

## Improvement of separation process of synthesizing MIBK by the isopropanol one-step method

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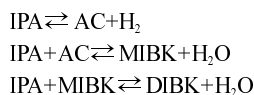
**Abstract**—The separation process of synthesizing MIBK (methyl isobutyl ketone) by an isopropanol one-step method, in which the multi-component mixture contains AC (acetone), IPA (isopropanol), water, MIBK, MIBC (methyl isobutyl carbinol), DIBK (di-isobutyl ketone), etc., was studied. As a high-purity of MIBK over 99.5 wt% is required in industry, the development of an effective separation method is urgent. In this work, first, by means of VLE (vapor-liquid equilibrium) experiments and PROII simulation, the possible azeotropes formed in the investigated system were tested. Then, the separation process was simulated with the result that the calculated and designed values were in good agreement, which indicated that the calculated results were reliable. On this basis, the original separation process was improved. In the original separation process, the yield of MIBK for a concentration of MIBK over 99.5 wt% was small, only 32.5%. In the improved separation process (step two), two columns (one extractive distillation column and the other solvent recovery column) were added and some simplification was made so as to recycle MIBK. In this case the yield of MIBK was 91.7%. Moreover, about 27.6% water stream per kilogram MIBK product is saved.

Key words: Isopropanol, MIBK, One-step Method, Process Improvement, Distillation

### INTRODUCTION

MIBK is a valuable chemical that is used as a solvent for cellulose and resin based coating systems and also for vinyl, epoxy and acrylic resins. Recently, the demand for MIBK has been large in chemical markets. In general, it is produced from AC in a three-step catalytic process or from AC in one step in trickle-type reactors [Lin and Ko, 1996; Mulas et al., 1999; Narayanan and Unnikrishnan, 1996], in which AC must be obtained from other sources, such as IPA in a previous step. However, the synthesis of MIBK in one step directly using isopropanol as reactant is a recent development [Cosimo et al., 2002; Mattos et al., 2002], and has been applied in one plant in China [Liang, 1999; Wang, 2002]. This method would be attractive since it is relatively simple. However, in this method the energy consumption is somewhat high and the purification of MIBK and intermediate cannot be solved well by far.

In the synthesis of MIBK by the isopropanol one-step method, the main reaction network is written as follows:



It is possible that some products, such as MIBC, also form. But those are too small to be neglected in the above reaction network.

However, the products from the reactor are a multi-component mixture containing AC, IPA, water, MIBK, MIBC, DIBK, etc. As a high-purity of MIBK over 99.5 wt% is required in industry, the development of an effective method is urgent. In this work a feasible separation process is put forward by a combination of experiment

and simulation.

### EXPERIMENTAL

The aim of VLE experiments is to identify the possible binary azeotropes in order to ensure a reliable process simulation. In terms of the separation principle of azeotropic distillation, the binary azeotropes form if at least one of the following criteria is satisfied.

1. At a certain concentration, the boiling point of the mixture is either higher or lower than that of any one of the two components consisting of the mixture.

This judgment is, herein, called the method of temperature measurement, which is especially suitable for immiscible or partly miscible systems because in this case it is relatively difficult to determine the composition in the liquid and/or vapor phases.

2. At the points of high and low concentrations in the  $x$  (mole fraction in the liquid phase) -  $y$  (mole fraction in the vapor phase) curve, the light component (relatively easy to volatile) and the heavy component (relatively difficult to volatile) exchange their volatility. That means that the  $x$ - $y$  curve intersects the diagonal at one point, i.e., the azeotropic point.

This judgment is, herein, called the method of concentration measurement, which is especially suitable for the completely miscible systems because in this case it is relatively easy to determine the composition in the liquid and/or vapor phases by GC (gas chromatograph) technique.

In fact, these two criteria should be satisfied at the same time for a binary system where the azeotrope can form. However, sometimes only one of them is convenient to evaluate. But it is enough for us to judge whether the azeotrope is formed or not.

In the separation process of synthesizing MIBK by the isopro-

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panol one-step method, many components, such as AC, IPA, water, MIBK, MIBC, DIBK, etc., are involved. Therefore, in order to determine the possible binary azeotropes, a combinatorial number  $C_6^2=15$  of VLE experiments under normal pressure must be done (assume that all the distillation columns in the separation process can be operated under normal pressure). In order to decrease the amount of experimental work, the experiment and calculation methods are combined.

