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# Green Process for Methacrolein Separation with Ionic Liquids in the Production of Methyl Methacrylate

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*Separation of methacrolein (MAL) is a critical technique for the production of methyl methacrylate, which is an important raw material for the preparation of acrylic resins applied in a variety of end-uses. In this work, an azeotropic distillation process and an ionic liquid (IL) green process were developed for the separation of MAL with $BmimBF_4$. The two processes were simulated with Aspen plus. The simulated results are in good agreement with the experimental results which were attained in a pilot plant. Also the economic and green degree analysis of these two processes was investigated. When compared with the azeotropic distillation process, the IL green process exhibits economic superiority and green degree superiority.* © 2010 American Institute of Chemical Engineers *AIChE J*, 57: 2388–2396, 2011

*Keywords: ILs, absorption, methacrolein, azeotropic distillation, green process*

## Introduction

Methyl methacrylate (MMA) is an important monomer, which is widely used for producing acrylic resins or polymer

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Additional Supporting Information may be found in the online version of this article.

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dispersions for paints and coatings.[1] And methacrylic polymer, which has the characteristics of good transparency and weather resistance, is used in many fields such as signboards, building materials, vehicles, and lighting equipment.[2] The production of MMA in the world has almost been doubled in the past 15 years as the demand of MMA grows steadily and speedily.[1]

The acetone cyanohydrine (ACH) process for MMA production was first commercialized in 1937, which is adopted by most manufacturers in the world even today. Although the ACH method was the only industrial process until 1982 for manufacturing MMA, there exist some problems, such as shortage of toxic hydrogen cyanide supply, discharge of large quantities of ammonium bisulfate waste. New commercialized processes have been developed till now, such as (1) the direct oxidation process which consists of catalytic oxidation of isobutylene (IB) or tert-butanol to methacrylic acid in two steps; (2) the BASF's method which uses ethylene, carbon monoxide, and formaldehyde as raw materials; (3) the new ACH process; (4) two-step selective oxidation process which selectively oxidizes IB to MMA via methacrolein (MAL).[3–5] Among these alternative routes, the two-step selective oxidation process is extensively regarded as a promising process[1] for its high-atomic efficiency. The separation and purification of MAL in which the water content should be controlled are critical in the two-step MMA production process. The most important units in this separation are the absorption and the purification of MAL. However, few studies have been focused to discuss this process. A method was disclosed, in which organic compounds having high-boiling points were used as the solvent. The mixture containing MAL and steam was absorbed into the solvent, then MAL was separated and recovered from liquid.[6] However, during the separation of MAL from the liquid, the mixture is kept under heated conditions, which leads to a polymerization of MAL consuming a large amount of MAL monomers. Another method for absorbing MAL with ethanol, and then performing extraction and rectification using water as an extracting agent, was invented.[7] However, water and MAL tend to form an azeotrope, which cannot meet the demand of the second step, that is, the oxidation and esterification reaction of MAL. A four-column combination process was reported in literature,[8] which contains water washing, methanol drying, methanol absorption, and rectification recovery. In this process, a great deal of methanol was demanded, which will cause great waste of methanol because of its high volatility. Furthermore, methanol is harmful to human beings and tends to cause environmental pollution problem.

