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Experimental investigations of the production of methyl acetate in batch catalytic distillation process in the presence of Indion 180

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As a novel study, esterification of acetic acid with methanol has been studied in a simple batch reactive distillation apparatus to produce methyl acetate as main product and water as byproduct. Novel solid catalyst named Indion 180 has been used in this esterification process. The product methyl acetate can be distilled out in two ways namely sequential and simultaneous reactive distillation. In the simple distillation batch process, first the reaction is carried out till the equilibrium with total reflux of vapours, and then distillation is carried out where the vapours are condensed and collected separately with zero reflux. In the second case, simultaneous reaction and distillation processes are carried out. During these experiments, the dynamics of bubble point temperature of the reboiler is recorded and analyzed. From the experimental results it is found that the maximum purity of methyl acetate in instantaneous distillate of reaction followed by distillation and simultaneous reaction and distillation are 0.847 and 0.782, respectively, as analyzed by gas chromatography. From these studies it is found that a batch distillation apparatus itself can be used in certain way to produce the desired product for the case of methyl acetate production by monitoring the temperature regime of the reboiler.

Keywords: Dynamics, Esterification, Ion-Exchange Resin, Reactive Distillation

Methyl acetate is produced from a reaction between acetic acid and methanol as follows.

$$CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O \quad \dots (1)$$

Without catalyst, the liquid state reaction is very slow [1]. But with catalyst such as Amberlyst or Indion ion exchange resins, the reaction rate increases [1-7]. The reaction rate increases but it is a reversible reaction therefore conversion reaches a constant value after some reaction time. The reaction rate data shows a substantial dependence on catalyst loading and temperature of the reaction mixture. Hence the catalytic reaction kinetics is to be understood in depth in order to obtain high conversion of the reactants in manufacturing [8-11].

The esterification kinetics between acetic acid and methanol was studied in presence of Amberlyst 36 solid resin catalyst by Mekala *et al.* [12]. The effect of temperature, mole ratio, catalyst loading, catalyst particle size and agitation speed on the acetic acid conversion were studied in a batch reactor. Mekala & Goli studied the production of methyl acetate in a packed bed reactive distillation column[13], where the column has 3 meter height and 50 mm diameter. The effect of reboiler temperature, feed flow rates, reflux ratio on the conversion of acetic acid and methyl acetate purity were also studied. A general framework for the dynamic simulation and optimization of global batch synthesis has been developed by Elgue *et al.*[14]. The authors discussed the application of global batch synthesis to the optimization of a methyl acetate production process[14]. Experiments performed on a batch pilot plant allow validating the dynamic model. Hence, optimal tuning of the operating parameters of the reactive batch distillation was investigated by means of the dynamic optimization procedure.

In another report[15], the authors performed the simulations for synthesis of methyl decanoate in a semi batch reactive distillation. Two batch distillation columns namely SBD and i-SBD are considered. They observed that the energy savings is more in i-SBD compared to SBD. The capital savings is 36.61%. The production and purification of levulinic acid was studied in a continuous reactive distillation[16]. Various alternative designs performed for reactive distillation. They found that from their designs 23% reduction in cost of equipment and 24% in energy consumption when compared to conventional process. The esterification of oleic acid with glycerol performed in presence of low cost and efficient Indion catalyst by Diana *et al*. [17]. The catalyst performance was studied for different temperatures, catalyst loading and mole ratios. At optimal conditions an acid conversion was reported as 78%.

Industrially, the product of interest that is, methyl acetate should be separated in as pure form as possible. Reaction as shown in Eq. (1) tells that when the reaction proceeds, there would be a total of four components in the reaction mixture that is acetic acid, methanol, methyl acetate and water. Now, the manufacture of methyl acetate could be done in two different methods broadly: (i) Distillation after the reaction going to equilibrium and (ii) simultaneous distillation while the reaction is proceeding. Again there could be variation of each of these methods i.e., batch[14], semi batch[15] and continuous (column) reactive distillation[16] or the distillation followed by reaction.

Feasibility of separation by distillation should be assessed primarily from boiling points and vapour liquid equilibrium (VLE) diagrams. The boiling points of the components here are 56℃ (methyl acetate), 65℃ (methanol), 100℃ (water) and 118℃ (acetic acid). The molecular weights are 74 g/mol, 32g/mol, 18 g/mol and 60 g/mol, respectively. There is good possibility that the main product methyl acetate could be selectively distilled since the boiling point of it is the lowest of all the four components. But, the purity and recoverability of methyl acetate in distillate is affected by azoetrope formation and multi component VLE. The methyl acetate/methanol azeotropic composition is 81.3 wt% methyl acetate and 18.7wt% methanol.

