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REACTIVE PACKED BUBBLE COLUMN FOR THE SYNTHESIS OF ISOPROPYL MYRISTATE

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Abstract
In this paper conceptual designs for the esterification of myristic acid with isopropanol through reactive distillation (packed and tray column) and bubble column are constructed, which are evaluated against the batch process based on required reaction volumes. The required reactor volume can be decreased with 27 or 79 %, allowing a maximum temperature of respectively 170 and 220°C, using a packed reactive distillation column. Using a tray reactive distillation column and a maximum temperature of 220°C, the required reactor volume can be decreased with 93 %. Due to the less favourable mass transfer characteristics of the bubble column, in here the required reactor volume can only be decreased with 78%. When a temperature of 220°C is allowed in the column, the tray reactive distillation is the preferable process for the esterification of myristic acid isopropanol, based on the required reaction volumes. The influence of the maximum column temperature and the influence of a larger liquid hold-up per stage as a result of a different column configuration are of equal importance for the required reaction volume.

Keywords: Fatty acids, Esterification, Reactive distillation, Bubble column, Conceptual design

1. Introduction

Fatty acid esters are natural-based chemicals used among other things in cosmetics, plastics and surfactants. Nowadays fatty esters are produced in batch reactors using strong acids like sulphuric acid as catalyst. Their production processes involve costly separations, large energy consumption and the production of polluting by-products. Because of equilibrium limitations high conversions can be only obtained by using a large excess of alcohol. For a more competitive process reactive distillation is considered a promising technique because the integration of reaction and separation in one unit means significant savings in equipment and operation costs.[1,2] Information on the esterification of long chain carboxylic acids such as fatty acids by reactive distillation is scarce. A few processes with various fatty esters and alcohols are described.[3-11] Most of them refer to methanol and primary alcohols. However, for the cosmetics industry the main fatty acid esters of interest are based on isopropanol, of which the typical reaction rates are 10-100 times lower compared to methanol and primary alcohols, causing excessive required reaction volumes. The available liquid hold-up in a column can be improved by looking at a reactive packed bubble column instead of reactive distillation.

The overall objective of this work is the establishment of a conceptual design for a multi-product reactive packed bubble column process for the synthesis of isopropanol based fatty acid esters, and evaluation of its attractiveness compared to the current batch technology and reactive distillation. For this purpose this study presents the development of a process model for the esterification of myristic acid with isopropanol. Furthermore, a parameter optimisation is performed to investigate the influence of the different process parameters. Finally all results are integrated in conceptual designs for the industrial scale packed and tray reactive distillation and reactive bubble column process, which are evaluated against the batch process.

2. Process Modelling

The process is attractive for the industry when a 99.0% conversion of myristic acid and a 99.0% product purity is obtained. The input parameters of the feed streams are based on a production

capacity of 1000 kg/hr (3697 mol/hr) ester, which is representative for an industrial process[11] and 99% conversion of the myristic acid. The kinetics of the reaction were experimentally determined[13].

Results are obtained by Aspen Plus simulations using the NRTL property model with the NRTL parameters taken from Aspen Plus. The packing used in the packed reactive distillation column is the Sulzer BX packing. The data for this packing is already included in the software. The number of stages is taken equal to the typical HETP values of ≈ 0.2 m^{-1} reported in the literature.The column diameter has been estimated using the commercial program SULPAK 3.1 from Sulzer Chemtech. The preferred operating point is situated at 80% capacity in proportion to flooding. This results in a diameter of 0.30 metres. For the tray column, the Aspen Plus the tray sizing section indicated that a diameter of 0.25 metres is a good choice. The bubble column is preferable operated in the homogeneous flow regime to ensure a large interfacial area which is beneficial for the mass transfer and subsequently the reaction rate. Lakota et al.[14] and Spicka et al.[15] reported that in the presence of internals the homogeneous regime is present up to a superficial gas velocity of 0.09 m s^{-1}. With this velocity and the production capacity of 1000 kg hr^{-1} isopropyl myristate, the column diameter is calculated. The liquid hold-up for the packed reactive distillation column is calculated in Aspen Plus using the relations of Stichlmair[16] For the tray reactive distillation column the liquid hold-up is calculated using the relations of Zuiderweg. [17] For the bubble column the liquid hold-up is calculated from the gas hold-up.[18]