Ionic liquids (ILs) will be used in many fields where conventional organic solvents are used today, because of the perceived benefit of substituting traditional industrial solvents. Traditional industrial technology based on traditional solvents, most of which are volatile organic compounds (VOCs), can be designed to be environmentally benign with nonvolatile ILs. This would prevent the emission of VOCs, a major source of environmental pollution.[9] Additionally, enhanced reaction rates obtained in ILs allows the reduction of solvent in the given technological process, thus reducing costs, risks and possible waste. These properties prompt the interest to replace common volatile organic solvent with ILs. Other important properties of ILs are the ability to dissolve an enormous number of organic, inorganic, and polymeric materials in a wide temperature range.[10] ILs have been used wildly as catalyst, solvent, etc. for their unique chemical and physical properties. Recent studies showed that imidazolium ILs have remarkable absorption capacities, and the phase-equilibrium of MAL-IL had been measured at the atmospheric pressure conditions.[11] $BmimBF_4$ is preferable potential alternative solvent for the absorption of MAL because of its low volatile. On the other hand, much work has been done to estimate their toxicity and degradability. Some important issues such as the lifecycle of an IL: purity, stability, biodegradability, and regeneration have been extensively investigated.[12,13] The toxicities of ILs on organisms have attracted much attention from researchers, who have reported results on bacteria,[14,15] animals,[16–18] and plants.[12,19,20] These studies mainly focus on the acute toxicity of ILs themselves, including effects on growth, behavior, and reproduction of organism. However, up to now, the toxicity of ILs is not completely clear and does not completely eliminate potential environmental risk. The greenness and economic analysis of a process with ILs have not been reported so far.

In this study, two processes for MAL separation were developed. One was called azeotropic distillation process, in which MAL was absorbed by a traditional solvent of water and purified through azeotropic distillation using methanol as entrainer. This separation process of MAL was simplified comparing with the four-column combination process, because only two columns were used and the entrainer was a reactant in the next reaction which did not need to be separated. In this process, the water content was well controlled below 500 ppm. For ILs are potential green solvent, another process called IL green process was developed. In this process, MAL was absorbed using $BmimBF_4$ and methanol as absorbent at normal pressure and then separated through flash evaporation. In this way, the whole process was further simplified and the equipment investment and operating cost were greatly reduced. These two processes were integrated. Results of simulation were compared with those of experiments, and economic and green degree analysis were also carried out.

## Simulation and Experimental Methods

### Simulation

*Properties: Phase-Equilibrium.* In this research, the physicochemical properties of pure components and mixture are calculated and analyzed. Most of the phase-equilibrium parameters were attained from Aspen Plus® (Aspen Tech, 2004). Some parameters are listed in Supporting Information Table S1. The other important phase-equilibrium parameters of methanol-MAL-IL system used in this research were obtained from experiments, which have been published in literature.[11] The thermodynamic properties of the components and process characteristics (such as relative volatility, the difference of boiling points between the two components, azeotropic pressure sensitivity) are calculated and revised. The qualitative and quantitative information is critical for the designs and simulations of processes. The suitable separation techniques were simulated based on the calculation and analysis results of the binary mixture properties. A number of experiments were proceeded to evaluate the feasibility of the separation techniques.

*Non-Random Two-Liquid (NRTL).* Among the modern equations for the excess Gibbs energy of mixing, the NRTL equation exhibits the outstanding features. It was proved to be suitable for some systems containing ILs, which has been reported in the literature.[21] The NRTL method was adopted in this article. Most of the parameters were attained from Aspen Plus except the NRTL parameters of methanol-MAL-$\text{BmimBF}_4$ system, which were obtained from the experimental data.[11] The parameters are also listed in Supporting Information Table S2.

*Process Integration, Design, Simulation, and Optimization.* Models of the system were built using Aspen Plus. Processes were designed and simulated under idealized heat integration. Parameter variations can be performed to investigate the sensitivity of the performance to uncertain variables.[22,23] The main operation units are absorption, distillation, and flash distillation.

In the process of MMA production, IB is first oxidized to MAL, where the product gas includes MAL (6.4%), $N_2$, $O_2$, etc. The temperature of the product gas is 633.15 K and the pressure is 120 kPa. To separate MAL from gas mixture, absorption operation was adopted. Before absorption, the temperature of the product gas was cooled to 318.15 K from 633.15 K. In the purity process, the purity of MAL should be considered.

Some of the parameters affecting the process of MAL separation were varied and their effects were studied. The following parameters were investigated:

- the solvent circulation rate,
- the number of absorber column stage, and
- the reflux ratio.

