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2-Methylpropylacetate synthesis via catalytic distillation

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Abstract

The paper deals with a 2-methylpropylacetate synthesis process development. The process is based on esterification of acetic acid with 2-methylpropanol by the reactive distillation method. A column in which separation of the reaction products takes place together with esterification in catalytic active separation packing is utilized in this process. Computer simulation of catalytic distillation has been performed to study the process and to evaluate the pilot plant experimental data. KATAPAK® S structural packing was used in the reaction zone, while stripping and rectifying sections of the column were packed by CY® packing. A good agreement between the simulation results and pilot plant data has been achieved. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 2-Methylpropylacetate; Esterification; Reactive distillation; Simulation; Experiment

1. Introduction

2-Methylpropylacetate is a solvent widely used in chemical industry. Its applicability as an extraction agent or a component of paint-solvents, adhesives, etc. is based on its extraordinary ability to dissolve both polar and non-polar compounds. Commercial technologies producing this acetate usually utilize the equilibrium reaction between alcohol and acetic acid. Esterification is traditionally catalyzed by acidic agents, e.g. sulphuric acid, *p*-toluenesulfonic acid, etc. Recently, heterogeneous catalysts like ion exchange resins were also used for this purpose. There are several problems resulting from the use of the liquid acidic catalysts, the main among them being severe corrosion problems as well as some difficulties with waste disposal. Furthermore, to increase conversion of starting components, either an excess of alcohol must be used, or at least one of the products must be constantly removed from the reaction system because the esterification of acetic acid by 2-methylpropylalcohol is a reversible reaction.

Solid acids, the typical example of which is a strongly acidic ion exchange resin, avoids the problems mentioned above, when used as the liquid phase esterification catalysts. The use of them can also simplify subsequent product separation process. Another solid catalyst, e.g. inorganic heteropolyacids, can also be utilized mainly in the gas phase esterification. But higher reaction temperature, which is inevitable in the gas phase reaction, can cause the alcohol to ether dehydration. This side reaction brings some operational difficulties [1].

To simplify the esterification process known in the art, a research program, aimed at integration of the esterification equilibrium reaction and the reaction mixture separation into one distillation column, was initiated (see [2]). Rectification of the reaction mixture, containing both reaction products (ester and water) and unreacted starting components (alcohol

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and acetic acid), can generally shift the chemical equilibrium in the desired direction. Nonetheless, this is very complicated in the case of 2-methylpropylacetate due to the existence of multiple azeotropes. Ternary heterogeneous azeotrope with minimum boiling point, containing ester, alcohol and water, is usually distilled out from the reaction mixture. Crude ester obtained this way must be dried and purified in a row of distillation columns. This is the main disadvantage of traditional technologies.

Catalytic distillation seems to be an energy-saving process with lower investment and operating costs in comparison to the traditional processes. A catalytic distillation technology configuration similar to that recommended in our previous study [3] for the butylacetate synthesis was utilized. There is a considerable difference between 2-methylpropanol and acetic acid boiling points (108.1 vs. 118.5°C). Therefore it seems to be necessary to inject starting components separately to different points. As 2-methylpropylacetate and acetic acid are compounds of almost the same boiling points, it is necessary to achieve total conversion of acetic acid to prevent difficulties with final product purification. Reaction water can be removed from the reaction zone in the form of heterogeneous azeotrope which distills overhead and can be separated into water and organic phases after condensation and subsequent cooling down to the ambient temperature. Major part of the organic phase (approximately 95%) is returned back to the top of the column as a reflux flow. Such arrangement makes it possible to overcome chemical equilibrium and to concentrate ester in the stripping section of the column. Pure ester is then withdrawn from the column reboiler.