Till now there are no studies available in the literature for the production of methyl acetate using simple distillation mode. In this paper, the experimental kinetics of multi-component distillation and simultaneous reactive distillation are presented for a batch process using simple distillation apparatus. The reaction is conducted at constant temperature till the equilibrium and the simple distillation is used to separate the components. In the second experiment the reaction and distillation are conducted in a simple batch distillation process. The interesting facts about the temporal variations of the composition of the distillate and residue are presented for the reactive batch distillation process.

Experimental Section

Chemicals

Methanol (purity=99% w/w) and Acetic acid (purity=99.95%w/w), supplied by SD Fine Chemicals Ltd. (Mumbai, India), were used in the present study. The solid acid catalyst, Indion 180, used for the esterification reaction was supplied by Ion-Exchange India Limited, Mumbai. Indion 180 has cross-linked three-dimensional structures of polymeric material, obtained by sulfonation of a copolymer of polystyrene and divinyl benzene (DVB). It is an opaque and dark grey colored solid spherical bead. The physical property of this catalyst is given in our earlier publication[6,11].

Experimental setup

The schematic diagram of a batch distillation apparatus used for conducting the experiments is shown in Fig. 1. It consists of a round bottom flask placed in a rota mantle with facility for magnetic stirring, electrical heating and temperature measurement by PT-100 thermocouple connected to a digital display with 0.1℃ resolution. There is a horizontal condenser connected to the top port of the reboiler flask. Water at room temperature is used as coolant (25℃). A collection vessel is provided for collecting the distillate.

Experimental procedure

The experiments were conducted in presence of the Indion 180 a novel catalyst in a batch reactive distillation in a simple distillation apparatus. Reactive distillation was carried out to produce methyl acetate from acetic acid and methanol using Indion 180 as a solid ion-exchange resin catalyst in a simple distillation apparatus as shown in Fig. 1. Unlike the reboiler-column combination, a simple distillation apparatus was used to conduct reactive distillation

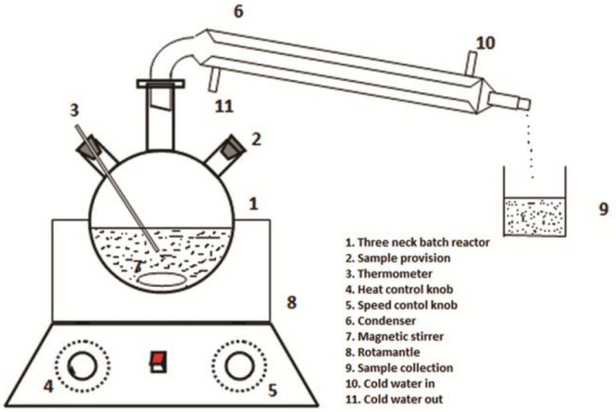

Fig. 1 — Schematic diagram of the batch distillation apparatus

where the vapours were condensed and collected as the catalytic reaction proceeds in the reboiler flask. The aim was to quantitatively measure the distillate or product purity in terms of the methyl acetate's mole fraction in it. The composition of instantaneous distillate, cumulative distillate and that of the reactant mixture in reboiler are monitored. Such data provided a very interesting experimental kinetics of simultaneous reactive distillation. In these experiments; the heat was supplied at an appropriate rate in order to maintain constant drop by drop condensation of distillate. The temperature of the mixture in round bottom flak was noted as a function of the time with the help of a thermocouple and digital indicator. The distillate and boiler flask samples were collected at various times or temperatures and analyzed using Gas Chromatography (GC) to determine the concentration of each of the four components.

Reaction followed by Distillation

The esterification reaction was carried out by taking 2.5 mol of pure acetic acid and 2.5 mol of methanol and catalyst (Indion 180) at loading of 0.025 g/cm^3 of the reaction mixture. Initially the reaction mixture was heated to 60°C and the catalyst was added. Based on a detailed kinetic study it was found that the conversion of the reactants goes to equilibrium within 3 h of time. The temperature is maintained at 60°C by controlling the heater in on/off mode. At end of 3 h, the reaction mixture was filtered to separate the catalyst particles. Now the resultant liquid mixture contains both the products (methyl acetate and water) and un-reacted reactants (acetic acid and methanol). This mixture is subjected to simple distillation. The second experiment was conducted at the same temperature of 60°C to study the reaction kinetics.

