Novel Packing-Enhanced Distillation Separation of Isoamyl Alcohol Isomer: Experimental and Pilot Scale Study

Yue Liu
School of Chemical Engineering and Technology, Tianjin University, No. 92 Wei Jin Road, Tianjin 300072, P.R. China
Henan Tianguan Group Co., Ltd, No.16 Jianshedong Road, Nanyang, Henan Province 473000, P.R. China

Hong Gao, Jinsheng Sun, Yanhong Wang, Peng Wu, Yanzhen Liu and Yulan Ji
School of Chemical Engineering and Technology, Tianjin University, No. 92 Wei Jin Road, Tianjin 300072, P.R. China

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Separation of isoamyl isomers by means of internally enhanced ordinary distillation was investigated in this work. Because of very close boiling points between the target components of the mixture, a novel paralleling spiral packing of extremely low HEPT was experimentally developed with success for this purpose. A coupled scheme of pilot scale was subsequently setup separating 2-methyl-butanol and 3-methyl-butanol from fusel oil, usually low-class byproduct of fuel bioethanol manufactures. Basically, batch distillation is used to remove light ends and the continuous partner to separate 2-methyl-butanol and 3-methyl-butanol. Operating results satisfactorily suggested that the concentration of 2-methyl-butanol was over 99 wt % with the yield over 80%. Computational flowsheet simulation was also done with the outcome in good agreement with the tested onsite to facilitate industrial design. © 2011 American Institute of Chemical Engineers *AIChE J,* 57: 3037–3041, 2011
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Introduction

Fusel oil, the mixture of higher alcohols, is a low-value byproduct of fuel ethanol factories with fermentation process, whereas high-value added active amyl alcohol (2-methyl-1-butanol) and isoamyl alcohol (3-methyl-1-butanol) are main components of it,[1] together with other constituents including ethanol, propanol, isobutanol, and water. Isoamyl alcohol is widely used in the product of solvents and synthetic fragrances, or the raw material of medicine intermediates, aldehydes, acetals, acids, esters, and other products for special industrial purpose as well. It is also worth noting that 2-methyl-1-butanol is involved in the synthesis of chiral compounds, especially chiral LED materials for popular green illumination.

Ordinary distillation can easily extract the mixture of isoamyl alcohol and active amyl alcohol, with total concentration of 95 wt %, from fusel oil. However, the concentration of active amyl alcohol is only 20–30 wt % at the most in the product.[2] It is very difficult to obtain the two alcohols with their concentration up to 95 wt %, respectively, because of their similar chemical structure, boiling point difference of 2.8°C, and the relative volatility of 1.036.[3] Basically, the current separation methods for this purpose are ordinary distillation,[4] precise distillation,[2,5] extractive distillation,[6–8] and

Correspondence concerning this article should be addressed to J. Sun at jssun2006@vip.163.com.