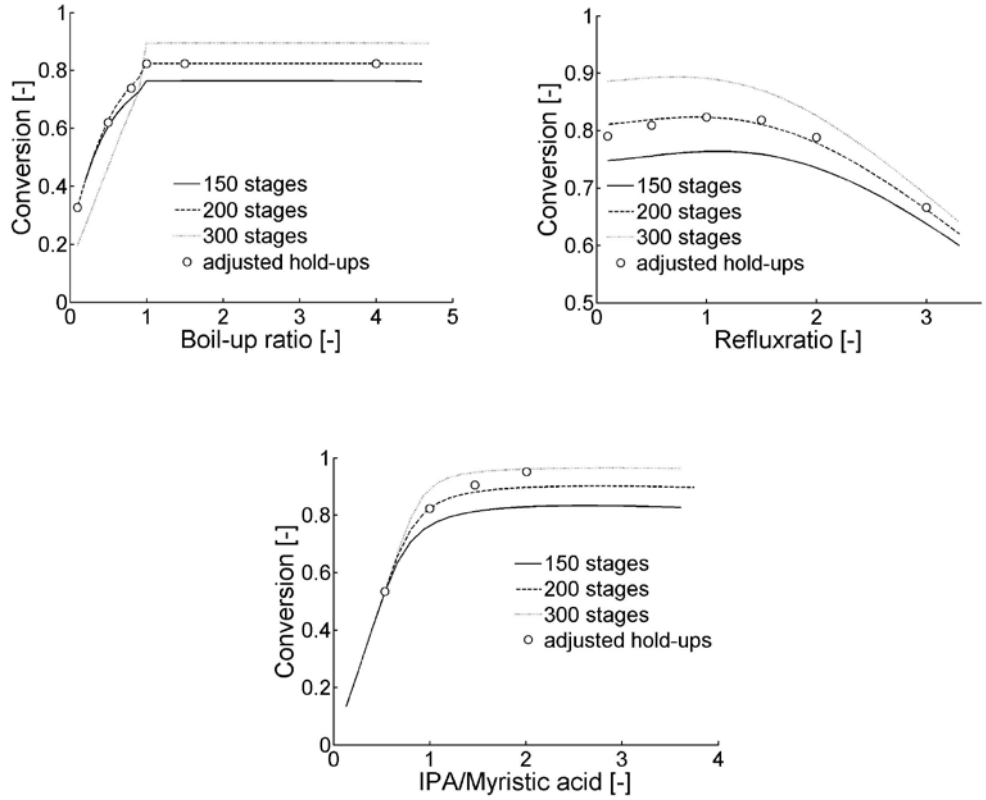

Figure 1. Influence of the boil-up ratio, reflux ratio and IPA/Myristic acid feed ratio on the conversion

3. Optimisation & Design

3.1 Packed Reactive Distillation column

In this simulation the influence of the following parameters is studied: Myristic acid to isopropanol feed ratio, pressure, catalyst concentration, boil-up ratio and reflux ratio. Three different number of stages are evaluated: 150, 200 and 300. In Figure 1 the influences are shown. First the parameters which cannot be optimised to obtain complete conversion are varied at constant stage liquid hold-up: Myristic acid to isopropanol feed ratio, boil-up ratio and reflux ratio. The results are verified by several simulations in which the average stage hold-up is adjusted to the operating conditions (e.g. feed flows,

pressure). For all parameters, except the reflux ratio, holds that an increase in the values of the parameter results in an increase of the conversion, until a maximum value is reached. For the reflux ratio this is a rather flat optimum laying around unity, depending of the number of stages. From these results suitable values can be selected for these parameters:

- The optimal reflux ratio is one.
- The optimal boil-up ratio is one; higher boil-up ratios do not result in a significant higher conversion. While increasing the boil-up ratio further, a maximum increase in conversion of 0.06% can be obtained, only more energy is required.
- The optimal ipa/myristic acid feed ratio is 1.5: higher ratios can result in an increase in conversion of approximately 2% but then more isopropanol is required which also results in a higher energy consumption.

The remaining parameters (number of stages, pressure and catalyst concentration) should be used to optimise the process further. These parameters are varied while the reflux ratio is 1, the boil-up ratio is 1 and the ipa/ma feed ratio is 1.5.

Higher catalyst concentrations result in higher conversion. However, the catalyst concentration cannot be increased endlessly. Therefore a catalyst concentration of 0.1 M is selected. This corresponds with 2.2 weight percent of the myristic acid amount, which is assumed to be applicable. With this catalyst concentration, a good combination of the pressure and number of stages needs to be found. In Figure 2 the conversion versus number of stages is given for different pressures. The reboiler temperature is set to 170˚C or 220˚C by changing the boilup-ratio. At low pressures the amount of stages has to be high, and with a small number of stages the pressure has to be high. An optimal combination can be found in the circled area. In this area 99% conversion can be obtained with the lowest possible number of stages and pressure. An operating pressure of 7 and 15 bar, respectively for the temperature restriction of 170˚C and 220˚C is chosen. Higher pressures hardly influence the number of stages to reach the same conversion of 99%.

