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Process Synthesis, Simulation and Optimization of Light Components Separation from Furfural Production

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Abstract The light components from furfural production consist of furfural, methanol, acetone and methyl acetate. Currently, these valuable chemical components in the furfural production tail gas are directly incinerated or vented, leading to environmental pollution and resource waste. Therefore recovering these chemicals is of great practical significance. Five schemes are synthesized and optimized for separating the light components by extractive distillation employing water, ethylene glycol, dimethyl sulfoxide and furfural as extractants, respectively, using Aspen Plus V15. The advantages and disadvantages of the five schemes are compared and discussed in terms of recovery and purity, energy consumption and column efficiency. This study may provide a valuable reference for furfural manufacturers to recover the light components.
Keywords Furfural , methanol , acetone, methyl acetate, light components.

1 Introduction

Furfural (2-furaldehyde) is one of the most significant renewable biomass platform chemicals, which is mainly produced from acid-catalyzed hydrolysis and dehydration of hemicellulose-rich agricultural residues including corn cobs, rice husks, sugarcane bagasse and cottonseed hulls[1]. As an indispensable fine chemical raw material, furfural is widely applied in the synthesis of furan resin, furfuryl alcohol, pharmaceutical intermediates, pesticides, spices and biofuel precursors, occupying an important strategic position in biomass refining and green chemical industry[2].

At present, global research on furfural production technology has formed a multi-directional development pattern covering catalytic mechanism, process optimization, raw material expansion and byproduct utilization. International early research focused on traditional inorganic acid catalytic technology, and scholars optimized reaction temperature, residence time and acid concentration to improve furfural yield and selectivity[3]. In recent years, foreign research has mainly concentrated on heterogeneous solid acid catalysts, ionic liquid pretreatment, microwave-assisted conversion and two-phase reaction system strengthening, aiming to solve the problems of serious equipment corrosion, high wastewater discharge and low raw material utilization in traditional processes[4,5]. Baktash et al. explored the preparation of furfural from industrial pre-hydrolysis liquor with solid acid catalysts and optimized the process parameters to effectively improve product yield[6]. Ojeda et al. systematically reviewed the application potential of furfural as a renewable platform molecule in high-value chemical synthesis and clean fuel preparation[7]. Mandalika et al. deeply analyzed the application advantages of ionic liquids in lignocellulosic biomass fractionation and furfural green preparation[8].

Domestic research on furfural started late but developed rapidly, mainly focusing on the improvement of traditional batch hydrolysis process, innovation of continuous production technology and low-cost modification of catalysts. Chinese researchers have optimized the traditional Chinese typical furfural production process, improved the heat integration and distillation refining process, and committed to reducing energy consumption and pollutant emission intensity. Wang et al. summarized the research progress of acid-catalyzed preparation of furfural from lignocellulosic biomass in China, and pointed out the bottlenecks of existing technical routes[9]. Xia et al. reviewed the research status of metal-based catalysts for furfural hydrogenation conversion in aqueous medium, laying a foundation for the high-value utilization of furfural[10].

In terms of global and domestic industrial production layout, China holds an absolute dominant position in furfural production capacity and output. The global annual furfural production capacity is about 1150000 tons, while China's annual furfural output is stable at 800,000 tons per year, accounting for ca. 70% of the global market share. Furfural production enterprises in China are mainly distributed in Hebei, Shandong, Inner Mongolia and other regions rich in agricultural and forestry waste raw materials, with mature production technology and complete industrial supporting facilities. Other major producing countries include India, Russia and Romania etc.[11]. However, the vast majority of domestic furfural enterprises still adopt the traditional one-step hydrolysis and atmospheric distillation process. A prominent problem in industrial production is that a large number of light component byproducts produced in the refining process are directly discharged or incinerated without effective separation and recycling, which not only causes serious waste of valuable chemical resources, but also brings serious environmental pollution problems such as volatile organic compound emission and wastewater organic pollution, and greatly reduces the economic benefit and green development level of furfural industry.

The light component byproducts produced in the furfural refining process are typical low-boiling near-boiling mixed organic systems, mainly composed of four key components: methanol, furfural, acetone and methyl acetate. The typical mass fractions of each component in the light fraction are as follows: methanol 0.5833, furfural 0.1950, acetone 0.1167, and methyl acetate 0.1050. These four components all have high industrial utilization value: methanol is a common solvent and chemical synthesis raw material; residual furfural in light components can be recycled to improve product yield; acetone is an important basic organic chemical raw material; methyl acetate is a green environmental protection solvent and fine chemical intermediate. Realizing efficient separation and recovery of the four components can turn waste into treasure and has remarkable economic and environmental benefits.

The formation of each component in light fractions originates from the complex hydrolysis, dehydration, degradation and side reaction mechanism of lignocellulosic biomass under high temperature and acidic catalytic condition. Furfural is generated by the acid-catalyzed dehydration reaction of xylose produced by hemicellulose hydrolysis. Under acidic conditions, xylose undergoes protonation, ring opening and continuous dehydration cyclization to form furfural molecules. Methanol is mainly derived from the breaking of methoxy ether bonds in lignin macromolecules under acid catalysis, and lignin methoxy groups are hydrolyzed and dissociated to release methanol.

Acetone is formed by the deep degradation, isomerization and carbon chain cleavage reaction of cellulose hydrolyzed glucose and partial xylose under high temperature acidic environment. Methyl acetate is generated by the esterification reaction between acetic acid produced by acetyl hydrolysis of hemicellulose and methanol produced by lignin degradation under in-situ acid catalysis. The coupled generation of multiple reaction paths makes the light component mixture form a complex azeotropic system, which is difficult to separate by conventional ordinary distillation.

According to the statistical data of furfural industrial production parameters, every 10,000 tons of furfural produced annually will generate 720 tons of light component byproducts[12]. Based on China's annual furfural output of 800,000 tons, the total annual production of light components in China is calculated as 57600 t/a. Combined with the mass fraction of each component, the annual output of methanol is 33,598.08 t/a, furfural 11232 t/a, acetone 6,721.92 t/a, and methyl acetate 6048 t/a. A large amount of high-value organic components is wasted every year due to the lack of mature separation and recovery technology, which restricts the green upgrading and high-quality development of China's furfural industry.

Given the difficulty of conventional distillation in separating azeotropic and near-boiling mixtures of methanol–furfural–acetone–methyl acetate, special distillation methods must be considered, including pressure swing distillation[13], extractive distillation[14], azeotropic distillation[15] and reactive distillation[16,17]. In this study extractive distillation is selected as the core separation technology. By screening high-efficiency selective extractants and designing different process flow schemes, multiple extractive distillation separation processes for light components from furfural production are synthesized and constructed in this work. Through process simulation and parameter optimization, each single component with high purity can be obtained, which provides a feasible technical scheme and theoretical basis for industrial recovery and resource utilization of furfural production light components, and is of great significance for energy saving, emission reduction and circular economy development of furfural enterprises.

2 Materials and Methods

2.1 Problem statement and feed basis

The light-component stream from the furfural refining section is a low-boiling, near-boiling mixture of four components. A typical mass composition reported for industrial furfural plants is methanol 58.33 wt%, furfural 19.50 wt%, acetone 11.67 wt% and methyl acetate 10.50 wt%. All simulations used a feed basis of 1000 kg/h (FEED1) at 25 °C and 1 atm. Methanol, acetone and methyl acetate form minimum-boiling binary azeotropes in every pairwise combination, and furfural forms a minimum-boiling azeotrope with water; the four components therefore cannot be recovered at high purity by ordinary distillation, which motivates the extractive-distillation and reactive routes developed in this work.