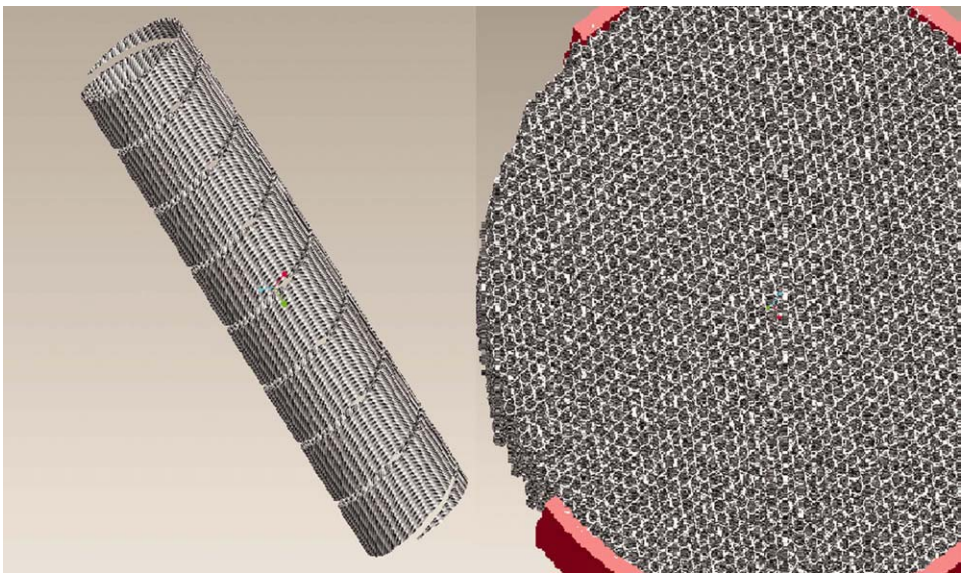

Figure 1. The paralleling spiral packing and its bundle section in column.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemistry separation method.[9] Using distillation to separate 3-methyl-butanol and 2-methyl-butanol requires a large number of theoretical plates, which significantly increases the difficulty of industrial unit construction. Extractive distillation to some extent improved the relative volatility, but a limited margin of this increase cannot reduce the required theoretical plates to an ideal range, not to mention the extractant defects. The large number of theoretical plates plus the recovery of extractant consequently lengthened the process and increased investment and operating costs.

This situation encourages the development of a novel paralleling spiral packing (PSP) with high efficiency in this study. Packed by this packing, batch distillation and continuous distillation for separation of 2-methyl-1-butanol and 3-methyl-1-butanol were evaluated, respectively, to determine a process with concentration of 2-methyl-1-butanol up to 99 wt % yielding more than 80% valuable products.

Packing and Experiments

Paralleling spiral packing

Packed column was widely used in unit operation, such as distillation, absorption, and extraction.[10] Packing is the core of packed tower, which is strongly related to the effective contact of gas–liquid phase and directly affects the separation performance. Therefore, great importance was attached to the development and research of packing.[11] To separate 2-methyl-butanol and 3-methyl-butanol, a novel PSP was developed, as shown in Figure 1. It is well known that spiral packing has been used for many years. For example, Herbert[12] developed a spiral screen packing for laboratory fractioning column, which was easily done by screwing a spiral of heavy wire into the spiral packing, and a sealed glass tube or nickel rod was installed in the center hole of the spiral to provide support and to prevent the vapors' rising directly up the center of packing, inserting this into a close-fitting outer glass tube assembly, then unscrewing the wire spiral. Minghan Han[13] also presented a novel internal for reactive distillation with spiral springs used as the retaining screen of the porous passages. Nevertheless, they are different from PSP in both unit structure/material itself and their incrementally installation manner instead of the squeezed one for PSP.

The PSP utilizes multilayer gauze wire to improve the forming ability of liquid film, and also to increase the capillary action and mechanical strength. Each PSP unit with a diameter of 4 mm and a clearance of 1 mm was constructed of stainless steel gauze, which has a width of 4 mm and thickness of 0.3 mm. This packing possessed a void fraction (v) of $\sim$0.91 and a specific surface area (α) of 1700 m^2/m^3, both of the above determined the packing factor (ε) of 2256 m^{-1}, which is known as the ratio of the specific surface area and the cubic of void fraction.

To determine the internal characteristics of this packing, hydrodynamic parameter in terms of pressure drop per unit height ($\Delta p/\Delta z$) and mass-transfer efficiency represented as height equivalent to a theoretical plate (HETP) were determined by total reflux laboratorial experiments using ethanol/water system at atmospheric pressure. The result was reported as a function of the F-factor, which defined as the product of the superficial vapor velocity and the square root of vapor density and is based on the column bottom conditions.

The pressure drop curve for ethanol/water, in a 0.1 m column equipped with 30 cm height of PSP, was shown in Figure 2. It displays an increase in pressure drop with the rising of vapor velocity. When the vapor velocity increases, the vapor flow disturbs and holds up liquid gravity flow, the hold-up increases, and the available flow area for upflowing vapor is squeezed and diminished as the pressure drop increases. Moreover, the trends are similar to those observed for classical structured packing, where the pressure drop is proportional to the square of the gas flow (for a given liquid load).[14] At higher pressure drop, a discontinuity divides the curve into two distinct zones. The location of the discontinuity corresponds to the loading point. If the vapor flow

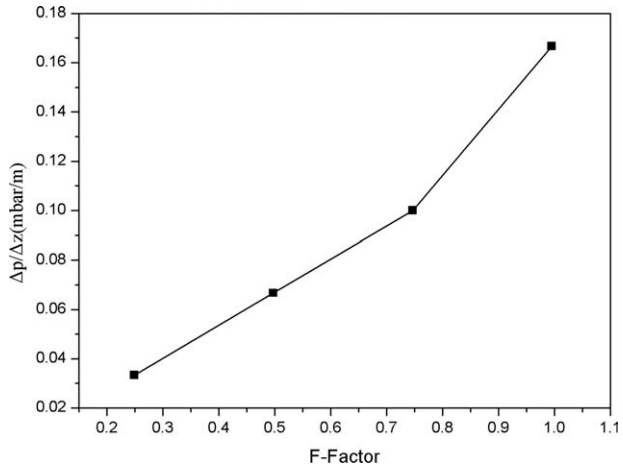

Figure 2. Effect of operating velocity (F-Factor) on hydrodynamic performance.