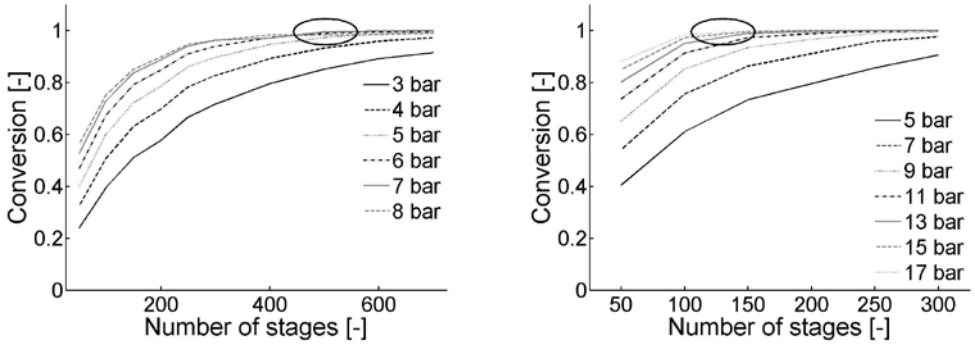

Figure 2. Influence of the pressure on the conversion while the temperature is restricted to a maximum of 170˚C or 220˚C

At the chosen pressure the exact number of stages to obtain 99% is determined. For the temperature restriction of 170˚C this results in 379 reactive stages with an average liquid hold-up per stage of 1.28 L. For the temperature restriction of 220˚C this results in 108 reactive stages with an average liquid hold-up per stage of 1.42 L. In Table 1 an overview is given of the resulting dimensions of the conceptual design of a packed reactive distillation column with two possible temperature restrictions, namely 170˚C and 220˚C. When the temperature restriction is 170˚C the height of the reactive section of the column is 76 metres, which is not desired in this application. With a temperature restriction of 220˚C the height of the reactive section becomes 22 metres, which is more realistic. However, first it should be investigated if higher temperatures are allowed at this short residence times.

A way to decrease the height of the column further is to increase the liquid hold-up per stage. Now, the liquid volume, in which the reaction takes place, is only 10% of the total volume. It is expected that with larger liquid hold-ups the total volume decreases as well as the column height. The liquid hold-up

can be increased by using a tray reactive distillation column or a reactive bubble column. These will be evaluated in the next paragraphs.

3.2 Tray Reactive Distillation column

For the tray column the outcome of the parameter optimisation will be the same as for the packed column. Only the internals have changed, which results in a different number and size of equilibrium stages. Therefore only the influence of the pressure on the number of stages is investigated. In Figure 3 the conversion versus number of stages is given for different pressures. The reboiler temperature is set to 220˚C by changing the boilup-ratio. At low pressures the number of stages has to be high, and with a small number of stages the pressure has to be high. An optimal combination can be found in the circled area. In this area 99% conversion can be obtained with the lowest possible number of stages and pressure. An operating pressure of 15 bar is chosen. Higher pressures hardly have any influence on the number of stages to reach the same conversion of 99%. This is the same operating pressure as for the packed column. At a pressure of 16 bar, the average increase in conversion is 0.3%, depending of the number of stages. The same effect of thermodynamics on the conversion is seen as for the packed column.

At the chosen pressure the exact number of stages to obtain 99% conversion is determined. This results in 22 reactive stages with an average liquid hold-up per stage of 9.57 L and a pressure of 15 bar. In Table 1 an overview is given of the resulting dimensions of the conceptual design of a tray reactive distillation column with a temperature restriction of 220˚C. The resulting liquid volume is 40% larger compared to the packed column. At small values for the number of stages the number of equilibrium stages does play a role. The tray column contains a lower number of stages than the packed column (22 versus 108), therefore the required liquid volume is larger than in the packed column. The column volume has decreased with 65% compared with the packed column. This results from the fact that the used liquid hold-up of 39% is much higher than the 10% for the packed column. The liquid hold-up can be increased even more by using a reactive bubble column.