2.2 Thermodynamic model and validation

All simulations were performed in Aspen Plus V15. The non-random two-liquid (NRTL) activity-coefficient model was selected to describe the highly non-ideal, polar vapor-liquid equilibria of this alcohol-ketone-ester-aldehyde-water mixture; binary interaction parameters were taken from the built-in Aspen VLE databank. The adequacy of the model was validated by comparing the predicted pure-component boiling points and the temperature, type and composition of all relevant azeotropes

against literature values (Table 1). The model reproduces the furfural-water minimum-boiling azeotrope (96.9 °C at 1 atm) and the methyl acetate-water azeotrope (about 57 °C) that govern the separation, confirming that NRTL is adequate for the subsequent design.

2.3 Flowsheet synthesis and unit-operation models

Five separation schemes (SCHEME 1-5) were synthesized by conventional extractive-distillation design logic. Shortcut DSTWU calculations provided initial estimates of the stage number and reflux ratio, which were then refined with the rigorous RadFrac equilibrium-stage model (total condenser, kettle reboiler) for all distillation columns B1-B7; in the extractive-distillation columns the entrainer was introduced above the feed stage. SCHEME 5 additionally employs an RStoic reactor (R1) to model the complete saponification of methyl acetate by NaOH at 60 °C, a Flash2 separator (V1, 69 °C) and heater blocks (H1, B6). The column stage numbers, feed and entrainer stages, mass reflux ratios, distillate flow rates and entrainer temperatures are summarized in Table 2. Convergence was obtained with the standard sequential-modular (Wegstein) solver and default tolerances.

2.4 Sensitivity analysis and design variables

The feed stage, entrainer stage, entrainer flow rate and entrainer temperature of each extractive column were optimized with the built-in sensitivity-analysis tool, in which each variable was varied over its practical range while the recoveries of the relevant light components were recorded. The optimum is defined as the condition that maximizes the recovery of the key component(s) while keeping all recoveries at or above 0.98.

2.5 Performance metrics

For each scheme, the recovery Ri and purity Pi of component i in its product stream are defined as Ri = (mass flow of i in the product stream)/(mass flow of i in FEED1) and Pi = (mass flow of i in the product stream)/(total mass flow of the product stream). For SCHEME 5, the methanol recovery is based on the methanol plus the methanol-equivalent generated from methyl acetate (accounting for the 32/74 molar-mass ratio). Energy performance is expressed by the reboiler duty, condenser duty and entrainer-cooling duty of each block. The overall column efficiency was estimated with the O'Connell correlation Eo = 50.3 (α×μ)^(-0.226), where α is the average relative volatility of the key components and μ (cP) is the viscosity of the liquid feed.

3 Separation of the light components using water as the extractant

3.1 The related properties of the light components plus water system

The boiling points and azeotropes of the light components plus water system are shown in Table1. Methanol, acetone and methyl acetate in the light components have close boiling points. In addition, they form minimum-boiling binary azeotropes with one another, indicating that the separation and purification of these three components by ordinary distillation alone is difficult and infeasible. Furfural and water form an azeotrope with a minimum boiling point of 96.923 ℃, as predicted by Aspen Plus V15 using the NRTL property method.

Table1 Boiling points and azeotropes of the light components plus water system

	TEMP	CLASS	TYPE	CODE	CH4O	ACE	MET	FUR	H2O
1	64.535	Saddle	Homo.	1	1.000	0.000	0.000	0.000	0.000
2	56.128	Saddle	Homo.	1	0.000	1.000	0.000	0.000	0.000
3	57.054	Saddle	Homo.	1	0.000	0.000	1.000	0.000	0.000
4	161.355	Stable	Homo.	1	0.000	0.000	0.000	1.000	0.000
5	100.018	Stable	Homo.	1	0.000	0.000	0.000	0.000	1.000
6	55.236	Saddle	Homo.	2	0.222	0.778	0.000	0.000	0.000
7	53.618	Unstable	Homo.	2	0.332	0.000	0.668	0.000	0.000
8	55.598	Saddle	Homo.	2	0.000	0.579	0.421	0.000	0.000
9	56.982	Saddle	Homo.	2	0.000	0.000	0.959	0.000	0.041
10	96.923	Saddle	Homo.	2	0.000	0.000	0.000	0.122	0.878

Notes: 1 Table1 was produce by Aspen plus V15 using property method NRTL. 2 TEMP=Temperature,℃;CH4O=methanol,ACE=acetone,MET=methyl acetate, FUR=furfural.

3.2 The separation sequence synthesis

Before the separation sequence synthesis, the choice of extractant must be considered for the extractive distillation. Water should be considered primarily since it is the cheapest and greenest solvent. Fig.1 is the flowsheet for separating the light components by extractive distillation using water alone as a solvent[18], which is referred to SCHEME 1 in this study.

SCHEME 1 is described as follows: 1000kg/hr of FEED1 consists of CH4O 0.5833, FUR 0.195, ACE 0.1167 and MET 0.105 with a temperature and pressure of 25 ℃ and 1 atm, respectively. The ordinary distillation column B1 recovers furfural from its bottom. Then the top stream FEED2 is separated in B2 using water as the extractant (WATER2) to recover CH4O into the bottom stream FEED3, which is further purified by ordinary distillation column B3 to get the high purity CH4O in stream CH4O-3 and the bottom stream H2O-3 could be recycled to WATER2 with some make up water. MET and ACE are recovered together in FEED4, which is further separated by extractive distillation column B4, again using water as the extractant (WATER4), thus, purified MET could be obtained in stream MET-4, while ACE is recovered with water in FEED5 which is finally purified by ordinary distillation column B5 and H2O-5 could be recycled to WATER4 with some make up water.

The structure and operation condition specification for each column in Fig.1 is shown in Table 2.

The flow rate of streams WATER2 and WATER4 is 1500 kg/h. The feed temperatures of streams WATER2 and WATER4 are 25 ℃ and 50 ℃, respectively. The pressure of all blocks and streams is 1 atm.

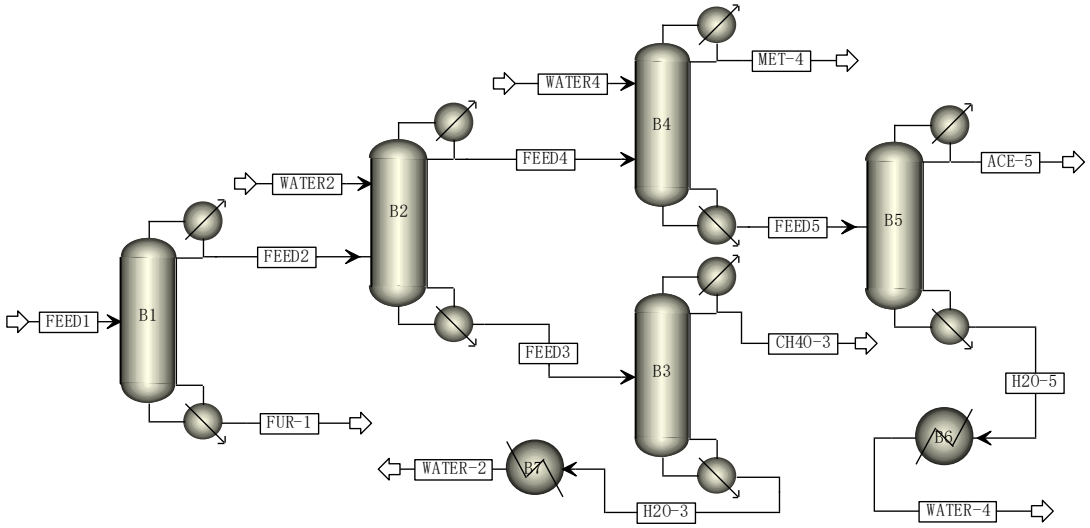


Fig.1 Flowsheet for separating the light components by extractive distillation using water as extractrant(SCHEME 1)