The processes were simulated with the MMA production of $10^7$ kg per year. The detailed heat integration was also performed. In heat integration, it is assumed that the hot resources are used in the theoretically best way using a $\Delta T_{\min} = 20$ K. This means an assumption that streams can be exchanged without constraints. The number of heat exchangers has no constraints. This is sufficient to obtain the clarity of the potential for the processes.[24]

This sensitivity analysis and optimization were performed with Aspen Plus[25–27] as mentioned before, and the results were used as an input for the economic evaluation and green degree analysis.

## Experimental

*Materials.* $\text{BmimBF}_4$ (99 wt %) was obtained from Henan Lihua Pharmaceutical Co., China. Methanol (99.5 wt %) was obtained from Beijing Chemical Works, China. MAL was produced in our laboratory in the MAL catalytic reactor.

*Equipments.* Absorption tower is a packing tower and the size is Φ 20 mm × 1500 mm. The azeotropic distillation column is also a packing tower, and the size is Φ 20 mm × 1300 mm. The stage number of them was changed along with the height of packing. The size of a flash tank is Φ 110 mm × 150 mm.

*Experiments.* Experiments were performed in a pilot plant under the MMA production of 1 kg/day. The experiments of each process contained two parts. One part was the absorption unit. The other part was purification or desorption unit. In the azeotropic distillation process, the product gas containing MAL, $N_2$, $O_2$, IB, etc. from MAL reactor was fed into the absorbing tower using water as the absorbent. Then MAL was purified and separated in the azeotropic distillation column. In the IL green process, the product gas was fed into the absorbing tower with $\text{BmimBF}_4$. Then the $\text{BmimBF}_4$ with MAL was added into the flash tank, and the MAL was flashed out of it. The operational conditions of those two processes were obtained from the simulation results.

The content of the streams was analyzed by gas chromatograph (GC; Agilent 6890 with TCD detector).

## Economic evaluation

Economic evaluation is essential to any proposed solution. To compare the azeotropic distillation process with the IL green process in economic analysis, several factors such as equipment cost, solvent cost, and cost of energy consumption were concerned.

Equipment cost was calculated by depreciation. The total equipment cost is the investment of the major device including installation charge. Assuming that the equipment life is 20 years and $10^7$ kg MMA is produced per year, the equipment cost is converted to unit cost. The equipment cost means the cost of depreciation of equipment per $10^3$ kg MMA.

$$C_{\text{Eq}} = \frac{\Sigma A_i}{m \times n} \tag{1}$$

Solvent cost was calculated by consumption of absorbent in two parts. One part of the cost is from the depreciation of the one-time investment of solvent and the other part is from replenishment for the loss of solvent. The solvent cost can be converted to unit cost like the equipment cost, assuming that the solvent can be used for 20 years and $10^7$ kg MMA is produced per year. Then the solvent cost means the cost of solvent loss and depreciation of the one-time investment, per $10^3$ kg MMA.

$$C_{\text{S}} = \frac{S_0}{m \times n} \times D + \frac{S}{n} \times D \tag{2}$$

Cost of energy consumption refers to the cost for cooling and heating, and energy consuming of pump and compressor in process per $10^3$ kg MMA.

$$C_{\text{E}} = \frac{\Sigma \text{Co}_i + \Sigma H_j + \Sigma P_k}{n} = \frac{\Sigma W_i \times D_i + \Sigma S_j \times D_j + \Sigma E_k \times D_k}{n} \tag{3}$$

Total cost is the summation of the three kinds of cost mentioned above. That is the main cost in the MAL separation process, and can be obtained from the following equation.

$$C_{\text{T}} = \Sigma C_i = C_{\text{Eq}} + C_{\text{S}} + C_{\text{E}} \tag{4}$$

## Green degree analysis

Green degree analysis of the processes is based on the green chemical principles. The environmental impacts were