As we know, water has a tendency to form azeotropes with other components. Therefore, the VLE experiment is done mainly to investigate the binary systems containing water: water (1)/isopropanol (2), water (1)/MIBK (2), water (1)/MIBC (2) and water (1)/DIBK (2). It is known from the reference [Chen, 1997] that water cannot form an azeotrope with acetone, and thus this system of water (1)/acetone (2) is excluded.

In the VLE experiment, the GC technique was used for composition analysis. The type of stainless packing column was: the size of  $\phi 4$  m (long)  $\times$  4 mm (I.D.), and the fixed agent consisting of A, B and C with the weight proportion of A : B : C = 25 : 20 : 55. A was prepared with poly(glycol) 1500 and silicon-alkyl support (the weight proportion 1 : 10), which was dissolved in chloroform. B was prepared with dibutyl sebacate and silicon-alkyl support (the weight proportion 1 : 10), which was dissolved in chloroform. C was prepared with double-glycerol and silicon-alkyl support (the weight proportion 1 : 5), which was dissolved in anhydrous methanol.

All chemicals used in this work were of analytical purity over 99.5%wt, and were purchased from the Beijing Chemical Regents Shop, Beijing, PRC, except that water was purified with ion-exchange resins.

An all-glass vapor-liquid equilibrium apparatus, manufactured by Tianjin University, was used for the VLE measurement. It was a circulation still of the Rose type. Circulation stills were designed to determine VLE of totally miscible mixtures. However, the systems of water (1)/MIBK (2), water (1)/MIBC (2) and water (1)/DIBK (2) showed an immiscible liquid-liquid region. In this case, the liquid phase was taken on as a pseudo-homogeneous phase, and its composition could be determined beforehand when preparing the solutions of water with MIBK (MIBC, DIBK). At the same time, the composition in the vapor phase was determined by adding the solvent, isopropanol, as internal standard into the withdrawn vapor sample in order to avoid immiscibility.

Details of the apparatus used and its operation have been described previously [Blanco et al., 2000; Lei et al., 2002a; Resa et al., 1999]. The boiling point temperature in the equilibrium still was monitored with a mercury-in-glass thermometer ( $\pm 0.05$  K), calibrated against a standard thermometer. Pressure remained constant by a manual regulator. Composition analyses of vapor and liquid samples were done by a GC (type 4000A) equipped with a thermal conductivity detector. Hydrogen was the carrier gas with the flowrate  $20 \text{ ml} \cdot \text{min}^{-1}$ . Temperature of the column packing was  $85^\circ\text{C}$ , the detector  $150^\circ\text{C}$  and the vaporization  $160^\circ\text{C}$ . Data analysis was performed by using an East-West workstation. The relative mass calibration factors for all components were:  $f_{\text{H}_2\text{O}}=1.00$ ,  $f_{\text{IPA}}=1.367$ ,  $f_{\text{MIBK}}=1.050$ ,  $f_{\text{MIBC}}=1.629$  and  $f_{\text{DIBK}}=1.802$ . Therefore, the sample compositions of the mixtures were deduced in terms of peak area of the components.