Table 2 The structure and operation condition specification for each block in SCHEME 1

ITEM	B1	B2	B3	B4	B5	B6	B7
STAGE NUMBER	8	30	17	40	30	/	/
FEED STAGE	3	15	12	31	19	/	/
EXTRACTANTSTAGE	/	7	/	19	/	/	/
MASS REFLUX RATIO	0.8	3.5	3	6	6	/	/
DISTILL FLOW(Kg/hr)	805	225	583	104.999	116.237	/	/
EXTRACTANT TEMP (℃)	/	/	/	/	/	50	25

3.3 The optimization of the feed stages

The feed stage of a distillation column is crucial. The sensitivity analysis of FEED2 stage and WATER2 stage is conducted by varying both from the 2nd to the 29th stage to observe the recovery of the related light components. The feed stage windows of distillation column B2 that enable the recoveries of all the three light components (RCH4O,RACE and RMET) to be greater than 0.99 include (12^{th},6^{th} -7^{th}), (13^{th},5^{th} -8^{th}), (14^{th},5^{th} -9^{th}), (15^{th},5^{th} -10^{th}), (16^{th},5^{th} -11^{th}), (17^{th},5^{th} -12^{th}), (18^{th},5^{th} -12^{th}), (19^{th},5^{th} -12^{th}), in which the former number in each bracket stands for the fixed FEED2 stage, while the latter number range stands for the corresponding WATER2 stage range. For example, (12^{th},6^{th} -7^{th}) means WATER2 stage 6^{th} and 7^{th} are both feasible for enabling the recoveries to be greater than 0.99 when the FEED2 stage is fixed at 12^{th}.

When FEED2 stage varies from 11th to 19th, WATER2 stage window 5^{th}-10^{th} leads to high recovery for all the three components, among which 7^{th} gives the highest as shown in Fig.2. The recovery of methanol（RCH4O）, methyl acetate(RMET) and acetone(RACE) is 0.99926, 1 and 0.99777, respectively at the optimum feed stage location.

The recovery of acetone (RACE) is most sensitive to the stage location of the extractant WATER2. When WATER2 is around 7^{th}, the extractant goes downward and contacts the FEED2 upward fully, which gives the best vapor-liquid mass transfer. When the WATER2 location is below the FEED2 stage, RACE deteriorates immediately. This is because in this situation considerable part

of the extractant leaves from the bottom without contacting the feed stream. When the WATER2 location is too faraway from the FEED2 stage(i.e. the WATER2 location=2^{ed} to 5th) , some of the extractant is easily transferred to the distillation stream causing lower RACE.

The recovery of methanol(RCH4O） changing trend is similar to that of acetone when the WATER2 location is 2^{ed}-10th,. It deteriorates slower and with a smaller extent while the WATER2 location varies from 10th to 29th compared with RACE.

The recovery of methyl acetate(RMET) is not so sensitive to the WATER2 stage location. This might be due to its much less solubility in water than methanol and acetone, which means that it is hard to be carried to the bottom of B2 by water.

Sensitivity analysis of WATER4 stage and FEED4 stage in SCHEME1 indicates that the optimal result is WATER4 stage = 19th and FEED4 stage = 31st. RMET attains the maximum 0.9871 and RACE= 0.9997(Fig.3).

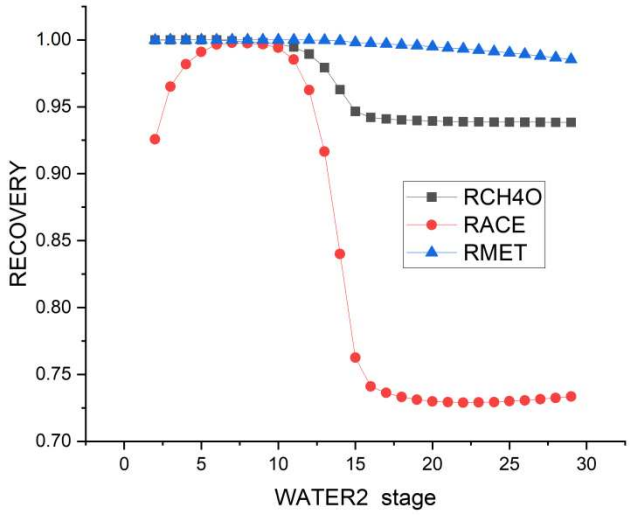


Fig.2 Sensitivity analysis of WATER2 stage in SCHEME1(FEED2 stage =15th)

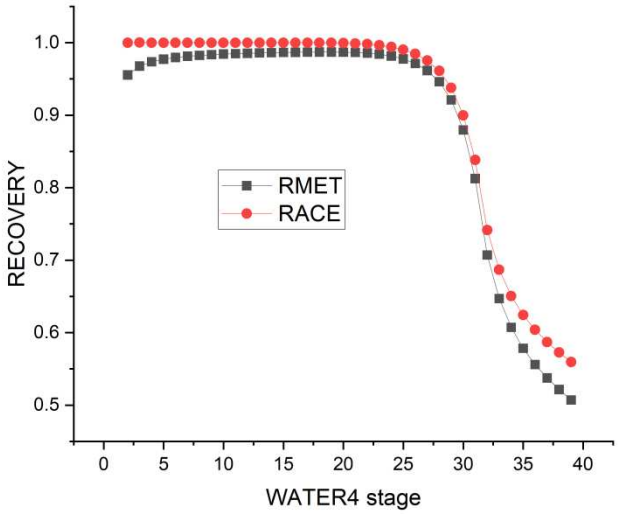


Fig.3 Sensitivity analysis of WATER4 stage in SCHEME1(FEED4 stage =31st)

3.4 The optimization of the extractant dosage

The extractant dosage, i.e., the mass flow rates of WATER2 and WATER4, is optimized by sensitivity analysis. Fig.4 indicates that when the flowrate of WATER2 varies from 300 to 1500Kg/hr, the recoveries of the three light components(RCH4O,RACE and RMET) attain nearly 100%. So the optimum flow rate of WATER2 is set at 1500 kg/h. Fig. 5 indicates that the optimum flow rate of WATER4 is also 1500 kg/h.

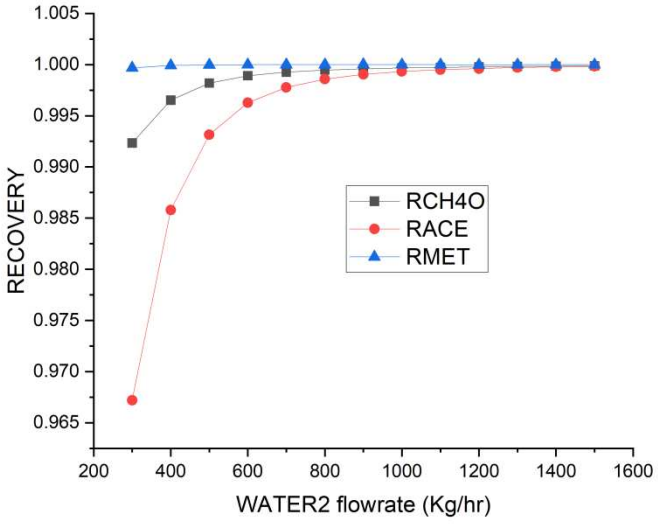


Fig.4 Sensitivity analysis of WATER2 flowrate in SCHEME 1.

