[IMP2 01] Reactive Distillation Column for the Production of Palm Oil Fatty Acid Ester: Modeling and Simulation

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Introduction

Reactive distillation (RD) which integrates distillation with reaction in a single unit offers distinct advantages of increased conversion, lower capital investment, lower energy consumption and higher product yields. Recently, theoretical and experimental studies of fatty acid esterification processes in RD column are an important focus of both industrial and academic research. It is a suitable case for RD column because of its formation being affected by chemical equilibrium. Conventionally, fatty acid esters are produced in batch reactors using homogeneous catalysts such as sulphuric acid or p-toluene sulphonic acid. Conventional processes are penalized by important shortcomings including relative high alcohol consumption, product quality degradation and necessity of catalyst neutralization and removal (Moritz, 2003).

The utilization of heterogeneous catalysts as the replacement is gaining importance due to their ecofriendly nature. Steingeweg and Gmehling (2003) described the esterification of decanoic acid with methanol in a packed column. The reaction was catalyzed heterogeneously by a strong acidic ion exchange resin in low temperature and reaction kinetics was reported along with the process data from pilot plant experiments. On the other hand, solid catalyst based on sulphated zirconia which may provide sufficient thermal stability was used by Omota *et al*. (2003) to investigate the possibility of applying RD to the esterification of decanoic acid with 2-ethylhexanol and methanol respectively.

Although RD has been industrially applied in various processes, such as synthesis of methyl tertiary butyl ether (MTBE) and methyl acetate, the design of RD processes still remains a challenge. During the last decades, several design methods have been developed. The available approaches for the design of RD may be categorized into three main groups: those based upon graphical/ topological considerations, those based upon optimization techniques and those derived from heuristic/ evolutionary considerations.
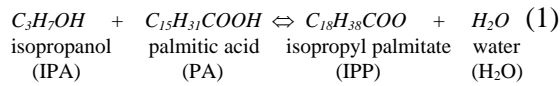
Detailed design applying post-design algorithm was presented by Subawalla and Fair (1999), a detailed step-by-step guideline for designing a solid catalyzed reactive distillation systems was discussed. It was used to generate initial estimates for several key design parameters. The authors accounted the effects of column internals on design and recommended using non-equilibrium or rate-based models for this purpose.

In the present study, a detailed design using post-design algorithm is applied to the reactive distillation column for production of isopropyl palmitate. The reaction has been catalyzed heterogeneously by zinc acetate supported on functionalized silica. Several design key parameters for the heterogeneously catalyzed reaction are estimated. The reactive distillation design is proposed and simulated based on the developed kinetic model.

Data Sources

All simulations are carried out with the rate-based model Ratefrac from the process simulator Aspen Plus (Version 12.1). Ratefrac assumes that the vapor-liquid equilibrium occurs only at the interphase. The model explicitly accounts for the underlying interphase mass and heat transfer processes to determine the degree of separation and this approach avoids uncertainties that result when the equilibrium approach is used with estimated efficiencies or HETP.

Experimental values of reaction kinetic parameters are incorporated into Aspen Plus. The heterogeneous experimental kinetic data were reported by Aafaqi *et al*. (2004). Esterification reaction is assumed to be reversible and second order reaction. It can be represented as:

C_3H_7OH + $C_{15}H_{31}COOH$ ⇔ $C_{18}H_{38}COO$ + H_2O (1)
isopropanol   palmitic acid   isopropyl palmitate   water
   (IPA)   (PA)   (IPP)   (H_2O)