2. Pilot plant experiments

A stainless steel apparatus operating continuously under atmospheric pressure was used to perform the esterification of acetic acid with 2-methylpropanol (Fig. 1). This apparatus consisted of a reboiler, the volume of which was 50 l, and a catalytic distillation column (i.d. 81 mm) equipped with a condenser and a phase separator. The catalytic distillation column consisted of the reaction zone equipped by structural packing KATAPAK® S with efficiency ca. three theoretical stages (TS) per meter containing 0.71 kg of an acidic ion exchange resin in H^+ form (5 equiv./kg). Measured value of esterification reaction rate for equimolar mixture of acetic acid and 2-methylpropanol at 60 and 80°C was 0.0131 and 0.033 kmol/h $kg_{cat.}$, respectively. The corresponding value of activation energy is equal to 45.2 kJ/mol.

Both the lower and upper separation zones were packed by high effective CY® structural packing, the efficiency of each zone (length 2 m) being equivalent to 20 TS. Both types of packing have been made by Sulzer Chemtech Winterthur.

Two different column arrangements were tested. A column with one feed point only was used in variant A, while variant B was characterized by the use of a column equipped with two feed points. The column was combined with a primary fixed bed reactor in both cases (see Fig. 1).

Nearly equimolar mixture of acetic acid and 2-methylpropanol was fed to an equilibrium reactor (operation temperature 70°C) packed with an acidic ion exchange resin catalyst (volume 9.50 l). The reaction mixture of almost equilibrium composition was

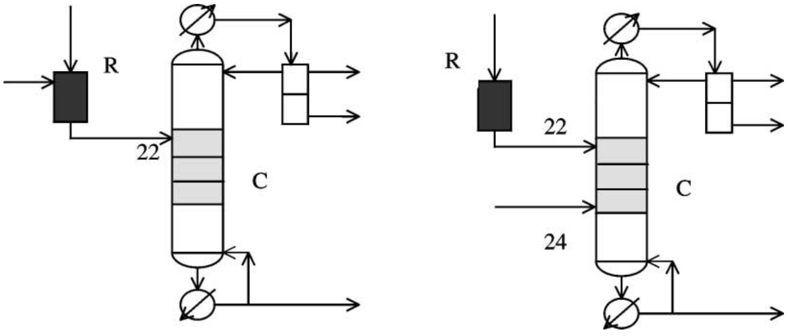

Fig. 1. Scheme of the catalytic distillation pilot plant, R: esterification fixed bed reactor, C: catalytic zone, variant A: left, variant B: right.

introduced into the reaction zone (variant A) while additional 2-methylpropanol was injected to the top edge of the lower separation zone in the amount assuring slight molar excess of 2-methylpropanol with respect to acetic acid (variant B).

The water formed by the reaction was taken off from the phase separator and the major part of the organic phase was refluxed back to the column, another part of the organic phase being withdrawn as distillate. Crude 2-methylpropylacetate (bottom product) was withdrawn at the rate assuring constant liquid holdup in reboiler. Typically, waterless product containing only a small amount of unreacted starting components was obtained. All technological streams were sampled and analyzed by GC method using HP 5890 II device. A 60 m/0.2 mm capillary column coated with SPB^{TM} (Supelco) was employed. An IS method using 2-methylbutanol as internal standard was applied.

3. Process simulation

Mathematical simulation of the catalytic distillation process producing 2-methylpropylacetate was made in the frame of this study. ASPEN PLUS software (model RADFRAC) was used by Smejkal [4] to simulate the process. Physicochemical properties, i.e. phase equilibrium, liquid- and vapor-phase enthalpies etc. were calculated utilizing the software data-base [5]. An equilibrium model assuming both vapor–liquid and chemical equilibrium on each TS of the reaction zone was applied. The NRTL equation was used for the calculation. The esterification equilibrium constant value was supposed to be 4.3. Pressure drop along the column was neglected and the pilot plant unit was simulated as operating under atmospheric pressure. The accuracy limit 10^{-6} was considered. Adequacy of these model assumptions was confirmed by the pilot plant experimental results.

