Simulation and Parametric Study of the Innovative Process to Produce High Purity Isopropyl Acetate with Ethylene Oxide Hydration as an Auxiliary Reaction

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Abstract. Production of high purity isopropyl acetate by esterification is a difficult process since the equilibrium conversion is relatively low and there are azeotropes between isopropyl acetate with water and between isopropyl acetate with the reactants. In this research, an innovative process to produce high purity isopropyl acetate with auxiliary reaction of ethylene oxide hydration was proposed. The process consisted of a reactor and a simple distillation column. The auxiliary reaction abolished the water/isopropyl acetate azeotrope and shifted the esterification equilibrium to the right. Impacts of the reactor type, the feed temperature, the reflux ratio, and the bottoms rate were investigated by simulating the process in Aspen Plus software. The results revealed that the innovative IpAc production with auxiliary reaction of EO hydration gave very high esterification conversion (up to 99.8%) and very high purity of IpAc (up to 99.7%). These results were achieved when the reactor type was isothermal at feed temperature, the feed temperature was 77°C, the reflux ratio was 1, and the bottoms rate was 10 kmol/h.

1. Introduction
Isopropyl acetate (IpAc) is a solvent with a wide variety of manufacturing uses that is miscible with most other organic solvents, and moderately soluble in water. It is a component of some printing inks and perfumes [1]. IpAc commonly produced by esterification of isopropyl alcohol (IpA) with acetic acid (AcH) as

\[
\text{CH}_3\text{CHOHCH}_3 + \text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO(CH}_3)_2 + \text{H}_2\text{O}
\]

The equilibrium conversion of this reaction is around 79% at room temperature and become smaller as the temperature rises, since it is an exothermic reaction. This makes at the end of reaction process, the purity of IpAc is relatively low. There are also azeotropes in the mixture (Table 1) that makes the separation process much harder to get high purity IpAc.

Table 1. Azeotropes in the mixture

| Temp (°C) | Mole Fraction | IpA | AcH | IpAc | Water |
|----------|---------------|-----|-----|------|-------|
| 78.44    |               | 0.6053 | 0   | 0.3947 | 0     |
| 74.22    |               | 0.1848 | 0   | 0.4247 | 0.3905|
| 79.99    |               | 0.678  | 0   | 0     | 0.322 |
| 99.7     |               | 0     | 0.0999 | 0   | 0.9001 |
| 74.98    |               | 0     | 0   | 0.5248 | 0.4752|
Conventionally, IpAc can be readily removed from mixtures containing it, IpA and water, by using extractive distillation in which the extractive agent is a mixture of a polyol and one or higher boiling oxygenated, nitrogenous and/or sulfur containing organic compounds [2]. However, the cost of extractive distillation is relatively high, because there are additional cost to provide the extractive agent and the cost for additional solvent recovery column. Therefore, an innovative IpAc production method that may have lower cost is proposed in this research.

Based on the Table 1, high purity IpAc can be achieved by shifting the reaction equilibrium to the right, so the fraction of AcH and IpA in the mixture can be reduced to near zero, and removal of water. These two steps can be conducted simultaneously, because if water is removed from the mixture, the equilibrium will shift to the right naturally. The idea of innovative IpAc production is that the removal of water can be done by adding ethylene oxide (EO) which can react with water and produce ethylene glycol (EG) as

\[ C_2H_4O + H_2O \rightarrow (CH_2OH)_2 \]  

(2)

Because the equilibrium shifts to the right, a near 100% conversion of IpA and AcH can be achieved. Therefore the mixture after reaction process mainly contain EG and IpAc. Since there is no azeotrope between EG and IpAc, the separation process afterwards can be done in a simple distillation column with IpAc as distillate product and EG as bottom product. The present of auxiliary reaction of EO hydration is also worthwhile, because the product, EG, is valuable chemical which is used as an antifreeze and coolant, in hydraulic fluids, and in the manufacture of low-freezing dynamites and resins [3].

This study is a part of a research about innovative IpAc production. In this study, the innovative IpAc production was simulated using Aspen Plus to investigate its feasibility and to study the effects of the process parameters in steady state condition. Based on the result of this study, the next parts of the research, which are about process design optimization, dynamic behavior, and process control, can be conducted.