The reaction rate can be expressed in the Langmuir - Hinshelwood - Hougen - Watson (LHHW) model. The LHHW formalism equation (Xu and Chuang, 1996) for a reversible esterification using zinc acetate supported over silica gel as a catalyst is represented as:

$$r = \frac{1}{v_i}\frac{dC_i}{dt} = k_f^* \left(K_{IPA}K_{PA}C_{IPA}C_{PA} - \frac{K_{IPP}K_{H_2O}C_{IPP}C_{H_2O}}{K_x} \right) \; molL^{-1}s^{-1} \quad (2)$$

where r is the rate of reaction, C_i is the concentration of component i in $molL^{-1}$ and K_i is the adsorption equilibrium constant for component i,

$$K_{IPA} = 4.00 \times 10^{-16} \exp^{10539/T} \quad (3)$$

$$K_{PA} = 8.68 \times 10^{-18} \exp^{12310/T} \quad (4)$$

$$K_{IPP} = 6.04 \times 10^{-14} \exp^{9927/T} \quad (5)$$

$$K_{H_2O} = 1.64 \times 10^{-15} \exp^{10250/T} \quad (6)$$

The reaction equilibrium constant, K_x and the forward rate constant, k_f^* are given by:

$$K_x = 75057 \exp^{-3949/T} \quad (7)$$

$$k_f^* = k_f m_{cat} = 1258 \exp^{-5002/T} \; Lmol^{-1}s^{-1} \quad (8)$$

where m_{cat} is the total amount of catalyst which equal to 1 g in this case and T is reaction temperature in Kelvin.

The physical properties and UNIQUAC parameters are estimated using the available models in Aspen Plus (Aspen Plus 12.1, 2003).

Base Case Simulations

The process base case consists of a packed reactive distillation column with rectifying zone, reactive zone and stripping zone. The reactive section is packed with catalytic structured packing, Sulzer Katapak-SP (approximate surface area= 125 m^2/m^3 and void fraction= 0.55). The rectifying and stripping sections are packed with sheet metal structured packing, Sulzer BX (approximate surface area= 500 m^2/m^3 and void fraction= 0.90). The design and operating parameters for the "base case" reactive distillation

column are presented in Table 1 and the simulation methodology flowchart is shown in Figure 1. The results of simulation are shown in Figure 2(a) and 2(b). Segments are numbered from the top.

As can be seen from Figure 2(a), the reactive zone temperature drops due to the endothermic nature of the reaction. The sudden increase in temperature at segment 5 is due to the introduction of palmitic acid into the column. The palmitic acid and alcohol concentration in liquid phase drop gradually over the whole reaction zone beginning from the feed segments (Figure 2(b)).

Process Optimization

The design guidelines of Subawalla and Fair (1999) have been applied for the process optimization of a reactive distillation column for production of IPP. They are used to generate initial estimates for the optimum column pressure, reactive zone location, catalyst mass, reactant feed location, reactant ratio, column diameter, number of equilibrium stages and packed height.

Total Feed

Figure 3 shows the effect of total feed to the PA conversion. The total feed has been varied while other operating parameters are kept constant. The PA conversion decreases as the total feed increases due to the reduced residence time. However, one would see the decline at very low total feed because of the heat loss of the column, which is on the same order of magnitude as the reboiler duty at these very low feed flow rates. Hence, a moderate total feed of 50 mol/hr has been chosen for the further simulations.

Column Pressure

For endothermic reactions such as IPP synthesis, the increase in operating pressure raises the reactive zone temperature and increases the reaction equilibrium constant, thereby resulting in a higher conversion as well as higher purity (as shown in Figure 4). Thus, operation at the maximum possible pressure is beneficial for endothermic reaction from a chemical equilibrium and reaction rate standpoint.

Nevertheless, an intermediate pressure is favored to avoid the high reboiler duty and IPP degradation. According to Bock *et al.* (1997), a reduced temperature would produce

TABLE 1 Design and operating parameters for the "base case" of the reactive distillation column for production of IPP.