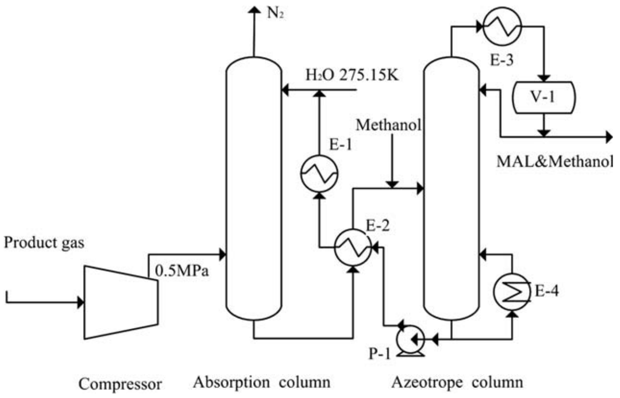

**Figure 1. Integration of the azeotropic distillation process.**

quantitatively determined by evaluating all of the material input and the chemicals output, and all the potential separation techniques were taken into account. The main advantage is that it applies the principle of mathematical solution approach but simplifies the problem through thermodynamic insights.[27,28] The unit values of green degree for the material are listed out in Supporting Information Table S3.

Because we mainly care about the effect of organics volatilization and energy consumption to the environment, the method in literature[28–30] was simplified in calculation in this work. The green degree of a process can be calculated from the following equations.

$$GD^{P} = \sum GD_{i}^{\text{Energy in}} + \sum GD_{j}^{\text{Material}\Delta} \tag{5}$$

where

$$\sum GD_{j}^{\text{Material}\Delta} = \sum GD_{k}^{\text{Material out}} - \sum GD_{l}^{\text{Material in}} \tag{6}$$

(The details of simplification in the calculation of green degree can be seen in Supporting Information.)

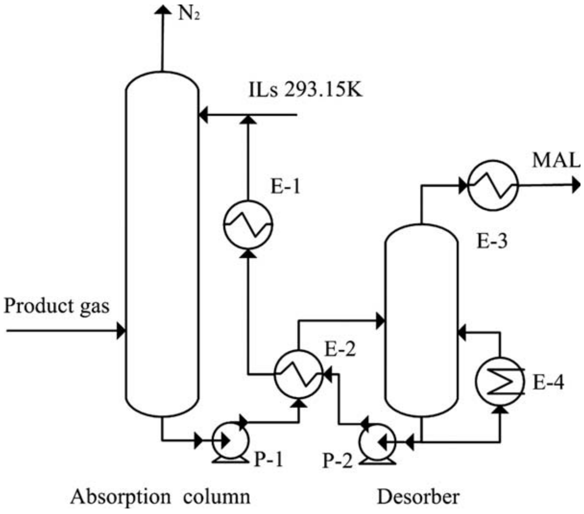

**Figure 2. Integration of the IL green process.**

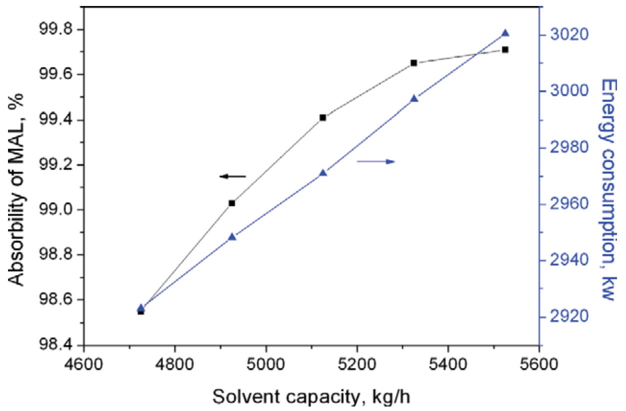

**Figure 3. Effect of solvent capacity on the absorbility of MAL and energy consumption.**

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

## Results and Discussion

### *Integration results*

The azeotropic distillation process and the IL green process were integrated, respectively, as seen in Figures 1 and 2.

In the azeotropic distillation process, MAL is first absorbed with water at 500 kPa, and then it is separated by azeotropic distillation with methanol, as seen in Figure 1. The temperature of water should be below 275.15 K, otherwise the absorption effect will be undesirable. MAL steam is heated to 333.15 K after methanol is added into it. The MAL purity and water content in MAL is controlled by the top temperature of the azeotropic tower. Water is discharged from the bottom. This process is more simplified than the four-column combination process, because only two columns were employed and the entrainer was a reactant in the next reaction, and its content can meet the demand of the next reaction without further separation.