2. Base simulation

2.1. Kinetics model

The kinetic model for IpAc production through esterification that takes place in liquid phase, in the presence of Amberlyst 15 as heterogeneous catalyst is adapted as follows [4]

\[ r = m_{cat} \frac{k_f(a_{AcH}a_{IpA} - a_{AcH}a_{IpAc}K_{EQ}^{-1})}{(1 + K_{AcH}a_{AcH} + K_{IpA}a_{IpA} + K_{IpAc}a_{IpAc} + K_{water}a_{water})^2} \]  

(3)

where:

\[ k_f(kmol.kg_{cat}^{-1}.s^{-1}) = 7.667 \times 10^{-5} \exp(23.81 - \frac{68620.43}{RT}) \]

\[ K_{EQ} = 8.7 \]

\[ K_{AcH} = 0.1976 \]

\[ K_{IpA} = 0.2396 \]

\[ K_{IpAc} = 0.147 \]

\[ K_{water} = 0.5079 \]

The auxiliary reaction of EO hydration may also produce unwanted by-product of diethylene glycol and triethylene glycol. However, the rate of the side reaction is much lower than that of the main reaction and consequently, the effect of this side reaction can be neglected [5]. The kinetic model of EG production from EO hydration in liquid phase is adapted as follows [5]

\[ r(mol.cm^{-3}.s^{-1}) = 3.15 \times 10^5 \exp(-\frac{9547}{T})x_{EO}x_{water} \]  

(4)

2.2. Process simulation

Innovative IpAc production was simulated in ASPEN Plus software, using packed bed reactor and separation process in distillation column as shown in Figure 1. The properties method that was used in
this study was NRTL (Non-Random Two Liquid), which has been confirmed to be accurate in simulating a system containing IpA, AcH, water, IpAc, EO, and EG [4, 5].

![Figure 1. Process configuration of intensified IpAc production](image)

In the reactor, it is assumed that the catalyst bed has bed void fraction of 50% and density of 770 kg/m³ [4]. In the conventional extractive distillation process, with the extractive agent is a mixture of glycerine, DMFA, and ethanolamine, it is found that the extractive distillation column needs around 18 stages to get IpAc with the purity of 98% [2]. Therefore, in this simulation, number of stages in the distillation column was set to 18, so the result may be compared to the conventional process.

The process variables that were examined first were feed temperature and reactor type (adiabatic or isothermal at feed temperature). The method of examination was by manipulating one variable at the time, by keeping any other variables constant at the initial condition of simulation. The initial conditions of simulation are shown in Table 2. The next variables that were examined were reflux ratio and bottoms rate of distillation column. The method of examination was also by manipulating one variable at the time, at the best feed temperature and reactor type which gave maximum conversion of AcH, and by keeping any other variables constant at the initial condition.

| Parameters | Value | Units |
|------------|-------|-------|
| Feed | | |
| AcH mole-flow | 10 | kmol/h |
| IpA mole-flow | 10 | kmol/h |
| EO mole-flow | 10 | kmol/h |
| Reactor | | |
| Diameter | 5 | m |
| Length | 20 | m |
| Distillation Column | | |
| Number of stages | 18 | - |
| Reflux ratio | 3 | - |
| Bottoms Rate | 10 | kmol/h |

Note that the initial conditions are not the optimum conditions. The optimum conditions will be covered in the next study.

3. Results and discussion

3.1. The effect of the feed temperature in the adiabatic reactor

In the adiabatic reactor, the reaction system is heated by the heat of reactions. The reactions are quite exothermic so that the heat of reactions is plenty enough to change the phase in the reactor from liquid
The conversion of AcH in adiabatic reactor is 95.7% at room temperature and not significantly increased at lower temperature, so the effort to provide refrigerant to decrease the feed temperature until below room temperature is not worth it. Therefore, it can be concluded that the room temperature is the best feed temperature that give optimum AcH conversion in adiabatic reactor.

3.2. The effect of the feed temperature in the isothermal reactor

In the isothermal reactor, the heat of reactions is transferred to the cooling jacket, so that the reactor temperature is constant at the feed temperature. It can be seen in Figure 4, when the feed temperature is increased from room temperature to around 77°C, the conversions of AcH and EO are increased, because the rates of reactions are higher at higher temperature. Above 77°C, the phase in the reactor begins to change from liquid to vapor, and because the reactions occurred in liquid phase, the conversion of AcH and EO are greatly decreased.