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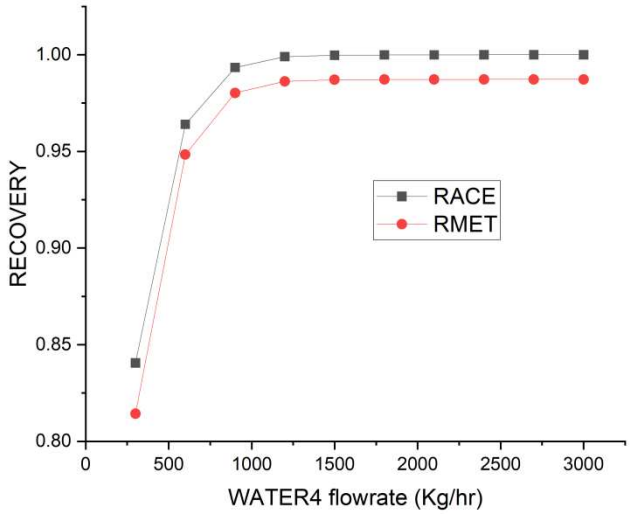


Fig.5 Sensitivity analysis of WATER4 flow rate in SCHEME 1

3.5 The optimization of the extractant temperature

Fig.6 shows sensitivity analysis of WATER2 temperature in SCHEME1. An increase in the extractant temperature leads to the fastest decrease of RACE, moderate decrease of RCH4O and slowest decrease of RMET. So the optimum temperature for WATER2 should be 25 ℃, and H2O-3 (99.9 ℃) should be cooled to 25 ℃ before it is recycled to WATER2 since RCH4O,RACE and RMET are at their maximum values which are approaching 100% .

Fig.7 shows sensitivity analysis of WATER4 temperature in SCHEME1. The extractant temperature increasing from 20℃ to 50℃ leads to a slight increase of the recoveries to the maximum values and then slightly decreasing the recoveries as it increases from 50℃ to 80℃, finally it quickly lowers the recoveries. So the temperature of H2O-5 (97.8 ℃) should be cooled to 50 ℃ before being recycled to WATER4.

The above analysis shows that a lower extractant temperature is advantageous for the separation, because most of the extractant should descend with the extracted component and leave from the bottom, whereas a higher temperature can cause a considerable part of the extractant to leave from the top stream, reducing the extraction efficiency.

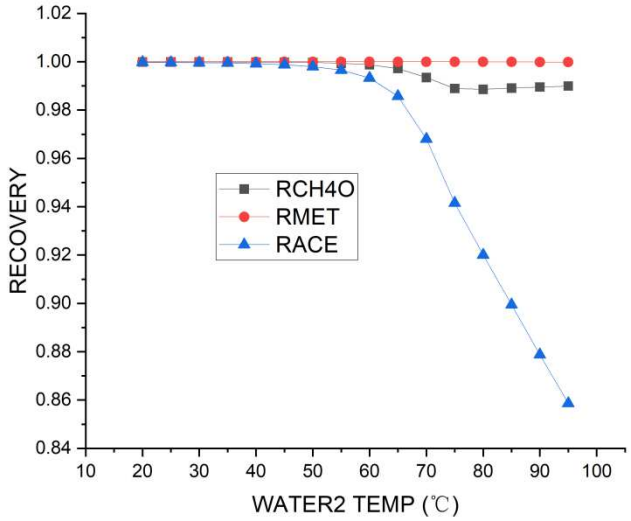


Fig.6 Sensitivity analysis of WATER2 temperature in SCHEME 1

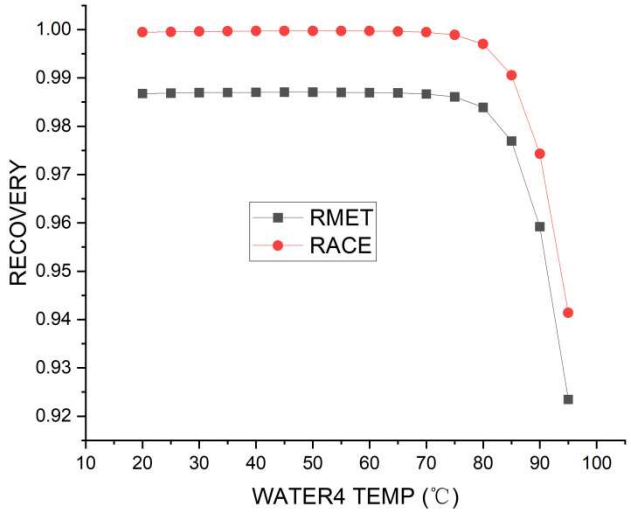


Fig. 7 Sensitivity analysis of the WATER4 temperature in SCHEME 1

3.6 The main results of SCHEME1 after optimization

Table 3 shows the mass fraction and recovery of light components in SCHEME1. The recovery and purity of furfural and methanol are both very high（> 99% on mass basis）,whereas those of methyl acetate and acetone are slightly lower than 99%. Table1 shows that water and MET can form binary minimum boiling point azeotrope at 0.959(MET):0.041(H2O). So MET will entrain minute water inevitably while water is used as the extractant to separate MET and ACE, which causes slightly lower recovery and purity of both components.

To increase the recovery and purity of MET and ACE to more than 99% level, two types of methods are put forward. One is to use other organic extractants; the other is to convert MET into CH4O and NaAc with NaOH. Both types of methods will be elucidated in the following sections.

Table3 The mass fraction and recovery of light components in SCHEME1

Component	Stream	Recovery (based on FEED1)	Purity (mass fraction)
Furfural	FUR-1	0.9992	0.9992
Methanol	CH4O-3	0.9983	0.9990
Methyl-acetate	MET-4	0.9870	0.9870
Acetone	ACE-5	0.9960	0.9815

Table 4 shows energy consumption and overall efficiency for each column in SCHEME1. The overall efficiency in the table is obtained using the O'Connell correlation[19]. The extract duty in the table is the cooling duty required to cool the extractant from the bottom bubbling temperature to the optimum extractant feed temperature.

Table4 Energy consumption and overall efficiency for each block in SCHEME1

ITEM	B1	B2	B3	B4	B5	B6	B7	∑
$Q_{reboiler}$(Mcal/hr)	350.7	214.8	642.4	130.8	125.2	/	/	1463.9
$Q_{condensor}$(Mcal/hr)	-321.6	-119.8	-613.8	-75.4	-102.6	/	/	-1233.2
Overall Efficiency(%)	27.01	53.50	44.80	61.54	56.82	/	/	243.67
Extract Duty(Mcal/hr)	/	/	/	/	/	-77.9	-115.5	-193.4