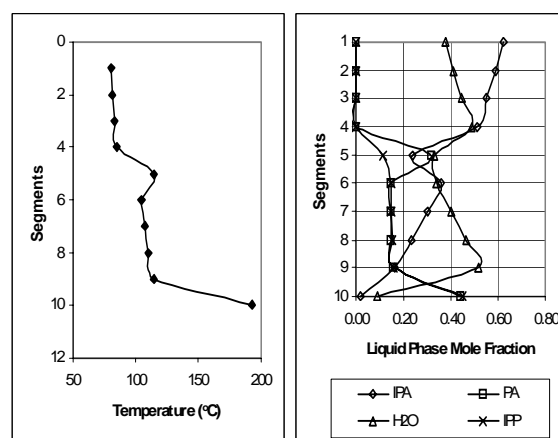| Description	Value	Description	Value
Rectifying section		Feed 1 (Palmitic acid)	
Height (m)	0.6	Flow rate (lit/hr)	6.7
Type of packing	Sulzer BX	Temperature (°C)	100
NTSM (1/m)	5	Feed segment	5
No. of segments	3		
Reactive section		Feed 2 (Isopropyl alcohol)	
Height (m)	2.0	Flow rate (lit/hr)	2.1
Type of packing	Sulzer Katapak-SP	Temperature (°C)	100
		Feed segment	6
NTSM (1/m)	1		
No. of segments	2		
Catalyst amount (kg)	4		
Stripping section		Distillate: feed ratio	0.5
Height (m)	0.6		
Type of packing	Sulzer BX		
NTSM (1/m)	5		
No. of segments	3		
Column diameter (m)	0.1	Reflux ratio (mol/mol)	1.0
Column pressure (bar)	1	Palmitic acid:isopropyl alcohol (mol/mol)	1: 1.3
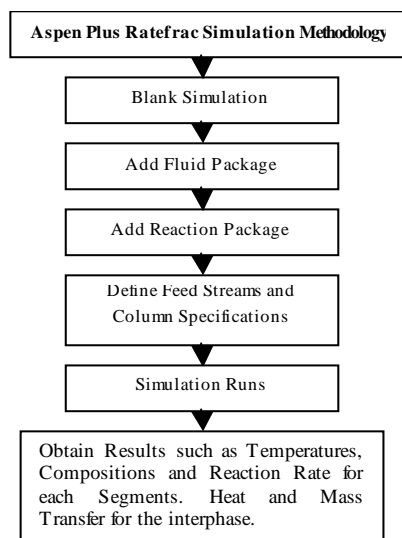
FIGURE 1 Aspen Plus Ratefrac simulation methodology flowchart.

(a)   (b)

FIGURE 2(a) Temperature profile for the RD unit. FIGURE 2(b) Liquid composition profile for the RD unit. Process Parameters as in Table 1.

a better colour products and less waste will be generated during the operation. Based on the simulation results as shown in Figure 4, a pressure of 3 bar is chosen for limiting the reboiler temperature below 250 ºC.

Reactive Zone Location

According to the design guideline by Subawalla and Fair (1999), the reactive section should be located where the concentration of at least one reactant (preferably the limiting reactant) is the maximum. The simulation of a non-reactive column with a feed as in the "base case" design was carried out. It was found that the concentration of isopropanol and the limiting
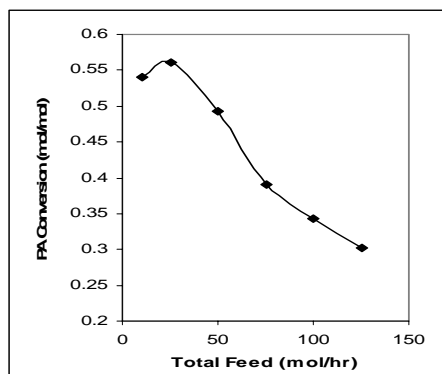
FIGURE 3 Effect of total feed to the PA conversion.

FIGURE 4 Effect of column pressure to the PA conversion, IPP purity and reboiler temperature.

reactant, palmitic acid were almost constant throughout the column. Consequently, the reactive zone was located between stages 3-4. The conversion and bottom product purity slightly increased when the reaction zone shifted towards the condenser (stages 3-4) because of the slightly higher concentration of palmitic acid near its' feed stage. Thus, the reactive zone for this system should be located at the top of the column. Therefore, for all further simulations, the reactive zone was fixed between stages 3-4.

Reactant Ratio and Feed Location

The choice of reactant ratio essentially becomes a compromise between conversion and product purity. Figure 5 shows the effect of increasing the reactant ratio on PA conversion and IPP purity. One can observe that the reactant ratio of 1.3-1.7 is considered sufficient to produce high PA conversion without having a significant effect on the IPP purity. Hence, the reactant ratio of 1.5 was used in further simulations.