First, we measured the VLE data of the water (1)/IPA (2) system

**Table 1. Results of the VLE experiments under normal pressure**

No.	T ( $^\circ\text{C}$ )	$x_1$	$x_2$	$y_1$	$y_2$
1. the system of water (1)/MIBK (2)					
1	112.6	0.0270	0.9730	0.0349	0.9651
2	90.4	0.5513	0.4487	0.5285	0.4715
3	85.4	0.9823	0.0177	0.7924	0.2076
According to the judgment method of temperature measurement, the system of water and MIBK can form a binary azeotrope.					
2. the system of water (1)/MIBC (2)					
1	117.4	0.0276	0.9724	0.0966	0.9034
2	91.7	0.5633	0.4367	0.6823	0.3177
3	89.9	0.9847	0.0153	-	-
According to the judgment method of temperature measurement, the system of water and MIBC can form a binary azeotrope.					
3. the system of water (1)/IPA (2)					
1	80.9	0.0256	0.9744	0.0306	0.9694
2	82.0	0.5616	0.4384	0.2345	0.7655
3	98.7	0.9840	0.0160	0.7125	0.2875
According to the judgment method of either temperature measurement or concentration measurement, the system of water and IPA can form a binary azeotrope.					
4. the system of water (1)/DIBK (2)					
1	134.6	0.0582	0.9418	0.1713	0.8287
2	97.6	0.5752	0.4248	0.5828	0.4172
3	98.2	0.9836	0.0164	-	-
According to the judgment method of temperature measurement, the system of water and DIBK can form a binary azeotrope.					
5. the system of MIBK (1)/MIBC (2)					
1	130.5	0.0183	0.9817	0.0397	0.9603
2	122.2	0.5398	0.4602	0.7693	0.2307
3	116.0	0.9721	0.0279	0.9980	0.0020
According to the judgment method of temperature measurement or concentration measurement, it seems that no azeotrope with the lowest boiling point is formed.					

under normal pressure, which corresponded well with the reference data [Chen, 1997]. It proved that the experimental apparatus was reliable. Then, measurements were made for water (1)/MIBK (2), water (1)/MIBC (2) and water (1)/DIBK (2) systems under normal pressure. The VLE data obtained from this work are listed in Table 1, where T, x and y represent temperature, molar composition in the liquid and vapor phases, respectively. In order to ensure accurate simulation, we use the Herrington method to verify the consistency of VLE data by MS Excel 2003 software that is convenient for this purpose. By this method it is proved that the data are consistent. In Table 1, only three points, respectively, in the low, middle and high concentrations were measured for each system, and the judgment method for azeotropes is also indicated. It can be seen that water can form an azeotrope with IPA, MIBK, MIBC and DIBK.

On the other hand, the calculation method is employed to test the azeotrope formation. The chemical engineering simulation software of PROII (5.61 version) is used [Lei et al., 2002b]. By means of its binary VLE prediction function (the UNIFAC, Wilson and NRTL equations which are commonly applied in the distillation

process simulation are selected), it is found that the experimental results given in Table 1 are in good agreement with the calculated results. On this basis, the other 11 systems, i.e., water (1)/acetone (2), acetone (1)/IPA (2), acetone (1)/MIBK (2), acetone (1)/MIBC (2), acetone (1)/DIBK (2), IPA (1)/MIBK (2), IPA (1)/MIBC (2), IPA (1)/DIBK (2), MIBK (1)/MIBC (2), MIBK (1)/DIBK (2) and MIBC (1)/DIBK (2), are investigated. It is found that no new azeotropes are formed except the system of MIBK (1)/MIBC (2) with the lowest boiling point. In this case, the VLE experiment for this system should be done. The results are in Table 1, from which it seems that MIBK and MIBC cannot form an azeotrope.

In order to go a step further to verify the azeotrope of the system of MIBK (1)/MIBC (2), a distillation column was set up. The mixture of MIBK and MIBC with a volume of 1,320 ml (the volume proportion of MIBK and MIBC 10 : 1) was added into the 2,500 ml distillation still. A distillation column with the size of 30 mm (diameter)×1,200 mm (height) was packed by a type of ring-shaped packing with the size 3 mm (width)×3 mm (height). The theoretical plates were determined by use of the system of n-heptane and methylcyclohexane at infinite reflux, having 25 theoretical plates (including reboiler and condenser). When the reflux ratio at the top of distillation column was 2.0, the top temperature was 115.0-116.0 °C, and the composition was MIBK 99.83 wt% and MIBC 0.17 wt%. It indicates that MIBK and MIBC cannot form an azeotrope with the lowest boiling point. Furthermore, they are easily separated by ordinary distillation. In a simulation of the distillation column where MIBK and MIBC are used as the key light and heavy components, it is better to select the VLE model of Ideal equation because MIBK and MIBC have similar molecular structure and cannot form an azeotrope. On the basis of experimental work, the next procedure is to simulate and improve the separation process.