4 Separation of the light components using organic solvents as the extractant for removing acetone from methyl acetate

4.1 Removing methyl acetate from acetone using ethylene glycol as the extractant

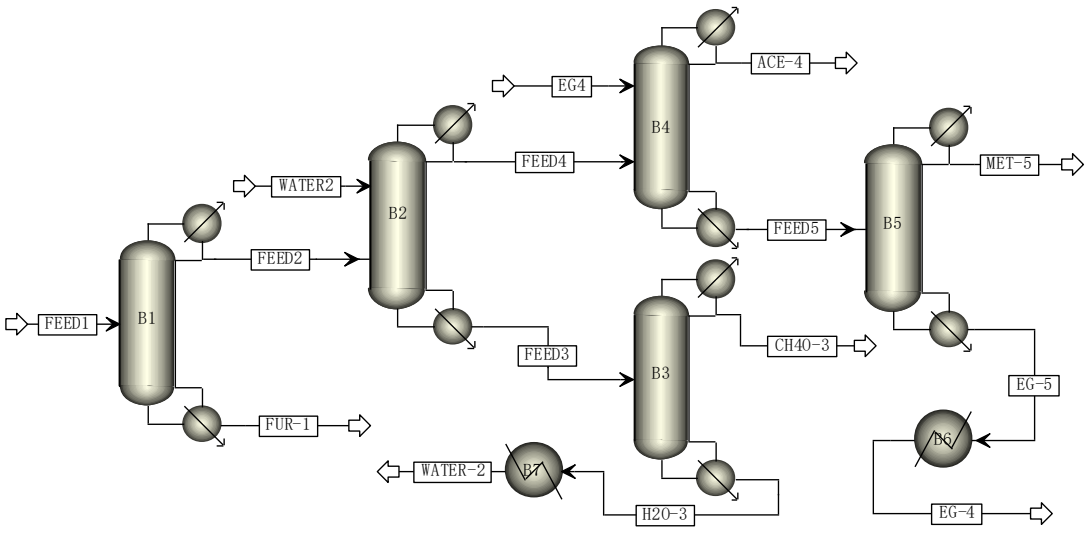


Fig.8 Flowsheet for separating the light components by extractive distillation using ethylene glycol as extractant(SCHEME 2)

Fig. 8 shows the flowsheet for separating the light components by extractive distillation using ethylene glycol [20] as the extractant (SCHEME 2). The feed and structure of B1, B2 and B3 in SCHEME 2 are the same as those in SCHEME 1, while ethylene glycol (EG) is used as the

extractant to remove methyl acetate (MET) from the bottom, and purified acetone is obtained from the top stream ACE-4 of B4. So the structures of B4 and B5 are different from those in SCHEME 1. The optimized EG4 flowrate is 1200Kg/hr.

The structure and operation condition specification for each block in SCHEME2 are shown in Table s1(in the supplementary material), among which B1,B2,B3 and B7 are identical to those in SCHEME1.

The sensitivity analysis of the FEED4 stage and the EG4 stage location was conducted by varying both from the 2nd to the 39th stage to observe the recovery of the related light components. The feed stage windows of distillation column B4 that enable recoveries of acetone(RACE) and methyl acetate(RMET) to be greater than 0.999 are quite wide. The feed stage of the extractant EG4 should be above the FEED4 stage. Fig.s1 shows both recoveries are nearly 100% when the EG4 stage location varies from 2^{th} to 25^{th} while the FEED4 stage is fixed at 31^{st}. The EG4 stage location is finally fixed at 19^{th} in the base case. When the EG4 stage location varies from the 25th to the 39th stage, the recoveries decrease sharply owing to inadequate contact between the extractant and the feed.

Fig.s2 indicates that when the flow rate of EG4 varies from 300 to 1200 kg/h, the recoveries of both components (RACE and RMET) attain their maximum values of 0.999815233 and 0.99981682, respectively. Further increasing the flow rate of EG4 from 1200 kg/h to 3000 kg/h causes a slight decrease in both recoveries. So the optimum flow rate of EG4 is 1200 kg/h.

Fig.s3 shows sensitivity analysis of EG4 temperature in SCHEME2. When the temperature of EG-5 (193.465 ℃) is lowered to 180 ℃, both recoveries reach very high values higher than 0.999; therefore EG-5 can be cooled to 180 ℃ before being recycled to EG4, and further cooling of the extractant is unnecessary.

Table s2 shows the mass fraction and recovery of light components in SCHEME2. The recovery and purity of all the four components are very high（> 99% ）. Compared with SCHEME 1, the recoveries and purity of methyl acetate and acetone are much higher in SCHEME 2. Table s3 shows the energy consumption and overall efficiency for each block in SCHEME2.

4.2 Removing methyl acetate from acetone using dimethyl sulfoxide as the extractant

Fig. s4 shows Flowsheet for separating the light components by extractive distillation using dimethyl sulfoxide(DMSO) as the extractant(SCHEME 3). The structures of B1, B2, B3 and B7 in SCHEME 3 are the same as those in SCHEME 1, while dimethyl sulfoxide (DMSO) is used as the extractant to remove methyl acetate (MET) from the bottom, and purified acetone is obtained from the top stream ACE-4 of B4. So the structure of B4 and B5 are different from those in SCHEME1. The optimized DMSO4 flow rate is 2700 kg/h.

Table s4 shows the structure and operation condition specification for each block in SCHEME3 among which B1,B2,B3 and B7 are identical to those in SCHEME1.

The sensitivity analysis of the FEED4 stage and the DMSO4 stage location was conducted by varying both from the 2nd to the 39th stage to observe the recovery of the related light components. The feed stage of the extractant DMSO4 should be above the FEED4 stage. Fig. S5 shows that both recoveries decrease monotonically as the DMSO4 stage location varies from the 2^{nd} to the 39^{th} stage while the FEED4 stage is fixed at 25^{th}. So the DMSO4 stage location is finally fixed at the 2nd stage in the base case to attain the maximum recoveries(RMET=0.997896074, and RACE= 0.978850899, both are lower than those in SCHEME2 using EG as the extractant).

Fig.s6 indicates that when the flow rate of DMSO4 varies from 300 to 9000 kg/h, the recovery of acetone(RACE) has a maximum value 0.9789 at 2700 Kg/hr, whereas the recovery of methyl acetate (RMET) at 2700 kg/h is 0.9979 and after that it increases slightly as the flow rate of DMSO4 varies from 2700 kg/h to 9000 kg/h. So the optimum flow rate of DMSO4 should be 2700 kg/h.

Fig.s7 shows sensitivity analysis of DMSO4 temperature in SCHEME3. When the temperature of DMSO-5 (188.9929 ℃) is lowered to 20 ℃, both recoveries reach their maximum values of 0.997382751 and 0.981967805, respectively. So DMSO-5 should be cooled to 20 ℃ before being recycled to DMSO4.

Table s5 shows the mass fraction and recovery of the light components in SCHEME 3. The recovery and purity of methyl acetate and acetone are lower than 0.99. Table s6 shows the energy consumption and overall efficiency for each block in SCHEME 3.

4.3 Removing methyl acetate from acetone using furfural as the extractant

Fig. S8 shows the flowsheet for separating the light components by extractive distillation using furfural (FUR) as the extractant (SCHEME 4). The structures of B1, B2, B3 and B7 in SCHEME 4 are the same as those in SCHEME 1, while furfural (FUR) is used as the extractant to remove methyl acetate (MET) from the bottom, and purified acetone is obtained from the top stream ACE-4 of B4. So the structure of B4 and B5 are different from those in SCHEME1. The optimized FUR4 flow rate is 2700 kg/h.

Table s7 shows the structure and operation condition specification for each block in SCHEME4 among which B1,B2,B3 and B7 are identical to those in SCHEME1.

The sensitivity analysis of the FEED4 stage and the FUR4 stage location was conducted by varying both from the 2nd to the 39th stage to observe the recovery of the related light components. The feed stage of the extractant FUR4 should be above the FEED4 stage. Fig. S9 shows that both recoveries remain at a high level greater than 0.99 as the FUR4 stage location varies from the 4th to the 25th stage while the FEED4 stage is fixed at 32^{ed}. So the FUR4 stage location is finally fixed at the 12th stage in the base case to attain the maximum recoveries(RMET=0.999998671, and RACE= 0.995543804, which are approaching those in SCHEME2 using EG as the extractant).