A right choice of feed location ensures high concentrations of reactants in the reactive zone. In the isopropyl palmitate column, the volatilities of the reactants, IPA and PA were very different. Hence, an additional feed location was required to ensure stoichiometric reactant quantities. Three reactive distillation arrangements with different feed points location were investigated in this study (as shown in Table 2). Other parameters were remained unchanged as stated in Table 1 during the simulation. The column configuration with separate feed of reactants to the lower and upper part of the reactive zone gave higher conversion as compare with the column with mixed feed of isopropanol
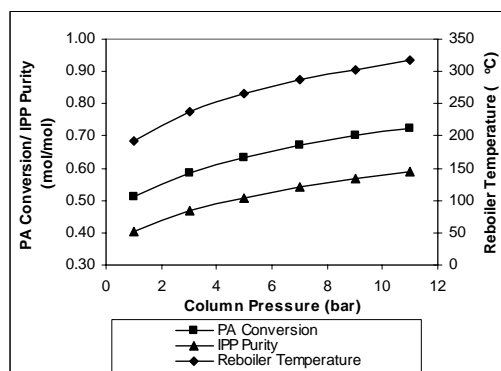
and palmitic acid to the same stage in the middle part of the reactive zone. Among the two-feed configurations, arrangement (b) gave the highest conversion. Thus, the column with two feeds right above and below the reactive zone is recommended and used in the further simulations.

Catalyst Mass

For equilibrium limited system like esterification reaction, excess catalyst may result in product decomposition when it is inappropriately located. In the present study, the minimum catalyst requirements was determined by simulating a series of isothermal plug flow reactors and ideal separators in series (HETES concept by D'Amico *et al.* (1990)). Four reactors containing 8 kg of catalyst were required for 92% acid conversion. The rate-based simulations of the same process required 10 kg of catalyst, an amount approximately 25% in excess of the ideal quantity (8 kg). The actual catalyst mass is 20-30 % greater than the minimum amount calculated using the ideal reactor-separator train because each reactive stage does not operate isothermally nor does it completely separate products from reactants. Adiabatic operation and imperfect separation are normal (Subawalla and Fair, 1999). The results indicate that the catalyst volume can be estimated with reasonable accuracy using the HETES concept and catalyst of 10 kg will be used in further simulations.

Number of Theoretical Stages

A short-cut Fenke-Underwood calculation with IPA as a light key component and IPP as the heavy key component indicated that only

TABLE 2   Effect of feed points location to the PA conversion and IPP purity.

Column Setup	(a)	(b)	(c)
	Rectifying Zone / Feed Stage: 4 IPA + PA / Reactive Zone / Stripping Zone	PA Feed Stage: 3 / Feed Stage: 4 IPA	PA Feed Stage: 2 / Feed Stage: 5 IPA
Conversion	0.65	0.68	0.66
Ester Purity	0.50	0.52	0.51
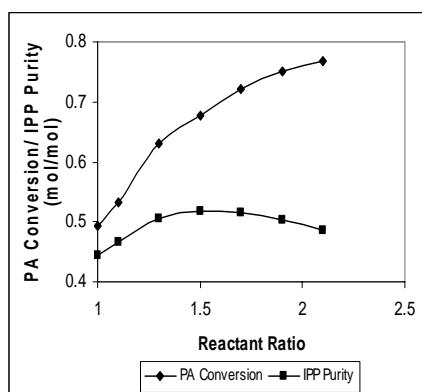
FIGURE 5 Effect of reactant ratio to the PA conversion and IPP purity

one theoretical stage is required. This result has been confirmed with a rigorous non-reactive column simulation. The easy separation of this system is due to the significant differences between their relative volatilities. The rate-based model Ratefrac was used to study the effect of number of rectifying and stripping stages to the column performance. One can observe from Figure 6 that the PA conversion does not change significantly even the number of rectifying stages increases. The concentrations of the PA and IPP can be ignored while the concentrations of the IPA and H_2O remain unchanged. IPA and H_2O cannot be separated effectively using rectifying stages because of the miscible system of IPA-H_2O. A special system such as membrane unit should be