## SEPARATION PROCESS SIMULATION

The original separation process of synthesizing MIBK by an isopropanol one-step method is illustrated in Fig. 1. The feedstock which comes from the fixed-bed reactor and is composed of AC, IPA, water, MIBK, MIBC, and DIBK is flowed into the column 1 (i.e., AC column), water separator that is a one-stage liquid-liquid separator, column 2 (i.e., IPA column) and column 3 (i.e., MIBK column) in series. The function of column 1, water separator, column 2 and column 3 is

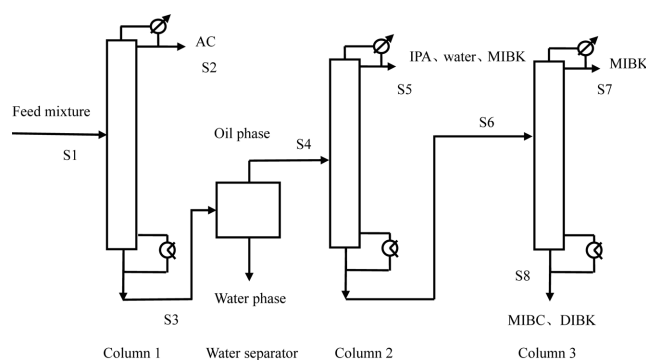


Fig. 1. The original separation process of synthesizing MIBK by an isopropanol one-step method: AC column (column 1); IPA column (column 2); MIBK column (column 3).

to separate AC, water, IPA and MIBK from the mixture, respectively.

There exists an obvious disadvantage in this process, that is, the yield of MIBK being over 99.5 wt% obtained at the top of column 3 is very low, only 32.5%, which leads to less competition of this method in the MIBK production even though the front fixed-bed reaction process of synthesizing MIBK may be attractive and promising. Herein the yield of MIBK,  $\eta$ , is defined as,

$$\eta = \frac{D_3 x_{D_3}}{F x_F} \quad (1)$$

where  $D_3$  is the flowrate at the top of column 3,  $F$  is the flowrate feeding into column 1,  $x_{D_3}$  is the weight fraction of MIBK at the top of column 3 and  $x_F$  is the weight fraction of MIBK feeding into column 1.

The reason for low yield of MIBK is that the water separator is only a one-stage liquid-liquid separator, with the result that much water is still left in the oil phase and then into MIBK column with oil phase. This is because the boiling point difference between the azeotropes formed by water and IPA (b.p. 80.3 °C) and formed by water and MIBK (b.p. 87.9 °C) is small, only 7.6 °C. It indicates that either the theoretical plates or reflux ratio of column 2 should be very large so as to separate these two azeotropes. In the actual plant, the theoretical plates are about 35 and reflux ratio about 3.0-4.0. Besides, water is residual after subtracting some forming azeotrope with IPA. Therefore, much MIBK is entrained by water into the top of column 2 so as to obtain high purity of MIBK being over 99.5 wt% at the top of column 3.

The whole separation process is simulated with PROII (version 5.61) software, in which the UNIFAC model is selected in column 1, water separator and column 2, and the Ideal model is selected in column 3. First, a comparison is made between the calculated and the designed values from one Chemical Engineering Design Institution. It is found that the calculated values correspond well with the designed values, which proves that the calculated values are reliable. Then, the process simulation is made, in which the operation condition comes from the plant. The calculated results are listed in Table 2 where the streams are marked in Fig. 1. Note that if other VLE models such as Wilson, NRTL are selected for column 1, water separator and column 2, similar results are also obtained.

Since our work is to provide useful information for a plant to modify the original separation process, it is necessary for us to verify the calculated values by experiment. In our laboratory, three distillation columns, in which columns 1, 2 and 3, respectively, had 25, 20 and 25 theoretical plates (including reboiler and condenser), have been set up. All of the theoretical plates were determined by use of the system of n-heptane and methylcyclohexane at infinite reflux. Those three distillation columns were operated in batchwise, and the reflux ratio of them was, respectively, 3.0, 2.0 and 3.0. At this time the yield of MIBK being over 99.5 wt% obtained at the top of column 3 was 35.3%, approximate to the calculated value.