4. Results and discussion

4.1. Start-up of the pilot plant unit

Before starting the collection of representative data, a stable column regime had to be achieved. Approximately constant distillate and bottom product compositions were the main stability criteria at the constant feed rate and composition. An example of time dependence of the distillate as well as bottom product compositions during the starting period are illustrated in Figs. 2 and 3. The column reboiler was full of 2-methylpropylacetate at the beginning of this experiment. As can be seen from the figure, it took about 50 h before the column had reached a steady state regime. After this time the concentration of unreacted 2-methylpropanol in the bottom stream dropped down to a minimum value depending on the molar excess of 2-methylpropanol in the feed stream.

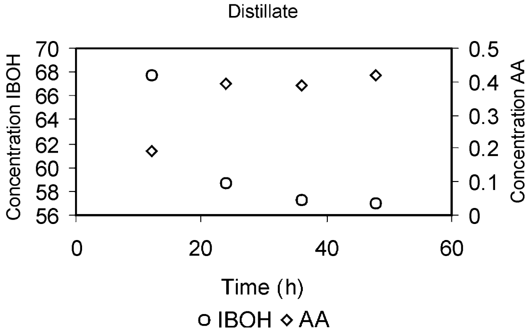

Fig. 2. Transient concentration of reaction components (wt.%) during start up period — distillate.

4.2. Effect of catalytic distillation column setup

Different results were obtained when columns of different setup were used. A comparison of typical results in both experimental variants are presented by Table 1. Lower acetic acid content in the bottom

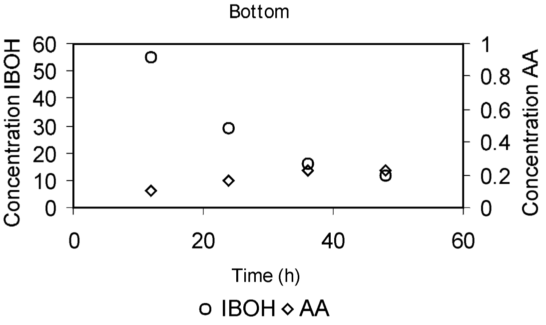

Fig. 3. Transient concentration of reaction components (wt.%) during start up period — bottom.

Table 1
Effect of catalytic distillation column setup on product composition (total efficiency of the column sections)

Parameter	Dimension	Variant A	Variant B
Catalyst weight	kg	0.71	1.07
Reaction mixture feed	kg/h	1.73	1.96
Second alcohol feed stream	kg/h	0	0.27
Alcohol molar excess	–	1.27	1.45
Reflux/total feed rates	–	5	5
Efficiency of column	TS		
Rectifying section		20	20
Reaction zone		3	5
Stripping section		20	11
Water phase flow rate	kg/h	0.36	0.28
Distillate flow rate	kg/h	0.21	0.29
Acetic acid concentration	wt.%	0.16	0.42
Alcohol concentration	wt.%	61.7	57.6
Ester concentration	wt.%	26.3	29.7
Bottom product flow rate	kg/h	1.08	1.50
Acetic acid concentration	wt.%	3.25	0.52
Alcohol concentration	wt.%	3.19	8.04
Ester concentration	wt.%	92.7	91.3

Table 2
Catalytic distillation column setup–comparison of experiment and simulation

Parameter (kg/h)	Simulation	Experiment
Feed of equilibrium mixture	1.775	1.775
Second alcohol feed stream	0.2932	0.2932
Distillate		
Organic phase	0.508	0.508
Water phase	1.57	1.546
Product stream	0.172	0.194
Reflux	8.9	9.3

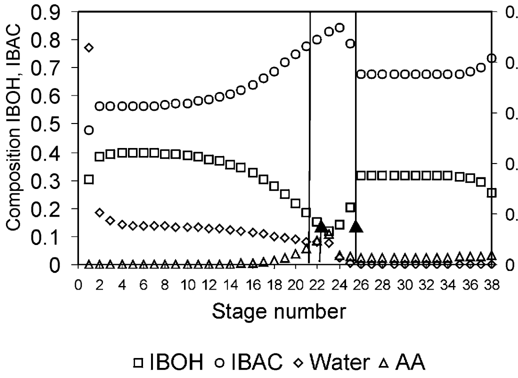

Fig. 4. Computed component mass fractions along the catalytic distillation column (variant B), details of the column setup — see Table 1.