applied for this purpose. Thus, it is not necessary to provide extra stages at the top of RD column due to the limited effects by introducing rectifying stages. Similar to the case in rectifying stages, the increase in number of stripping stages does not affect thePA conversion and the IPP purity (Figure 7). Although increasing the stripping stages up to 20 stages could minimize IPA loss with the IPP product, stripping stages are not preferable to be added because the loss of IPA could be minimized and recovered more efficiently with a flash unit.

Reactive Zone Height and Column Diameter

For reactive distillation column, the diameter of the column is determined by the flooding velocity, vapor-liquid traffic, pressure drop and packing catalyst density (catalyst mass per unit column volume). On the other hand, the reactive zone height depends on the catalyst mass, packing catalyst density and column diameter. Fenske-Underwood method was used to estimate initial reflux requirements for a nonreactive column fed with the prereacted equilibrium mixture as a reactive column. The minimum reflux ratio predicted using this method was 0.71. A reflux ratio of 0.84 (20% greater than the minimum) was used for our initial estimate and determined a preliminary column diameter (0.105 meter) at 80% flood (maximum permissible vapor velocity). The catalyst volume was calculated from the initial catalyst mass (10 kg) and catalytic packing
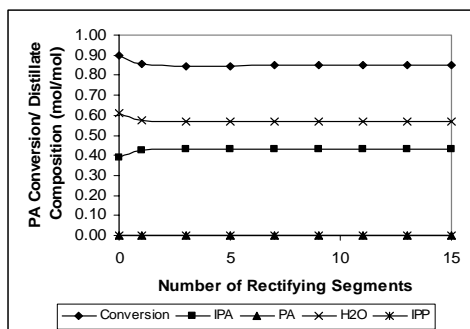
FIGURE 6 Effect of number of rectifying segments to the PA conversion and distillate composition.

FIGURE 7 Effect of number of stripping segments to the PA conversion and bottom composition.

density (155 kg/m^3) and used it to estimate the reactive zone height (8 m). Since catalytic packing HETP values are 1 m, the corresponding number of reactive stages is equivalent to 8 stages.

The initial estimates of rectifying, reactive and stripping stages were used to simulate a reactive distillation column and found that the conversion of 92% could be obtained. The procedure recommended by Subawalla and Fair (1999) was followed and kept increasing the reflux ratio until there was a negligible increase in conversion. One can find that the conversion did not change even though we kept increasing the reflux ratio. Hence, 10 kg of catalyst is accommodated in a reactive distillation column with diameter of 0.105 m and packed height of 8 m.

Conclusion

The heterogeneous kinetic model was incorporated into the process simulator Aspen Plus (Aspen Ratefrac). The influences of several important design parameters were investigated. It was found that it is viable to carry out the IPP synthesis in a reactive distillation column without adding the rectifying and stripping sections. It was shown that a reactive distillation column with diameter of 0.105 m, catalyst bed height of 8 m containing 10 kg of zinc acetate supported on functionalized silica gel, is necessary for total molar feed rate of 50 mol/hr. The resulting conversion is 92 %. A process proposed could serve as the basis of pilot plant scale-up of the reactive distillation unit. However, work on the IPP reactive distillation system is still in progress. Future developments will comprise an experimental data validation to determine the reliable model
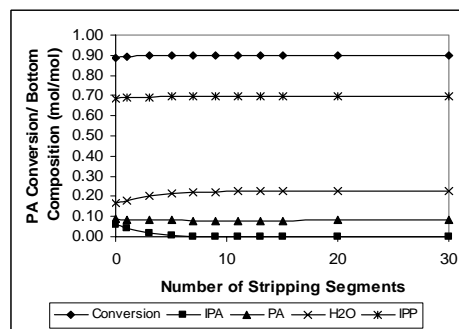
in order to ease the process scaling up to industrial scale.

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