Simultaneous RD in simple distillation apparatus

The experiment was started by taking equal number of moles (2.5 mol each) of acetic acid and methanol and charging them to the round bottom flask. Immediately, catalyst particles were added to the reactant mixture with a pre-calculated catalyst loading of 0.025 g/cm^3. The glass flask or the reboiler was heated by supplying heat through an electric heater placed in the rota mantle, which surrounds the flask up to halfway of its volume. The liquid level in the flak was maintained below height of electrical heating coil to get the uniform heat supply to the reactor. Simultaneously the magnetic stirrer was switched on to maintain an rpm of 240 for the magnetic stirrer. These operating conditions ensured uniform heating and availability of catalyst in the reactant mixture. Simultaneously the distillate was obtained and analyzed for methyl acetate concentration with GC. The experiment was repeated at the same conditions as mentioned above to find the deviation of the experimental data.

Analysis

The samples were analyzed using gas chromatography (GC-2014 ATF, Schimadju, Japan.) equipped with a thermal conductivity detector. Porapak-Q (2 m length and 3.17 mm id) packed column was used to analyze the sample. High purity hydrogen gas was used as a carrier gas at a flow rate of 30.0 mL/min. The oven temperature was programmed at 323.15 K for 1 min and then raised from an initial value of 323.15 K to 443.15 K at a ramp rate of 10 K/min and was held at 443.15 K for 2 min. The detector temperature was maintained at 473.15 K.

Results and Discussion

Reaction followed by distillation

The heating during simple distillation was maintained and adjusted such that there was only a drop by drop condensation of distillate. The time taken for every 10°C raise in the temperature of the residue mixture was noted and it is represented graphically in Fig. 2. The initial mixture was at room temperature of about 25°C. As it was heated, the temperature increased up to 55°C and condensation started. During condensation the temperature seems to rise slowly. This is the regime II where methyl acetate gets distillates majorly. After, some more heating, there is a steeper increase in temperature. This is

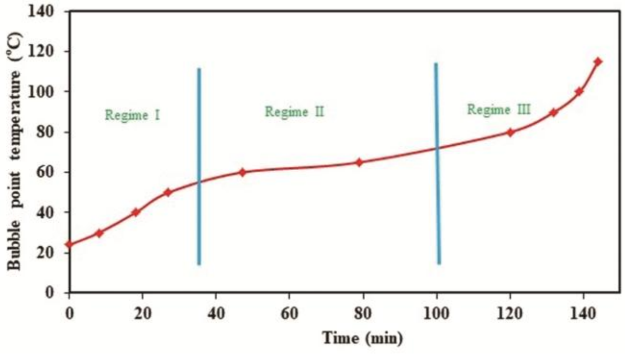

Fig. 2 — Residue's bubble point temperature versus time for case of reaction followed by distillation

because the high boiling components would be in higher fraction in the residue.

The composition of the residue as a function of time is recorded and represented in Fig. 3. The instantaneous composition of the distillate is represented in Fig. 4. Both these graphs give us a complete picture of the dynamics of distillation separation technique under quasi-equilibrium condition. These graphs are useful industrially to decide upon first cut as zone II. That is to say that the distillate collected between 55°C and 80°C offers higher purity of Methyl acetate. Beyond 80°C of the residue temperature, the concentration of methyl acetate would be very low. For further purification a second and third sequential simple distillation could be conducted.

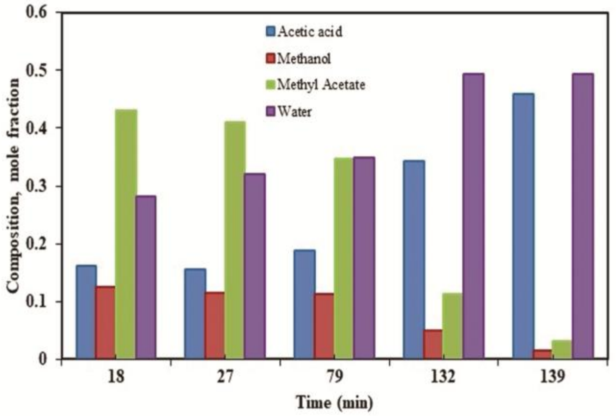

Fig. 3 — Composition of residue for the case of reaction followed by distillation

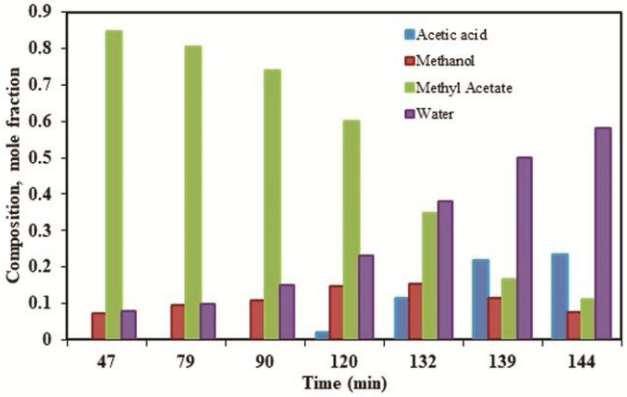

Fig. 4 — Composition of instantaneous distillate for the case of reaction followed by distillation