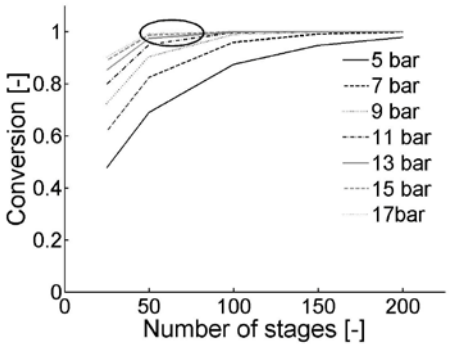

Figure 3. Influence of the pressure on the conversion in the tray column

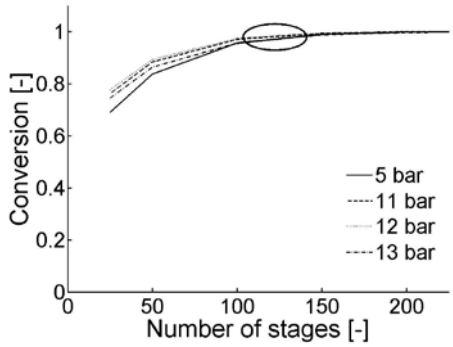

Figure 4. Influence of the pressure on the conversion the bubble column

3.3 Packed reactive Bubble Column

For the bubble column it will also be assumed that the outcome of a parameter optimisation will be the same as for the distillation column. Only the internals have changed. Therefore only the influence of the pressure on the number of stages is investigated.

In Figure 4 the conversion versus number of stages is given for different pressures. The reboiler temperature is set to 220˚C by changing the boilup-ratio. At low pressures the number of stages has to be high, and with a small number of stages the pressure has to be high. It can be seen that the pressure does not have a large influence on the number of stages as in the reactive distillation. For the bubble column the diameter depends on the pressure: at higher pressure the diameter decreases, thus without a decreasing number of stages the volume already decreases because of the diameter. A suitable combination can be found in the circled area. In this area 99% conversion can be obtained with the lowest possible number of stages and pressure. An operating pressure of 12 bar is chosen, this is the optimal pressure: at higher pressures the conversion decreases again. This is a lower operating pressure as for the packed column. This can be explained by the difference in the activity

coefficient of water. In the bubble column the activity coefficient of water is lower than in the reactive distillation. At 5 bar it has already a value of 2.0 in a part of the column, while in the reactive distillation this is obtained at 19 bar. Apparently, the slow mass transfer inhibits the liquid being pushed out of the liquid phase to the vapour phase. At the chosen pressure the exact number of stages to obtain 99% conversion is determined. This results in 115 reactive stages with an average liquid hold-up per stage of 40.53 L and a pressure of 12 bar. In Table 1 an overview is given of the resulting dimensions of the conceptual design of bubble column with a temperature restriction of 220˚C.

The resulting volume is larger than the reactive distillation columns, although the liquid hold-up has increased enormously to 73%. The larger required total liquid hold-up can be explained by the less favourable mass transfer characteristics of the bubble column compared to reactive distillation.

Table 1. Results conceptual design

	Packed Column		Tray Column	Bubble Colum
	170˚C	220˚C	220˚C	220˚C
Pressure [bar]	7	15	15	12
Reactive stage [-]	379	108	22	115
Column height [m]	76	22	11	23
Liquid hold-up per stage [L]	1.28	1.42	9.57	10.53
Total liquid hold-up [m^3]	0.49	0.15	0.21	1.21
Total volume [m^3]	5.36	1.53	0.54	1.63

3.4 Batch Process

Little has been published on the production of alkyl esters of fatty acids. Zhou[11] described a semi-batch process for the synthesis of methyl oleate, consisting of a reactor and a condenser or rectifying column. To prevent colouration of isopropyl myristate the temperature should not exceed 170˚C [3,10]. The estimation of the reaction volume is made based on the batch time, production capacity and the density of isopropyl myristate, assuming that the concentration of isopropanol is negligible due to the continuous feed and recycle. Depending on the batch time, the reaction volume will vary from 6 to 9 cubic metres. For the comparison the average of these batch times (ten hours) will be used.[19,20]

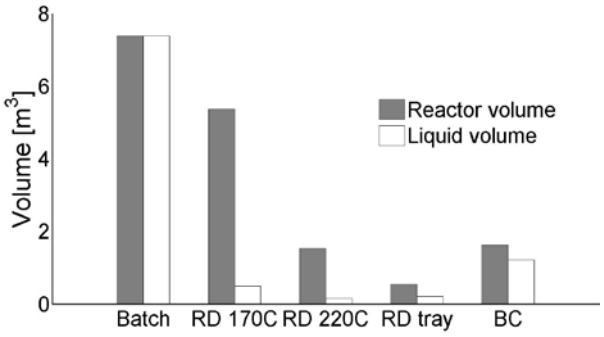

Figure 5, Required reaction and liquid volumes in the batch process and continuous processes