Fig. s10 indicates that when the flow rate of FUR4 varies from 300 to 3000 kg/h, the recovery of acetone(RACE) has a near maximum value 0.9955 at 2700 Kg/hr, whereas the recovery of methyl acetate(RMET) at 2700 Kg/hr is 0.99999. So the optimum flow rate of FUR4 should be 2700 kg/h.

Fig. S11 shows sensitivity analysis of FUR4 temperature in SCHEME4. When the temperature of FUR-5 (159.96 ℃) is lowered to 145 ℃, both recoveries reach their maximum values of 0.99999 and 0.9960, respectively. So FUR-5 should be cooled to 145 ℃ before being recycled to FUR4.

Table s8 shows the mass fraction and recovery of the light components in SCHEME 4. Both the recovery and purity of MET are lower than 0.99. Table s9 shows the energy consumption and overall efficiency for each block in SCHEME 4.

5 Separation of the light components by converting methyl acetate to methanol

5.1 Synthesis of the process

Fig.9 shows the flowsheet for separating the light components by converting methyl acetate to methanol, which is referred to as SCHEME 5. FEED1 and B1 are the same as those in SCHEME 1.

The distilled flow FEED-R1 is sent to block R1, in which methyl acetate is converted to methanol and NaAc by NaOH at 60 ℃. The stream NaOH+H2O consists of 1.41739 kmol/h NaOH and 2 kmol/h water. This is an irreversible reaction, and the conversion of methyl acetate is assumed to be 100%. The reaction product mixture FEED2 is transferred to V1, where the liquid is vaporized at 69 ℃ and subsequently cooled to 60 ℃ in H1. The resulting stream, referred to as FEED4, is the feed to B4. The subsequent extractive distillation uses water as the extractant to separate methanol from acetone by the combination of B4 and B5. The flow rate of WATER4 in SCHEME 5 is 1500 kg/h at 25 ℃ and 1 atm.

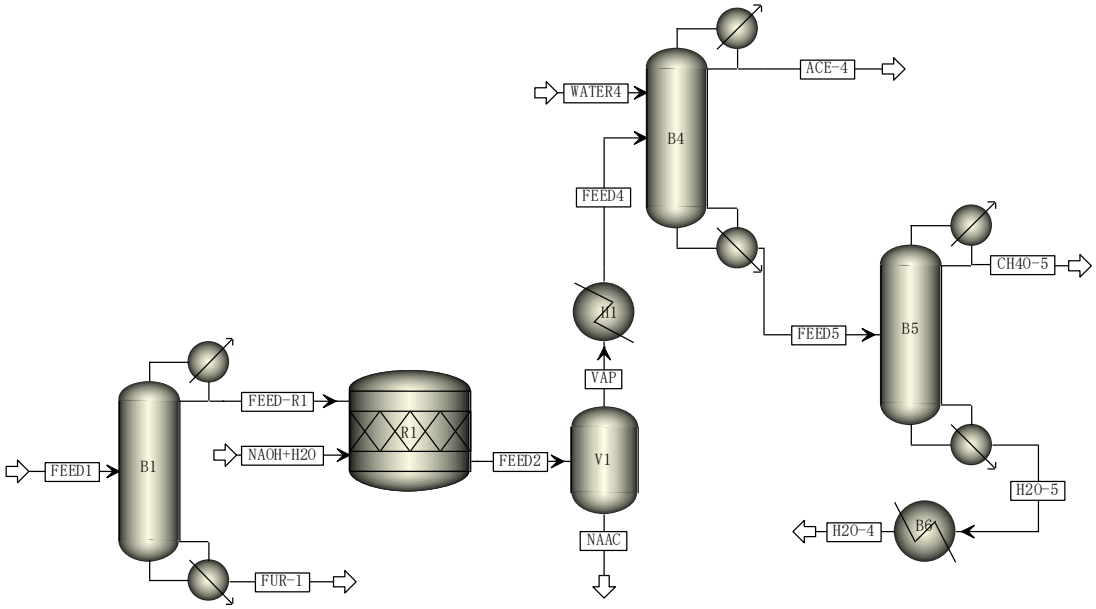


Fig.9 Flowsheet for separating the light components by converting MET to CH4O(SCHEME5)

5.2 The structure and operation condition specification for each block in SCHEME5

Table s10 shows the structure and operation condition specification for each block in SCHEME 5. B1 is identical to that in SCHEME1. R1 is an RStoic reactor, V1 is a Flash2 separator, and H1 and B6 are Heater blocks.

5.3 The optimization of WATER4 stage location

The sensitivity analysis of the FEED4 stage and the WATER4 stage location was conducted by varying both from the 2nd to the 39th stage to observe the recovery of the related light components. The feed stage of the extractant WATER4 should be above the FEED4 stage. Fig. S12 shows that the recovery of acetone (RACE) attains its maximum of 0.9930 while the recovery of methanol (RCH4O) is 0.9999 when the WATER4 stage location is the 18th stage and the FEED4 stage is fixed at the 25th stage. So the optimum stages for FEED4 and WATER4 are the 25th and 18th stages, respectively.

5.4 The optimization of the WATER4 dosage

Fig. S13 indicates that the optimum flow rate of WATER4 should be 1500 kg/h, since RACE attains its maximum of 0.992976112 while RCH4O is 0.999963737.

5.5 The optimization of WATER4 temperature

Fig. S14 shows the sensitivity analysis of the WATER4 temperature in SCHEME 5. H2O-5

(99.95 ℃) should be cooled to 25 ℃ before being recycled to WATER4, since the recovery of acetone (RACE) attains its maximum of 0.9930 while the recovery of methanol (RCH4O) is 0.99996.

5.6 The main results of SCHEME5 after optimization

Table s11 shows the mass fraction and recovery of the light components in SCHEME 5, in which the recovery and purity of acetone and methanol are all above 0.99. Table s12 shows the energy consumption and overall efficiency for each block in SCHEME 5.

6 Comparison of the five schemes for separating the light components

The five schemes for separating the light components are compared in terms of the recovery and purity of the light components, total energy consumption, overall column efficiency, and other aspects.

6.1 Comparison of the recovery and purity of the light components in the five schemes

Fig. 10 shows the recovery of the light components of the five schemes. The results are as follows:

For the recovery of furfural, SCHEME 1 = SCHEME 2 = SCHEME 3 = SCHEME 4 = SCHEME 5, since B1 for separating furfural is identical in the five schemes.

For the recovery of methanol, SCHEME 1 = SCHEME 2 = SCHEME 3 = SCHEME 4 < SCHEME 5, since the extractive distillation column B3 for separating methanol is identical in the first four schemes, whereas B5 for separating methanol in SCHEME 5 is an ordinary distillation column that can easily obtain a higher recovery.

For the recovery of acetone, SCHEME 2 > SCHEME 1 > SCHEME 4 > SCHEME 5 > SCHEME 3; SCHEME 2, which uses EG as the extractant, obtains the highest recovery of acetone.

For the recovery of methyl acetate, SCHEME 2 > SCHEME 1 > SCHEME 4 > SCHEME 3; SCHEME 2, which uses EG as the extractant, obtains the highest recovery of methyl acetate. Since SCHEME 5 converts methyl acetate to methanol, it is not included in this comparison.