In the IL green process, MAL is absorbed with $BmimBF_4$ and methanol at 100 kPa and then it is separated by flash distillation at 393.15 K as seen in Figure 2. The absorbent is a mixture of $BmimBF_4$ and methanol, considering that the

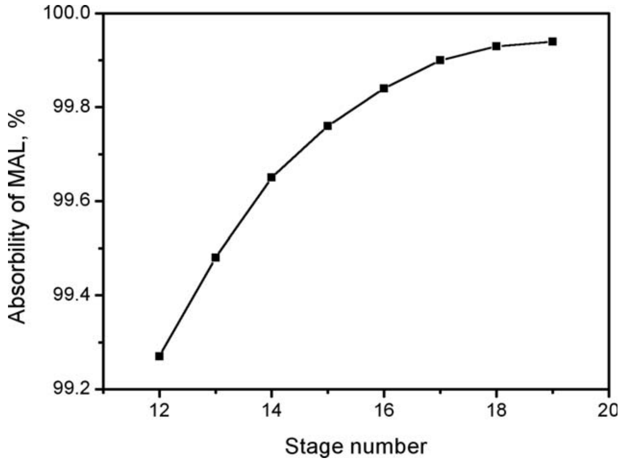

**Figure 4. Effect of stage number on the absorbility of MAL.**

Table 1. Comparison of Simulation and Experimental Results of Absorber Column in the Azeotropic Distillation Process

| | $N_2$ | | $O_2$ | | MAL | | $H_2O$ | | $CO_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. |
| Top product (wt %) | 89.45 | 89.66 | 5.05 | 5.24 | 61 ppm | 0 | 0.23 | 0.09 | 4.07 | 4.61 |
| Tower bottoms (wt %) | 1.02 | 0.96 | 0.18 | 0.15 | 5.87 | 5.66 | 91.52 | 91.68 | 0.61 | 0.45 |

addition of methanol can largely decrease the viscosity[31] and methanol is also a reactant for the next reaction, which does not need to be separated. In this process, the separation process of MAL is further simplified, because only one column was used and no compressor was needed. This process is more simplified than the azeotropic distillation process.

## Simulated and experimental results

### Azeotropic Distillation Process

### Absorber column

**Solvent capacity.** As seen in Figure 3, the absorbility increases with the capacity of water solvent. The whole energy consumption of the process is rather sensitive to the flow rate of the solvent. Because the water should be heated for distillation, the higher capacity of water solvent is used, the higher energy consumption will be needed. When the capacity of water solvent is over 5300 kg/h, the absorbility of MAL improves insignificantly. The preferred capacity of water is about 5300 kg/h.

**Absorber column stage.** The stage of the absorber column was varied from 12 to 19, resulting in a continuously increasing absorbility of MAL. However, when the column stage is more than 18 stages, the absorbility of MAL is not significantly affected by column stage, as seen in Figure 4. The column stage decides the column height. The higher is the column means, the higher is the pressure drop, so the stage defines the energy required for the fan and pump. A stage of 18 would be preferred.

**Contrast of simulation and experimental results.** Under the above preferred conditions, the simulation and experimental results were obtained and listed in Table 1.

As it can be seen in Table 1, the calculated results were close to those obtained from the experiments. Under the conditions of water capacity 5325 kg/h and column stage 18, the absorbility of MAL was over 99.6%. The content of MAL in the top product is 61 ppm in simulation results, whereas that cannot be detected by GC in experiments. That is to say, under these conditions the MAL can be completely absorbed. Thus, the parameters from simulation can be used in process design.