## SEPARATION PROCESS IMPROVEMENT

From the analysis of the original separation process, it is known that about 67.5% of MIBK in the feed mixture is withdrawn together with water and IPA from the top of column 2. So it is very straightforward to improve the original separation process by recycling MIBK,

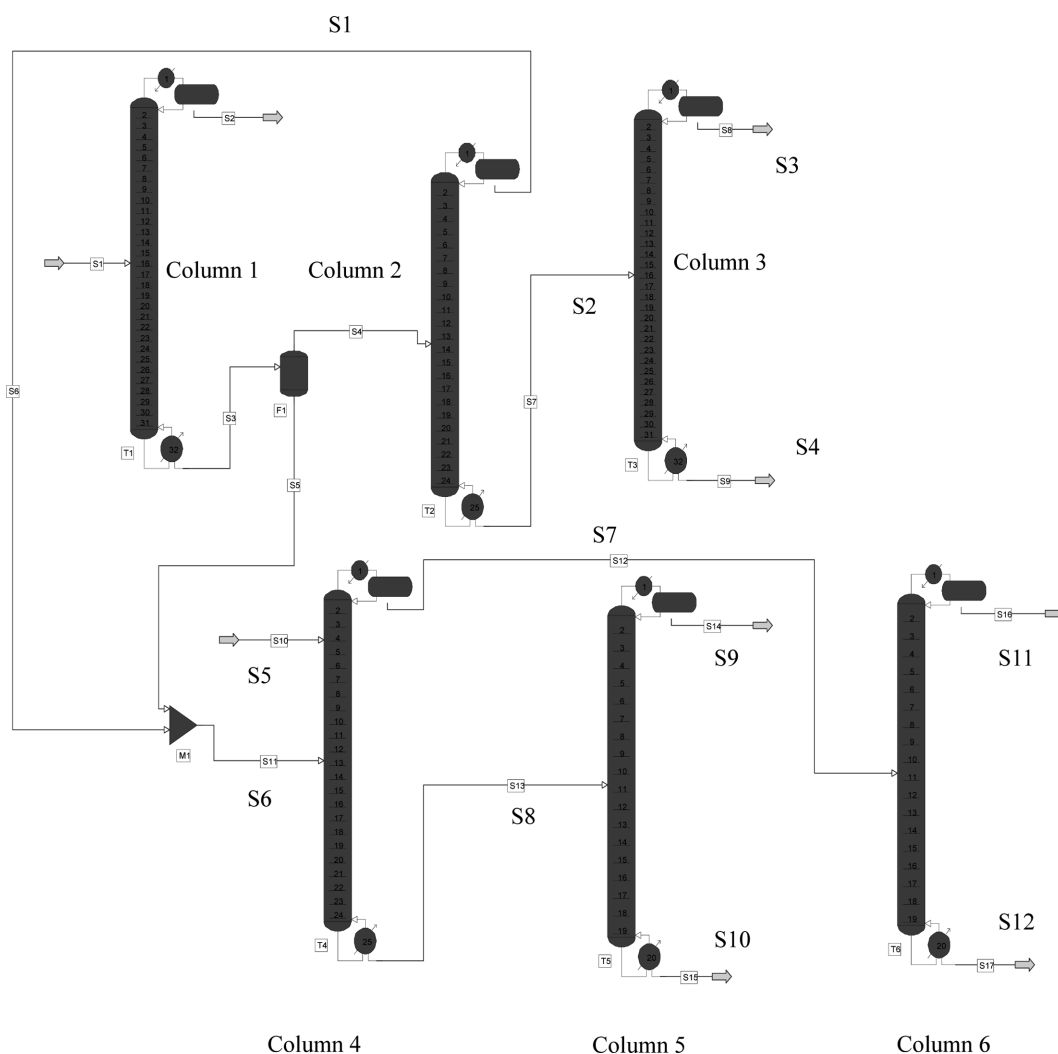
i.e., S5 in Fig. 1.