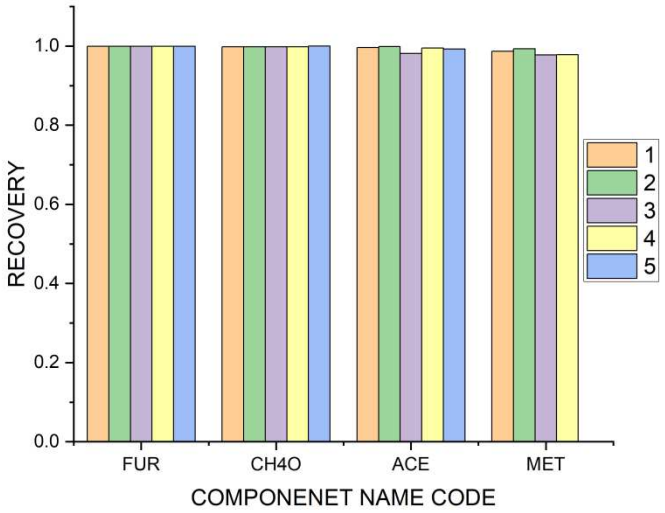


Fig.10 Recovery the light components of the five schemes

Fig. 11 shows the purity of the light components of the five schemes. The results are:

For the purity of furfural, SCHEME1= SCHEME2= SCHEME3= SCHEME4= SCHEME5.

For the purity of methanol, SCHEME1= SCHEME2= SCHEME3= SCHEME4<SCHEME5.

For the purity of acetone, SCHEME2>SCHEME4>SCHEME5>SCHEME3>SCHEME1.

For the purity of methyl acetate, SCHEME2>SCHEME1>SCHEME4 >SCHEME3.

In conclusion, SCHEME 2, which uses EG as the extractant, achieves the highest recovery and purity for all components, whereas SCHEME 5 achieves recovery and purity higher than 99% for all three recovered components without using any organic extractant.

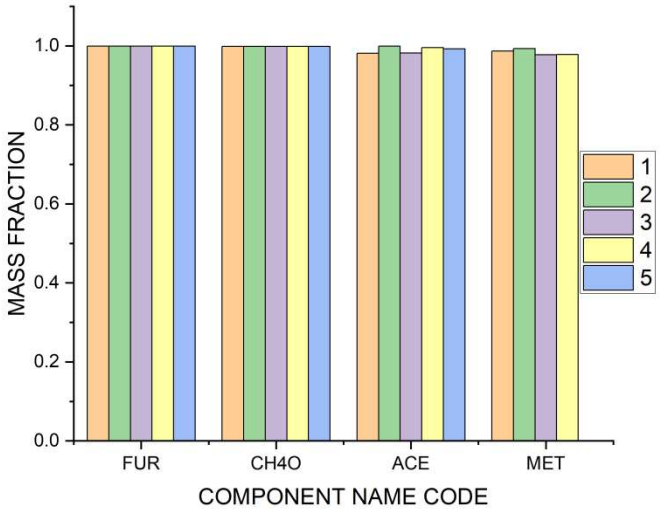


Fig. 11 purity the light components of the five schemes

6.2 Comparison of the total energy consumption in the five schemes

Fig. 12 shows the heating duty of the five schemes; the order of heating duty is SCHEME 4 < SCHEME 2 < SCHEME 1 < SCHEME 3 < SCHEME 5.

Fig. 13 shows the cooling duty of the five schemes; the order of cooling duty is SCHEME 4 < SCHEME 2 < SCHEME 1 < SCHEME 3 < SCHEME 5.

Fig. 14 shows the extractant duty of the five schemes; the order of extractant duty is SCHEME 2 < SCHEME 3 < SCHEME 4 < SCHEME 1 < SCHEME 5.

SCHEME 5 has the highest energy consumption, mainly because the added blocks V1 and H1 require cooling and heating, respectively.

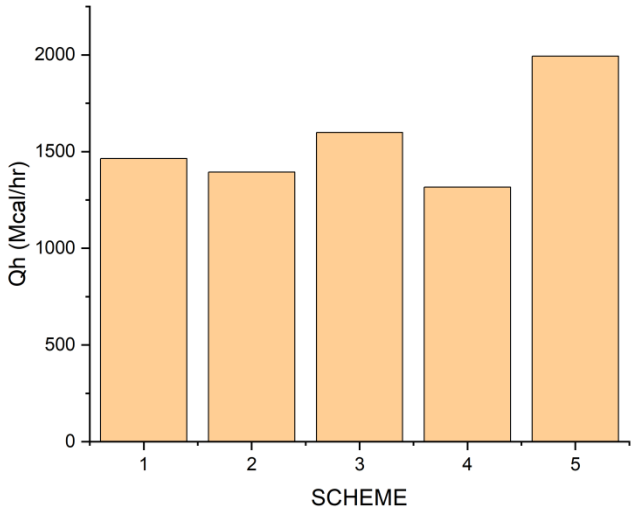


Fig. 12 Heating duty of the five schemes

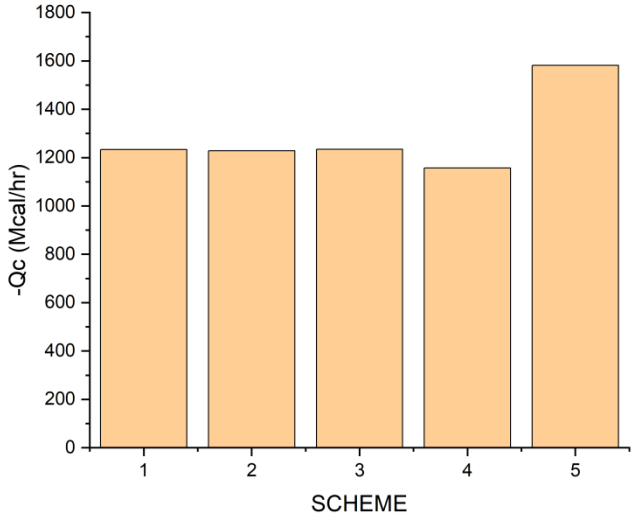


Fig. 13 Cooling duty of the five schemes

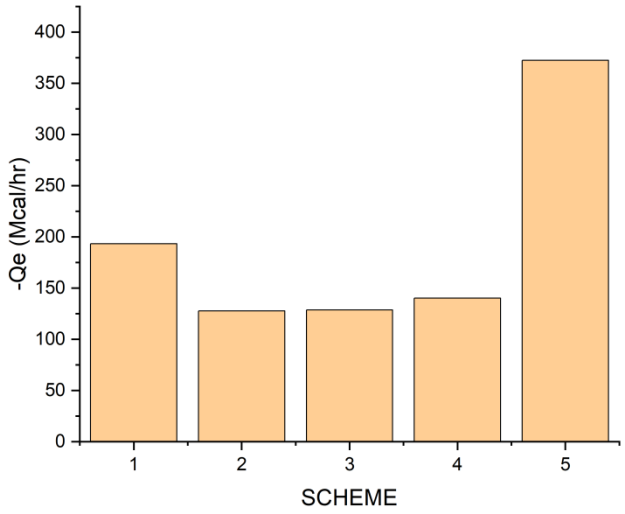


Fig. 14 Extractant duty of the five schemes

6.3 Comparison of the overall efficiency of each column in the five schemes

Fig. 15 shows the total column efficiency of the five schemes; the order is SCHEME 1 > SCHEME 5 > SCHEME 3 > SCHEME 2 > SCHEME 4.

Higher total efficiency means lower fixed cost, i.e., less investment in equipment.