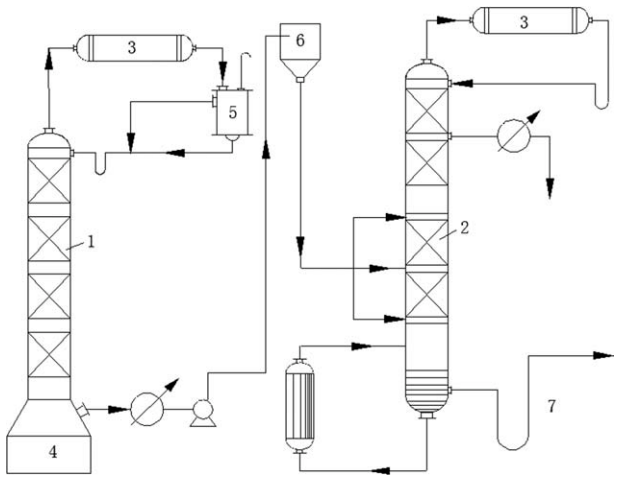

Figure 3. Flow sheet of batch distillation coupled with continuous distillation.

(1) Batch distillation column; (2) Continuous distillation column; (3) Condenser; (4) batch tower kettle; (5) decanter; (6) head tank; (7) automatic liquid discharge device.

continuous to increase, the hold-up increases until the flooding point is reached, corresponding to the last point. As presented in Figure 2, the pressure drop of PSP was less than 0.1 mbar/m, which was significantly lower than conventional structured packing. It is mainly attributed to the bundle of vertical hollow tubular structures along with the triangular pathway formed by three adjacent units, supplying largely limited frontal area, and multilayer gauze wire wall of PSP units suck and spread liquid on its surface to form a smooth film, which also attributes to the low pressure drop.

The HETP was ~0.05 m, corresponding to 20 theoretical stages per meter, for the F-factor around 0.8 $Pa^{0.5}$. As the F-factor increased to 2 $Pa^{0.5}$, the HETP decreased to 0.067 m or so, corresponding to 15 theoretical stages per meter. The theoretical stages per meter were much higher than that of the traditional structured packing whose theoretical stages per meter are often below 10.[15]

Apparatus and procedures

The distillation equipment for pilot study is shown in Figure 3, which consists mainly of a batch distillation tower, a decanter, and a continuous distillation tower. The batch tower is of ID 200 mm with a rectifying section of 8 m and four-bed isotonic PSP. The continuous tower is of ID 200 mm with a rectifying section of 15 m and a stripping section of 10 m, and filled with two-bed PSP.

Fusel oil was added to the batch tower kettle as raw material and the column operated in the situation of total-reflux for 30 min. Mixed propanol in the fusel oil was recovered from the top of tower at reflux ratio of 3:1 when the column reached gas–liquid equilibrium. Once tower top temperature reached 89°C, decanter was used to remove water, and isobutanol can be used as entrainer itself to bring out of water. The process was finished until the temperature reached 105°C, and then the reminding isobutanol is extracted at reflux ratio of 10:1. After the temperature reached 128°C, increasing the amount of gasification and using total-reflux operation, then mixed amyl alcohol (MAA) was taken from tower kettle quickly to avoid contamination of light ends.

Concentration of 2-methyl-butanol and 3-methyl-butanol in MAA that is obtained from batch tower were 20 and 80 wt %, respectively. First, MAA was pumped into head tank and then entered into continuous tower at the controlled flow rate. Sequentially, after the entire column was operating normally, the feed was closed and total reflux carried on for 8 h until the column reached equilibrium. Finally, the feed was reopened, and then qualified 2-methyl-butanol and 3-methyl-butanol can be obtained continuously from lateral line and bottom of tower, respectively. As shown in Figure 3, three inlets at the different height were placed in the centre of continuous tower to meet different composition of raw material. Lateral line was placed near the top of tower to collect qualified 2-methyl-butanol, a little amount of isobutanol and water was concentrated on the top of tower and recovered in intermittent or continuous way.