In terms of our experience on special distillation processes, the method of extractive distillation is more suitable for the separation of organic aqueous solutions with azeotropic point than azeotropic distillation [Arlt et al., 2004; Ko et al., 2002; Lei et al., 2003a, b, 2005; Li et al., 2005a, b]. In extractive distillation the separating

agent does not need to be vaporized. For azeotropic distillation, however, both the separating agent and the components to be separated must be vaporized into the top of an azeotropic distillation column. Moreover, the amount of the separating agent in azeotropic distillation is usually large, which leads to high energy consumption compared with extractive distillation. For this reason, extractive distillation

**Table 2. The calculated results for the streams in Fig. 1 (the original separation process)**

No.	T (°C)	Flowrate (kg h <sup>-1</sup> )						Total
		H <sub>2</sub> O	AC	IPA	MIBK	MIBC	DIBK	
Stream 1	34.7	81.20	472.9	164.6	184.7	1.44	53.7	958.0
Stream 2	37.1	1.34	468.6	0	0	0	0	470.0
Stream 3	65.6	79.9	4.23	164.5	184.7	1.44	53.7	488.0
Stream 4	30.0	69.1	4.18	163.3	184.5	1.44	53.7	476.0
Stream 5	81.2	69.1	4.18	163.3	123.4	0.06	0	360.0
Stream 6	128.3	0	0	0	61.1	1.38	53.7	116.0
Stream 7	116.5	0	0	0	60.0	0.01	0	60.0
Stream 8	163.5	0	0	0	1.08	1.37	53.7	56.1



**Fig. 2. The improved separation process of synthesizing MIBK by an isopropanol one-step method (Step one): AC column (column 1); IPA column (column 2); The first MIBK column (column 3); Extractive distillation column (column 4); Solvent recovery column (column 5); The second MIBK column (column 6).**

is used more often than azeotropic distillation.

The process improvement is fulfilled in two steps. In step one, the original separation process is improved by setting an extractive distillation system, as shown in Fig. 2. The extractive distillation system is composed of an extractive distillation column (column 4), a solvent recovery column (column 5) and a second MIBK column (column 6), which is used to deal with the S5 from the top of column 2. It is evident that for extractive distillation, the selection of a suitable selective separating agent is fundamental to ensure an effective and economical design. In the simulation, the solvent of ethylene glycol (EG) is used as the separating agent.

The calculated results for streams in the improved separation process (step one) are listed in Table 3. Here the yield of MIBK  $\eta$  is defined as,

$$\eta = \frac{D_3 x_{D_3} + W_6 x_{W_6}}{F x_F} \quad (2)$$

where  $W_6$  is the flowrate at the bottom of column 6, and  $x_{W_6}$  is the weight fraction of MIBK at the bottom of column 3.

In this case, the yield of MIBK being over 99.5 wt% obtained at the top of column 3 as well as at the bottom of column 6 is up to 97.4%, greatly higher than that of the original separation process.

In Fig. 2, there are two MIBK columns (columns 3 and 4), and their function is to recover MIBK. Both columns may be incorporated into one MIBK column so that the equipment investment can decrease in the plant modification. Moreover, a water separator is unnecessary because water will be withdrawn from the top of the solvent recovery column. Thus, a further improved separation process (step two) is put forward on the basis of step one, and illustrated in Fig. 3.

The calculated results for streams in the improved separation process (step two) are listed in Table 4. Here the yield of MIBK  $\eta$  is defined as,

$$\eta = \frac{W_6 x_{W_6}}{F x_F} \quad (3)$$

In this case, the yield of MIBK being over 99.5 wt% obtained at the bottom of column 6 is up to 91.7%, greatly higher than that of