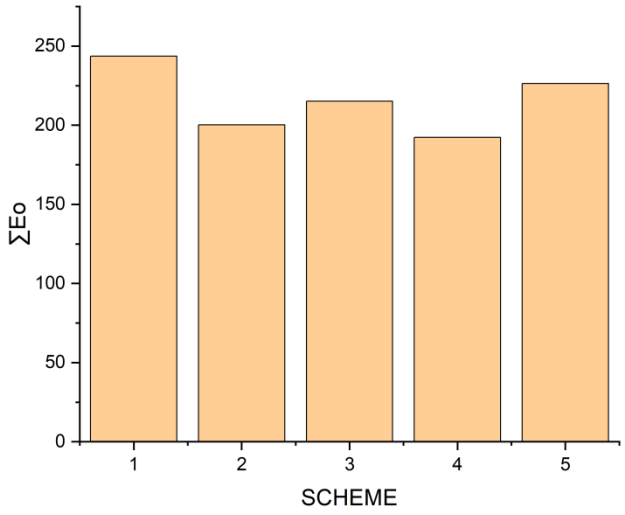


Fig. 15 Total column efficiency of the five schemes

6.4 Others

Other factors to be considered include the environmental friendliness, stability and cost of the extractant. Water is the best choice in terms of these factors, but using water as the extractant to separate acetone and methyl acetate cannot achieve very high purity for acetone and methyl acetate. Using EG as the extractant to separate acetone and methyl acetate can achieve very high purity and

recovery. Besides, EG is stable under the operating conditions, and the price of EG is the lowest among the three organic solvents. Furfural polymerizes easily under the operating conditions, which might prevent it from being used as a satisfactory extractant.

7 Conclusions

Five schemes are proposed to separate the light components recovered from furfural production, which consist of furfural, methanol, acetone and methyl acetate; the latter three components form minimum-boiling binary azeotropes in all pairwise combinations.

The major conclusions are:

7.1 Furfural is the heavy key component, which is separated first in all schemes using a simple distillation column, and both the recovery and purity of furfural are as high as 0.9992.

7.2 Methanol is best separated by extractive distillation using water as the extractant, and the recovery and purity of methanol are as high as 0.9983 and 0.9990, respectively.

7.3 Water can also be used as the extractant to separate acetone and methyl acetate, as shown in SCHEME 1, but the purity of acetone and methyl acetate is slightly lower than 0.99 because methyl acetate inevitably entrains a small portion of water via the binary azeotrope.

7.4 Among the three organic solvents, ethylene glycol is the best in terms of recovery and purity, both of which exceed 0.99. The energy consumption of this scheme (SCHEME 2) is at a lower level compared with the other schemes, whereas its total column efficiency is slightly lower than those of SCHEME 1, SCHEME 3 and SCHEME 5.

7.5 SCHEME 1 has the highest total column efficiency and relatively low energy consumption; therefore, if the purity of acetone and methyl acetate (0.9815 and 0.9870, respectively) satisfies the customer, SCHEME 1 is strongly recommended.

7.6 SCHEME 5 has the advantage of using water alone as the extractant to obtain high recovery and purity for methanol and acetone; however, it has the highest energy consumption and requires NaOH to convert methyl acetate to methanol.

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Conflict of Interest Statement

No competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors declare that they have no known competing financial interests or personal affiliations in the past three years that could have affected the research, analysis, and writing of this manuscript.

Data Availability Statement

All data generated or analysed during this study are included in this published article. The simulation models, process parameters, and optimized operating data that support the findings of this study are available from the corresponding author on reasonable request.

References

[1]Rachamontree P, Douzou T, Cheenkachorn K, Srinophakun P. Furfural: A sustainable platform chemical and fuel, Applied Science and Engineering Progress, 2020, 13(1): 3-10.

[2]Edumujeze D, Fournier-Salaün M, Leveneur S, Production of furfural: from kinetics to process assessment[J]. Fuel, 2025, 381: 133423.

[3]Rönnebro E, Chen J G,Selective hydrogenation of furfural to furfuryl alcohol over supported metal catalysts, ACS Sustainable Chemistry & Engineering, 2017, 5(1): 744-751.

[4]Luo Y P, Li Z, Li X L, Wang H, The production of furfural directly from hemicellulose in lignocellulosic biomass: A review, Catalysis Today, 2019, 319: 14-24.

[5]Zhang G S, Zhu M M, Zhang Q, Wang X, Towards quantitative and scalable transformation of furfural to cyclopentanone with supported gold catalysts, Green Chemistry, 2018, 20(12): 2764-2773.

[6]Baktash M M, Ahsan L, Ni Y H, Production of furfural from an industrial pre-hydrolysis liquor[J]. Separation and Purification Technology, 2015, 149: 407-412.

[7]Ojeda M, Sadaba I, Lopez Granados M. Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels, Energy & Environmental Science, 2016, 9(4): 1144-1189.

[8]Mandalika A, Morais A R C, Bogel-Łukasik E, Bogel-Łukasik R, Ionic liquids as a tool for lignocellulosic biomass fractionation[J]. Sustainable Chemical Processes, 2013, 1(1): 1-31.

[9]Wang Q, Wang W, Qi W, Zhang Y. Research progress on acid-catalyzed preparation of furfural from lignocellulose, Transactions of the Chinese Society of Agricultural Engineering, 2017, 33(15): 1-10.

[10]Xia H H, Zhou M H, Chen C Z, Li J. Research progress on metal-based catalysts for furfural hydrogenation in aqueous media, Biomass Chemical Engineering, 2022, 56(4): 39-48.

[11]Zhou S S, Miao X T, Yao X, Zhang Y. Research progress on electrocatalytic oxidation catalysts for furfural, Hans Journal of Catalysis, 2025, 12(1): 1-8.

[12]Yu Y M, Wan J, Wang J, Simulation and optimization of furfural distillation process[J]. Journal of Anhui University of Science and Technology (Natural Science), 2021, 41(3): 1-6.

[13] William L. Luyben, Comparison of Extractive Distillation and Pressure-Swing Distillation for Acetone-Methanol, Separation. Ind. Eng. Chem. Res. 2008, 47, 2696-2707.

[14]Badra Mahida, Malika Medjahdi, Ikram Khelifa, Samiha Mazouzi, Houaria Maghdouri, Separation of acetic acid and ethanol from wastewater by distillation process with addition of side draw stream, Chemical Papers (2023) 77:837–846.

[15] Jinglian Gu, Yukun Ma, Xinqiang You, Energy efficient extractive distillation process design and optimization for separating quaternary mixture with four azeotropes based on thermodynamic insight,Chemical Engineering Research and Design 230 (2026) 203–218.

[16] I Gede Pandega Wiratama, Zong Yang Kong, Basil T. Wong, Ao Yang, Agus Saptoro,Jaka Sunarso, New hybrid reactive-extractive distillation with two reactants for separating water-free ternary azeotropic mixtures, Chemical Engineering Research and Design 221 (2025) 369–382.

[17] Jianlin Yan, Jiyan Liu, Junyao Ren, Yang Wu, Xinnong Li, Tao Sun, Lanyi Sun, Design and multi-objective optimization of hybrid reactive-extractive distillation process for separating wastewater containing benzene and isopropanol,Separation and Purification Technology 290 (2022) 120915.

[18] Iva´n D. Gil, Diana C. Botı´,Pablo Ortiz,and Oscar F. Sa´nchez, Extractive Distillation of

Acetone/Methanol Mixture Using Water as Entrainer. Ind. Eng. Chem. Res. 2009, 48, 4858–4865.

[19] J.D.Seader, Ernest J. Henley, Separation Process Principles, Beijing：Chemical industrial press，2002.

[20] Jesús Alonso Cruz Valdez, Rosalba Pati˜no-Herrera, Adriana Avil´es Martínez, Elías P´erez, Separation of the cyclohexane-benzene mixture by the extractive distillation process using ethylene glycol as a solvent, Chemical Engineering and Processing- Process Intensification 196 (2024) 109686-109698.

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