Analytical method

The water content of fusel oil was analyzed by Karl-Fisher titration, and the purity of product was determined by gas chromatography.

Results and Discussion

Separation of light ends using batch distillation

Table 1 revealed product's quality and yield of batch distillation. Fusel oil (1500 kg) was fed into batch distillation

Table 1. Product Quality and Yield of Batch Distillation at Different Distillation Range

Fraction	DR (°C)	*W*	*M* (Kg)	*Y*
Mixed propanol	74 ~ 89	–	650	–
Oil-water	89 ~ 105	–	80	–
Isobutanol	105 ~ 107	≥95%	50	30%
Middle fraction	107 ~ 128	–	50	–
MAA	128 ~ 130	≥99.5%	670	90%

Table 2. Effect of 2-Methyl-butanol Concentration on Yield

Feed (wt %)	Product (wt %)	M (Kg)	Y
20	98.0	100	10
40	98.5	220	22
60	99.0	350	35
80	99.0	450	45
90	99.0	600	60

tower, in which the concentration of MAA was 50 wt %, and products were collected at different distillation range. The MAA were obtained at 128–130°C with the yield of 90%.

Separation of 2-methyl-butanol and 3-methyl-butanol by batch distillation

Different concentration of 2-methyl-butanol in the MAA directly affected the yield of itself, as can be seen in Table 2. Batch distillation can concentrate 2-methyl-butanol to 98 wt % or even higher, but the yield of qualified products is only 10%. Besides, a lot of intermediates, of which mass fraction fell between 0.4 and 0.8, need to be retreated.

Results indicated that batch process was more suitable for the production of MAA. Especially, when batch distillation was combined with decanter and rapid adoption device, the concentration of MAA was more than 99.5 wt % and the yield over 90%. However, it is not economical to utilize batch distillation to separate 2-methyl-butanol and 3-methyl-butanol.

Separation of 2-methyl-butanol and 3-methyl-butanol by continuous distillation

The MAA, including 20 wt % 2-methyl-butanol, entered into continuous tower. 2-Methyl-butanol of yield over 99.5 wt % was collected from the side stream below top of the tower, and 3-methyl-butanol over 99.5 wt % was recovered from the bottom of tower. Table 3 provides experiment data of different feed rates.

Results shows that continuous distillation, which owned suitable feeding rate and reflux ratio over 80, can get qualified 2-methyl-butanol and 3-methyl-butanol products one-time simultaneously. Based on Underwood equation, minimum reflux ratio is just related to relative volatility, when the feed and distillate condition is determined. Consequently this large minimum reflux ratio is always required by no matter what kind of packing and how large the NTSM, due to the relative volatility immensely close to 1 between the target components. That is, the large reflux ratio was determined by the nature of the mixture under certain theoretical plates. However, the HETP of PSP is significantly lower than that of traditional commercial packings, so the height of commercial-packed column will be largely lowered through usage of PSP to achieve the same separation efficiency. In the appropriate range of reflux ratio (80–150), packed by PSP can lower the height of tower effectively, reducing energy consumption through avoid connecting pumps necessary for serial columns.

It is favorable to use relatively pure isomer as raw material because of the complexity of fusel oil components. Small amount of light ends and water was excluded from the top of tower to ensure the purity of 2-methyl-butanol. If concentration of 2-methyl-butanol in MAA is too low, the amount of feed and recovery of tower kettle are relatively large, which will increase the pressure of stripping section and reduce the distillate of top and consequently the yield of 2-methyl-butanol. When concentration of 2-methyl-butanol was over 40 wt %, top product quality is stable, chromatographic purity exceeded 99 wt %, and the yield stayed over 80% (2-methyl-butanol concentration in bottom close to 5 wt %).

Table 4. Simulation Results of Continuous Distillation

F (L/h)	D (L/h)	R	N	Nr	W_1	W_2
5	1.0	200	193	85–110	0.991	0.9997
6	1.2	166	200	85–110	0.991	0.9997
7	1.4	142	210	85–105	0.991	0.9997
8	1.6	124	220	90–105	0.991	0.9997
9	1.8	110	230	90–105	0.991	0.9997
10	2.0	99	245	95–105	0.991	0.9997
11	2.2	90	260	100–105	0.991	0.9997
12	2.4	83	280	103–120	0.991	0.9997
13	2.6	76	300	107–150	0.989	0.9992
14	2.8	71	350	112–190	0.988	0.9990
15	3.0	66	500	109–340	0.985	0.9983
17	3.4	59	700	122–527	0.976	0.9965

Simulation results of continuous distillation

By using numerical simulation software ASPEN PLUS, process simulation of continuous distillation for separation of 2-methyl-butanol and 3-methyl-butanol was carried out. The operating parameters of feed and column are the same as experiment data and WILSON equation was selected as thermodynamic model, which was sifted as the most accurate one in agreement with experimental results from process simulation with different model in terms of the practical point to facilitate the coming industrial scaling-up. Simulation results of continuous distillation are summarized in Table 4.