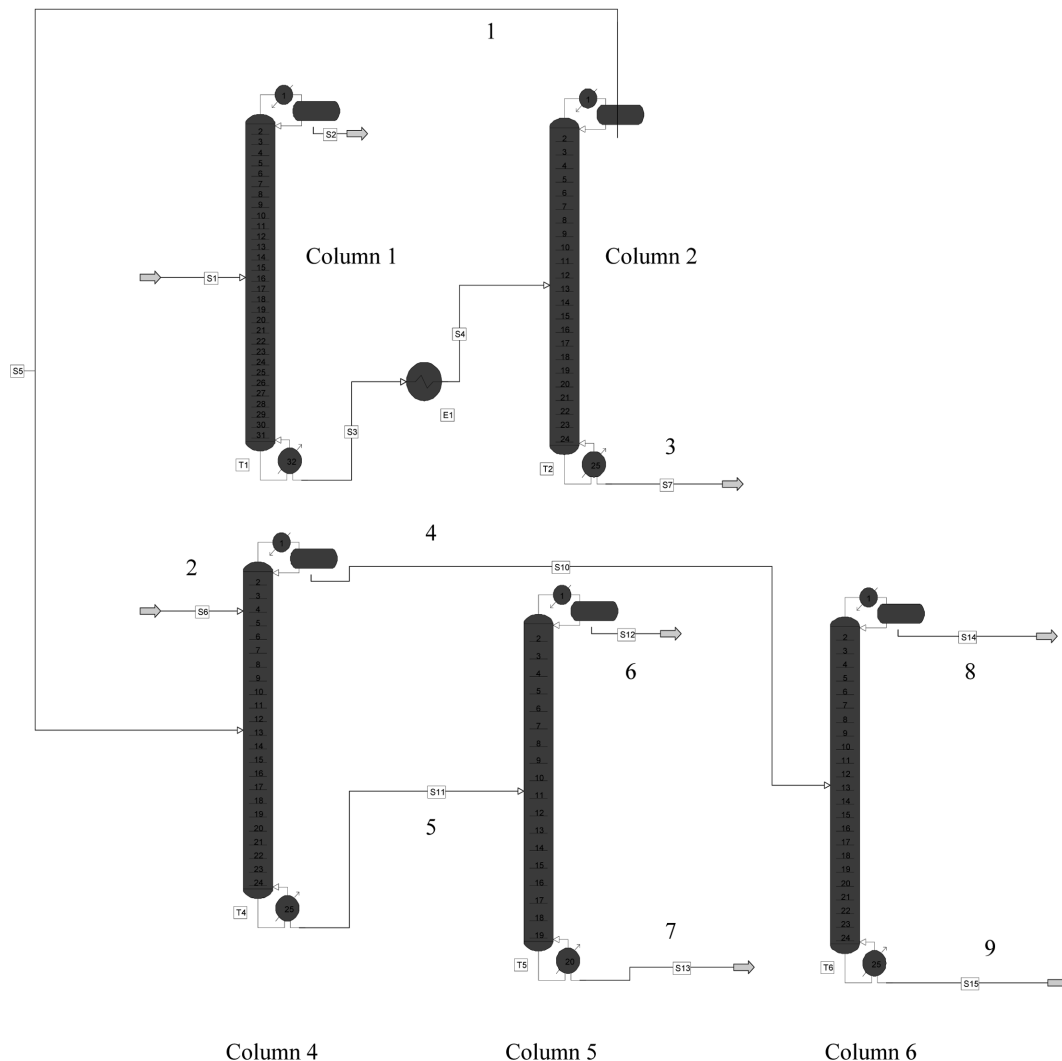


Fig. 3. The improved separation process of synthesizing MIBK by an isopropanol one-step method (Step two): Acetone column (column 1); IPA column (column 2); Extractive distillation column (column 4); Solvent recovery column (column 5); MIBK column (column 6).

the original separation process and close to that of the improved separation process (step one). Compared with Figs. 2 and 3, the improved separation process (step two) with 5 columns is more simplified than the improved separation process (step one) with 6 columns.

On the other hand, a comparison of heat duties on reboilers  $Q_R$  and condensers  $Q_C$  among the original, improved (step one) and improved (step two) separation processes is given in Table 5. It can be seen that total heat duties of the original separation process on reboilers  $Q_R$  and condensers  $Q_C$  are the lowest, and for the improved (step one) and improved (step two) separation processes,  $Q_R$  and  $Q_C$

are approximately equal. But it is 8.27 kg water stream per kilogram MIBK product in the improved (step two) separation process, while 11.42 kg water stream per kilogram MIBK product in the original separation process. Therefore, much energy is saved by comparison of water stream consumption per kilogram MIBK product. So it is advisable for the plant to adopt the improved process (step two).