The maximum conversion of AcH in isothermal reactor is 99.9% at 77°C. This is greater than the conversion of AcH in adiabatic reactor, because in isothermal reactor, the temperature is kept at
optimum reaction temperature and the phase in the reactor is maintained as liquid. Therefore, it can be concluded that the best type of reactor is isothermal at the feed temperature of 77°C.

### Figure 4

The effect of the feed temperature AcH and EO conversion in the isothermal reactor

### 3.3. The effect of the reflux ratio

The influence of the reflux ratio was investigated by fixing the reactor condition at optimum condition (isothermal at the feed temperature of 77°C) and any other parameters in distillation column at initial condition. It can be seen in Figure 5, when the reflux ratio is increased from 1 to 20, the reboiler duty is significantly increased, because there is more liquid that is recycled into the column and therefore more energy is needed to boil up the liquid and maintain the bottom flow rate at initial condition (10 kmol/h).

### Figure 5

The effect of the reflux ratio on reboiler duty

However, as can be seen in Figure 6, the increasing of reflux ratio does not significantly increase the molar composition and molar flow rate of IpAc at distillate and EG at bottom, because even at a low reflux ratio, the molar composition of IpAc at distillate and EG at bottom are already very close to its maximum value of 100%. Thus, it is more efficient if the distillation is operated at a low reflux ratio.
Figure 6. The effect of the reflux ratio on (a) molar flow rate and (b) molar composition

3.4. The effect of the bottoms rate

Figure 7 shows the influence of bottoms rate of distillation column on reboiler duty. The reboiler duty is decreased when the bottoms rate is increased, because the greater bottoms rate means the lesser liquid in the reboiler should be boiled up.

In Figure 8, it can be seen that when the bottoms rate is increased from 8 to 10 kmol/h, the more EG as heavy component flows to the bottom, leaving IpAc as main component at distillate. Therefore, the molar flow rate of EG at bottom and the molar composition of IpAc at distillate are increased.

Figure 7. The effect of the bottoms rate on reboiler duty
When the bottoms rate is greater than 10 kmol/h, the molar composition of IpAc at distillate is not significantly increased, since it is already very close to 100%. However, when the bottoms rate is greater than 10 kmol/h, IpAc begins to flow down to the bottom, so that the molar composition of EG at bottom and molar flow rate of IpAc at distillate are decreased.

![Figure 8](image1.png) ![Figure 8](image2.png)

**Figure 8.** The effect of the bottoms rate on (a) molar flow rate and (b) molar composition

From Figure 7 and 8, it can be concluded that the best bottoms rate is 10 kmol/h. It gives highest purity and molar flow rate of IpAc at distillate, highest purity and molar flowrate of EG at bottom, and relatively low reboiler duty.

### 3.5. Comparison

The innovative IpAc production is compared to the conventional configuration which is the combination of reactor and extractive distillation, without the auxiliary reaction of EO hydration. With the operating conditions that are shown in Table 3, by the innovative IpAc production, the AcH conversion of 99.8% and IpAc molar composition of 99.7% can be achieved. These results are better than the results by the conventional process which gives AcH conversion of 79% and IpAc molar composition of 98% [2].

| Table 3. Operating conditions that give maximum AcH conversion and maximum IpAc purity |
|---------------------------------|-----------------|----------------|
| **Parameters** | **Value** | **Units** |
| Feed Temperature | 77 | °C |
| Reactor Type | isothermal at feed temperature | - |
| Distillation Column | | |
| Reflux ratio | 1 | - |
| Bottoms Rate | 10 | kmol/h |

### 4. Conclusions

The simulation results revealed that the innovative IpAc production with auxiliary reaction of EO hydration is highly prospective. It gives very high esterification conversion (up to 99.8%) and very high purity of IpAc (up to 99.7%). These results are achieved when the reactor type is isothermal at feed temperature, the feed temperature is 77°C, the reflux ratio is 1, and the bottoms rate is 10 kmol/h.
Nomenclature

\( a_i \) = activity of component i
\( k_r \) = rate reaction constant
\( \text{K}_{\text{EQ}} \) = reaction equilibrium constant
\( K_i \) = adsorption constant of component i
\( R \) = ideal gas constant
\( T \) = temperature

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