The comparison results between experiments and simulation data are listed in Table 5. It shows that a good agreement between experiment data and simulation results. Little differences of experimental and simulation yield can be

Table 3. Experiment Data of Different Feed Rate

F (L/h)	D (L/h)	R	P (KPa)	T_1 (°C)	T_2 (°C)	W_1 (%)	W_2 (%)
5.0	1.0	200	4.0	127.8	134.5	99.0	99.5
6.0	1.2	160	4.0	127.9	134.5	99.0	99.5
8.0	1.5	130	4.0	127.8	134.3	99.5	99.0
10.0	2.0	100	4.0	127.8	134.0	99.5	99.0
12.0	2.3	90	4.0	127.9	133.9	99.5	99.0
15.0	2.8	80	5.0	127.9	133.5	99.0	98.4
20.0	4.0	60	5.0	128.0	133.1	99.0	98.0

Table 5. Comparison of Experiments and Simulation Data

		Experiment			Simulation		
F (L/h)	D (L/h)	R	W_1	W_2	R	W_1	W_2
5.0	1.0	200	0.990	0.995	200	0.991	0.9997
6.0	1.2	160	0.990	0.995	166	0.991	0.9997
8.0	1.5	130	0.995	0.990	124	0.991	0.9997
10.0	2.0	100	0.995	0.990	99	0.991	0.9997
12.0	2.3	90	0.995	0.990	83	0.991	0.9997
15.0	2.8	80	0.990	0.984	66	0.985	0.9983

explained by the phase equilibrium for theoretical stages. In the case of pilot plant experiment, the phase equilibrium was not reached. Another reason is experimental errors of the flow rate measurements.

Conclusions

Through this pilot work, the novel structured packing, PSP, was developed both experimentally and industrially, and by means of application to separate 2-methyl-butanol and 3-methyl-butanol from fusel oil by batch distillation and continuous distillation. It demonstrated that PSP has an excellent performance in the distillation separation of iso-amyl isomers, for its low pressure drop and high-theoretical stages, and it is feasible to apply batch distillation to remove light ends and then continuous partner to separate 2-methyl-butanol and 3-methyl-butanol, with the concentration of 2-methyl-butanol is over 99 wt % and yield over 80%. Commercial software ASPEN PLUS has been used in this study, a good agreement between experiment data and simulation results was obtained, which further verified the reliability of this couple scheme and also indicated WILSON equation represents this isomers system properly.

Despite the excellent performance of PSP in this special purpose and substantial system, this packing need further acknowledged test by total reflux experiments with an standard cyclohexane/*n*-heptane system at atmospheric pressure. To achieve complete appraisal system of PSP as a commercial structured packing of extremely high-separative efficiency, further testing is indispensable for HEPT and pressure drop *versus* F-factor and specific liquid flow under different pressure. When all the work is covered, PSP is expected to give a new industrial option for reducing size of the distillation equipment and/or solution to revamp energy consuming columns for technical or economical purpose.

Notation

D = distillation rate (L/h)
DR = distillation range (°C)
F = feed rate of mixed amyl alcohol (L/h)
HETP = height equivalent to a theoretical plate (m)
ID = internal diameter
M = mass of product of batch distillation (Kg)
N = number of actual stages
Nr = feed stages
NTSM = number of theoretical stages per meter (m^{-1})
P = overall column pressure drop (KPa)
R = reflux ratio
T_1 = tower top temperature (°C)
T_2 = tower bottom temperature (°C)
W = product mass fraction of batch distillation
W_1 = mass fraction of 2-methyl-butanol
W_2 = mass fraction of 3-methyl-butanol
Y = product yield of batch distillation

Greek letters

α = specific surface area
v = void fraction
ε = packing factor
$\Delta p/\Delta z$ = pressure drop per unit height (mbar/m)

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