## CONCLUSION

The separation process of synthesizing MIBK (methyl isobutyl

**Table 3. The calculated results for the streams in Fig. 2 (the improved step-one separation process)**

No.	T (°C)	Flowrate (kg h <sup>-1</sup> )							
		H <sub>2</sub> O	AC	IPA	MIBK	MIBC	DIBK	EG	Total
Stream 1	81.2	123.42	4.18	163.29	123.42	0.06	0.00	0.00	360.00
Stream 2	128.3	0.00	0.00	0.00	61.07	1.38	53.67	0.00	116.11
Stream 3	116.5	0.00	0.00	0.00	59.99	0.01	0.00	0.00	60.00
Stream 4	163.5	0.00	0.00	0.00	1.08	1.37	53.67	0.00	56.12
Stream 5	140.0	3.98	0.00	0.00	0.00	0.00	0.00	796.02	800.00
Stream 6	79.0	9.54	4.23	164.54	123.61	0.06	0.00	0.00	372.28
Stream 7	82.1	9.54	4.23	152.45	123.61	0.02	0.00	0.16	290.01
Stream 8	137.0	74.28	0.00	12.09	0.00	0.04	0.00	795.85	882.27
Stream 9	41.8	69.86	0.00	12.09	0.00	0.04	0.00	0.00	82.00
Stream 10	132.2	4.41	0.00	0.00	0.00	0.00	0.00	795.85	800.27
Stream 11	79.1	9.54	4.23	152.45	3.80	0.00	0.00	0.00	170.02
Stream 12	116.5	0.00	0.00	0.00	119.82	0.02	0.00	0.16	120.00

**Table 4. The calculated results for the streams in Fig. 3 (the improved step-two separation process)**

No.	T (°C)	Flowrate (kg·h <sup>-1</sup> )							
		H <sub>2</sub> O	AC	IPA	MIBK	MIBC	DIBK	EG	Total
Stream 1	81.7	79.83	4.23	164.54	180.52	0.88	0.00	0.00	430.01
Stream 2	140.0	3.98	0.00	0.00	0.00	0.00	0.00	796.02	800.00
Stream 3	157.1	0.00	0.00	0.00	4.16	0.56	53.67	0.00	58.38
Stream 4	83.2	8.99	4.23	155.66	180.52	0.19	0.00	0.42	350.01
Stream 5	137.9	74.83	0.00	8.88	0.00	0.69	0.00	795.60	880.00
Stream 6	42.7	72.43	0.00	8.88	0.00	0.69	0.00	0.00	82.00
Stream 7	136.3	2.40	0.00	0.00	0.00	0.00	0.00	795.60	798.00
Stream 8	79.3	8.99	4.23	155.66	11.14	0.00	0.00	0.00	180.02
Stream 9	116.5	0.00	0.00	0.00	169.39	0.19	0.00	0.42	170.00

**Table 5. Comparison of heat duties on reboilers and condensers among the original, improved (step one) and improved (step two) separation processes (unit: ×10<sup>6</sup> kJ·h<sup>-1</sup>)**

No.	The original separation process		The improved separation process (step one)		The improved separation process (step two)	
	$Q_R$	$Q_C$	$Q_R$	$Q_C$	$Q_R$	$Q_C$
Column 1	1.2787	1.2450	1.0321	0.9883	1.0321	0.9883
Column 2	0.2962	0.2352	1.3603	1.2812	1.5555	1.4751
Column 3	0.2595	0.2554	0.0909	0.0876	-	-
Column 4	-	-	0.3727	0.3574	0.4235	0.4082
Column 5	-	-	0.3134	0.3565	0.3287	0.3644
Column 6	-	-	0.5246	0.5170	0.4094	0.3991
Total	1.8344	1.7356	3.6940	3.5880	3.7492	3.6351

ketone) by an isopropanol one-step method is improved by means of the combination of experiment and simulation. In order to ensure accurate simulation, the possible azeotropes are identified by VLE experiments. On this basis, the whole separation is simulated by PROII simulation software. The improved separation process (step two), in which an extractive distillation system is incorporated and EG is used as the separating agent, is put forward in this work. The yield of MIBK was 91.7% in the case of concentration of MIBK being over 99.5 wt%, greatly higher than that of the original separation process. In addition, much energy was saved from 11.42 kg water stream per kilogram MIBK product in the original separation process to 8.27 kg water stream per kilogram MIBK product in the improved separation process (step two). So it is advisable to use the improved separation process to modify the original separation process in industry.

Although the improved separation process is more advantageous, it should be mentioned that the original separation process in product yield and energy consumption, investment cost may increase due to setting an extractive distillation system. This factor should be considered when the original process is modified in industry.

#### ACKNOWLEDGMENT

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