product could be achieved when a major part of 2-methylpropanol was injected below the reaction section while partly converted mixture of acetic acid and 2-methylpropylacetate, containing only small amounts of 2-methylpropanol, was fed to the upper part of the reaction section (variant B). Lower efficiency of the stripping zone (11 vs. 20 TS) in this variant was the reason for somewhat higher alcohol content in the bottom product compared to variant A. The distillate composition was in both cases nearly the same because of the existence of 2-methylpropanol–2-methylpropylacetate–water ternary azeotrope. This azeotrope was split into organic and water phases after condensation and cooling to the ambient temperature, the water phase being withdrawn. The chemical reaction equilibrium was thus shifted in the desired direction. Major part of the organic phase was refluxed back to the top of the column. Only small stream of this organic phase was withdrawn as distillate.

4.3. Comparison of simulation and experiment

Pilot plant experimental data were compared with the simulation results of the catalytic distillation column (see Table 2). The feed stream flow rates, compositions and temperatures as well as relevant numbers of TS of the reactive and separation sections were taken as the input parameters for the process simulation. Fig. 4 illustrates an example of the reaction

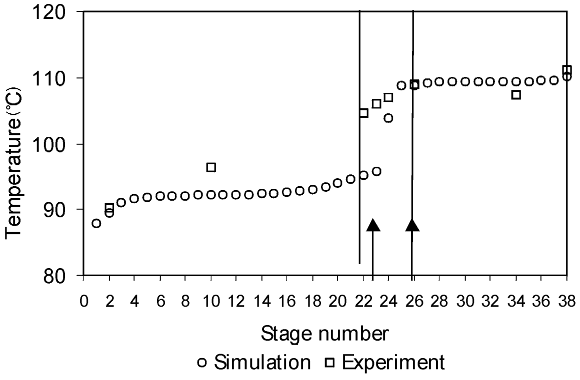

Fig. 5. Comparison of experimental and simulated axial temperature profiles in the catalytic distillation column (identical parameters as for Fig. 3).

mixture composition profile along the column for variant B. Vertical solid lines represent borders of the reaction zone inside the column and the arrow positions correspond to the feed stages. Both concentrations and axial temperature profiles were the numerical simulation results. As apparent from Fig. 5, relatively good agreement between simulated and experimental axial temperature profiles measured in the catalytic distillation column was observed. Stepwise character of the temperature profile inside the reaction zone was caused by location of the feed stages in them.

5. Conclusion

Viability of the new 2-methylpropylacetete process, based on catalytic distillation, has been verified by the pilot plant experiments as well as the simulation results. This process can be an alternative to the traditional technologies. In principle, the process is similar to that applied in the butylacetate synthesis which was described in our previous paper [3]. The arrangement in which dry product is withdrawn from the column bottom or reboiler while reaction water is distilled overhead in the form of heterogeneous azeotropic mixture is the common feature of both processes. In contrary to the butylacetate process, at least a part of the alcohol should be fed separately to the point below the acetic acid feed point to achieve optimum results in the 2-methylpropylacetate synthesis. Because the reaction mixture contains close boiling components, the use of highly efficient packing, mainly in the rectification section, is necessary to achieve high performance of the catalytic distillation column. Even at relatively low liquid load, it is difficult to obtain a product of commercial quality, particularly to meet very tough acetic acid concentration limit (0.01 mass% at maximum). The stripping section efficiency has no effect on acetic acid separation. Its concentration in the bottom product depends on the reaction conversion only. Though it is possible to increase conversion at the value close to 100% by increasing the height of the reaction zone, it seems unlikely to achieve the acetic acid concentration limit safely. Therefore final purification of the crude product will be necessary in an industrial 2-methylpropylacetate production via catalytic distillation.

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