4. Comparison

In Figure 5 the required reaction volumes and the corresponding liquid volumes of the batch process, the packed reactive distillation column with a temperature restriction of 170˚C and 220˚C and the tray reactive distillation column with a temperature restriction of 220˚C, as discussed before, are depicted. The total required reaction volume for the reactive distillation with a temperature restriction of 170˚C has decreased with 27% compared to the reaction volume in the batch process. Despite this decrease in volume, the height of the reactive distillation column is 76 metres, which is too high to realise. When the temperature restriction is 220˚C instead of 170˚C, the reaction volume can be decreased even

more (79% in relation to the reaction volume in the batch process), and the height of the reactive distillation column is now more realistic: 22 metres. However, first it should be investigated if higher temperatures are allowed at these short residence times.

The resulting liquid volume of the tray column is 40% larger compared to the packed column. Unlike stated before, at a small number of stages the number of equilibrium stages does play a role, therefore the required liquid volume is larger than in the packed column. The column volume has decreased with 65% compared to the packed column, and with 93% compared to the batch process. This results from the fact that the used liquid hold-up of 39% is higher than the 10% for the packed column.

It was expected that the required total liquid volume of the bubble column would be smaller than the reactive distillation column, due to the higher hold-up. However the required reactor volume has only decreased with 78% compared to the batch process, which is most likely caused by the less favourable mass transfer characteristics of the bubble column. When a temperature of 220˚C is allowed in the column, the tray reactive distillation is the preferable process for the esterification of myristic acid isopropanol, based on the required reaction volumes.

5. Conclusions

A conceptual design for the industrial scale reactive distillation process (packed and tray column) for the esterification of myristic acid with isopropanol was constructed and evaluated against the batch process. The required reaction volume can be decreased with 27 or 79%, allowing a maximum temperature of respectively 170 and 220˚C, using a packed reactive distillation. Using a reactive distillation tray column and a maximum temperature of 220˚C, the required reactor volume can be decreased with 93%. Due to the less favourable mass transfer characteristics of the bubble column, the required reaction volume can only be decreased with 78%. When a temperature of 220˚C is allowed in the column, the tray reactive distillation is the preferable process for the esterification of myristic acid isopropanol, based on the required reaction volumes.

References

1. C. Noeres, *Chem. Eng. Process.,* 43(2004) 43 421-434
2. G.P. Towler and S.J. Frey, *Reactive Separation Process*, Taylor & Francis (2002) 18-50
3. H. Bock et al., *Chem. Eng. Process.*, 36(1997) 101-109
4. L.M. Jeromin, N. Bremus, and E. Peukert, *Fette, Seifen, Anstrichmittel*, 83(1981) 493-504
5. B. Schleper, et al. *Chem. Ing. Tech.,* 62(1990) 226-227
6. F. Omota, et al. *Chem. Eng. Sc,.* 58(2003) 3159-3174
7. F. Omota etal. *Chem. Eng. Sc,* 58(2003) 3175-3185
8. S. Chin et al., *International Journal of Chemical Reactor Engineering,* 4(2006) 1-17
9. S. Bhatia et al., *Chem. Eng Sc,* 61(2006) 7436-7447
10. S. Bhatia et al., *Comp. Chem. Eng.,* 31(2007) 1187-1198
11. M. Zhou, *Modelisation de reacteurs d'esterification fonctionnement semi-continu et continu,* Thesis, L'institut national polytechnique de Toulouse (1983)
12. S. Steinigeweg and J. Gmehling, *Ind. Eng. Chem. Res,* 42(2003) 3612-3619
13. M.C. de Jong et al., *Applied Catalysis A: General,* 365(2009) *141-147*
14. A. Lakota et al., *Acta Chim. Slov.* 48(2001) 453-468
15. P. Spicka et al, *Chem. Eng. Sc.,* 54(1999) 5127-5137
16. J. Stichlmair, et al., *Gas Separation & Purification*, 3(1989) 19-28
17. F.J. Zuiderweg, *Chem. Eng. Sc.,* 37(1982) 1441-1464
18. S. Sawant et al, *Chem. Eng. J*., 18(1979) 143-149
19. D. Packet, *Email communication*, 2009
20. H. Roessler, *Email communication*, 2009