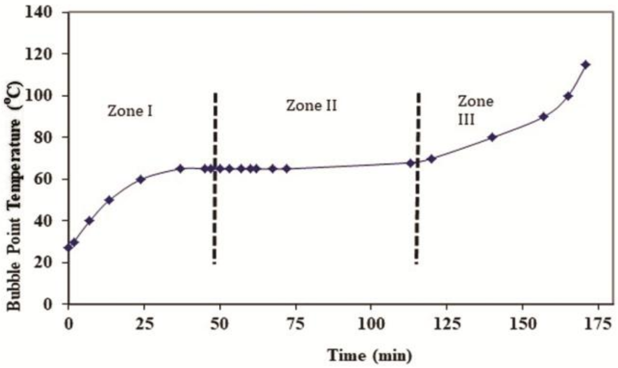

Fig. 5 — Residue's bubble point temperature versus time for simultaneous reaction and distillation

Simultaneous reaction and distillation

The resultant temperature variation of the residue in the flask is plotted against the time as shown in the Fig. 5. The temperature raised in the first zone and constant in the second zone. In the third zone suddenly the temperature raised to availability of high boiling acetic acid which comes lastly. Low boiling components have come first at low temperature; hence the temperature rose in the first zone, where as in the second zone the mixture of low and high boiling components separates.

The composition of residue in reboiler versus time is shown in Fig .6. As the reaction precedes the composition of the methyl acetate and water increased in the reboiler up to 180 min. After 180 min the methyl acetate composition could have decreased due to fast separation into vapor phase at solution temperature going much above its boiling point.

The composition of instantaneous distillate versus time is shown in Fig. 7. It can be observed that the mole fraction of methyl acetate is much higher (0.75) compared to the equilibrium mole fraction (0.345) obtained in a batch reactor. Such experimental dynamic data helps in designing large scale batch reactive distillation process.

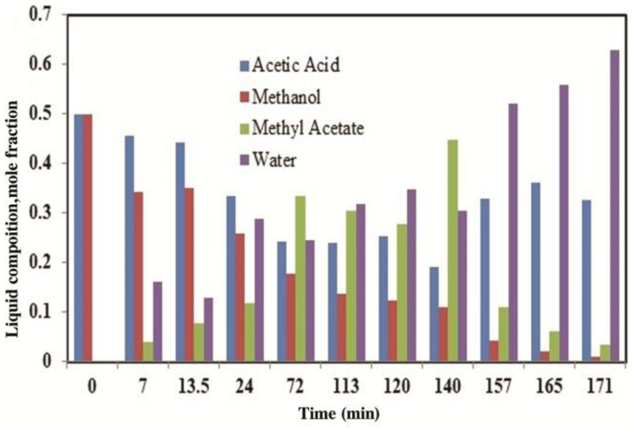

Fig. 6 — Composition of residue for simultaneous reaction and distillation

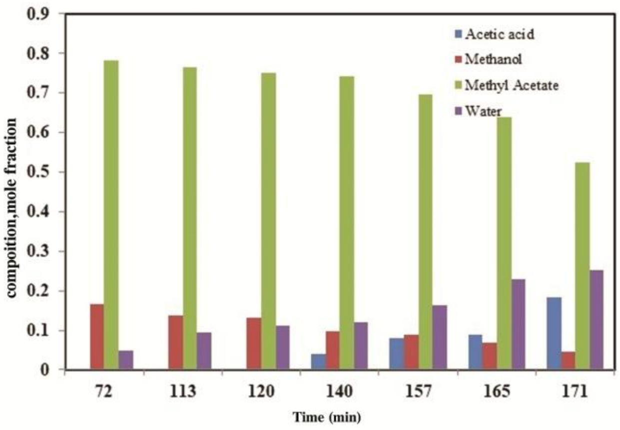

Fig. 7 — Composition of instantaneous distillate for simultaneous reaction and distillation

Conclusion

The production of the methyl acetate in presence of ion exchange resin catalyst Indion 180 in a simple batch distillation apparatus by two methods namely simultaneous and sequential reaction and distillation processes were reported. Mole fraction of methyl acetate in instantaneous distillate is the highest as 0.782 from sequential reactive distillation with 1:1 reactant mole ratio of acetic acid and methanol. Reactive distillation also presents interesting temperature and composition dynamics with regard to distilling the product. Methyl acetate could be produced in high purity by simple distillation conducted after reaction and it is found to be 0.847. From the experimental studies it was found that the purity of methyl acetate in instantaneous distillate of reaction followed by distillation and simultaneous reaction and distillation are comparable but the temperature dynamics of the reboiler has to be followed for an industrial process based on the choice.

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