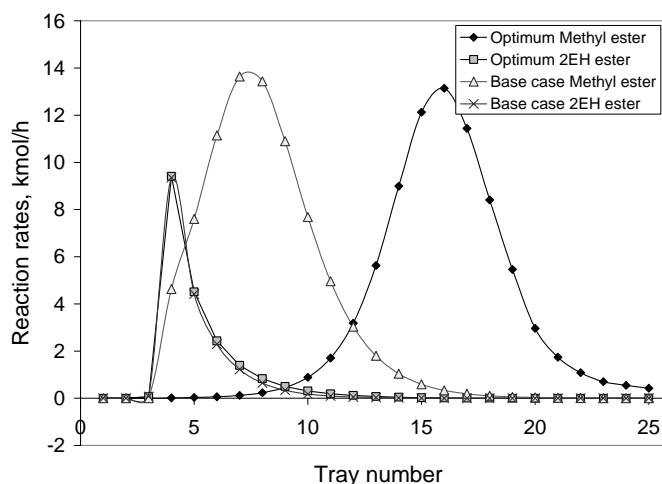Figure 5. Impurities in the top and bottom of the reactive distillation column.

Figure 6. Optimal reaction rate profiles.

Regarding the reaction rate, Figure 6 compares two situations: base-case and the stoichiometric feed. The heavy ester formation remains in place but the light ester migrates from an upper position to a lower position. By stoichiometric balance no 2EH is found in the base and no methanol in the top water. These are the optimal conditions for operating the reactive distillation column.

5. Conclusions

The process proposed here brings the innovation of using multi-reactions in reactive distillation for better matching of reaction and separation requirements. In particular, the removal of water in fatty acid esterification – used for production of oleochemicals and biodisel – is solved in a simple and effective manner. Compared to the conventional technology, this novel design has several key benefits: compact equipment, higher flexibility in production rate, product specifications and operation conditions, as well as reduced capital and operating costs due to the highly integrated design.

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