### Azeotropic distillation column

**Reflux ratio.** Reflux ratio is an important factor for distillation column, and the top product as well as energy consumption is sensitive to it. The recovery of MAL, water content in MAL product, and the energy consumption were investigated under the reflux ratio ranging from 2 to 5. The

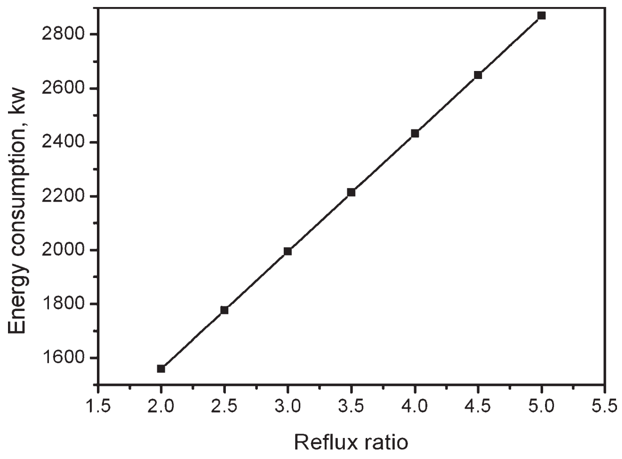

Figure 6. Effect of reflux ratio on energy consumption.

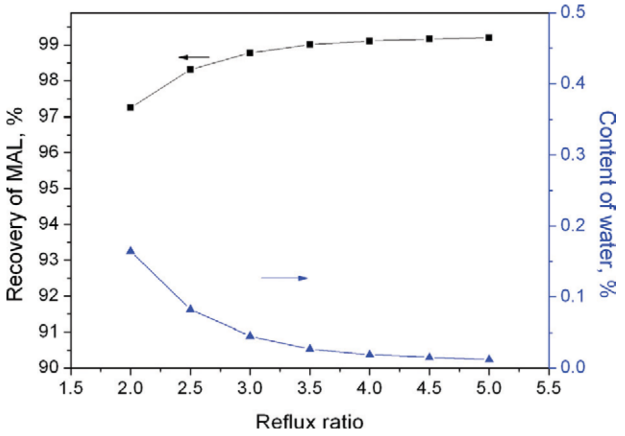

Figure 5. Effect of reflux ratio on the recovery of MAL and the content of water.

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

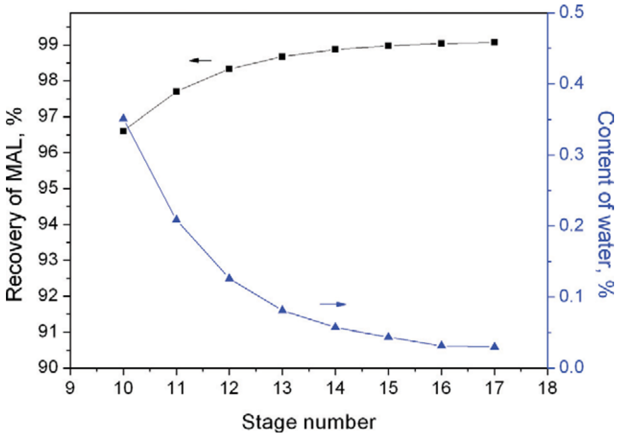

Figure 7. Effect of stage number on the recovery of MAL and the content of water.

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

Table 2. Comparison of Simulation and Experimental Results of Azeotropic Distillation Column in the Azeotropic Distillation Process

| | Methanol | | MAL | | $H_2O$ | | $CO_2$, CO, IB, etc. | |
|---|---|---|---|---|---|---|---|---|
| | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. |
| Top product (wt %) | 21.28 | 23.71 | 74.46 | 74.67 | 0.02 | 0.01 | 4.01 | 1.61 |
| Tower bottoms (wt %) | 0.029 | 0.23 | 12 ppb | 0.01 | 99.69 | 99.80 | 0 | 0 |

results are illustrated in Figure 5. It shows that the recovery of MAL and water content in MAL product are sensitive to the reflux ratio. At low reflux ratio, the recovery of MAL is low and the water content in MAL product is high. With the increase of the reflux ratio, the recovery of MAL increases and the water content decreases significantly. However, they change slowly when the reflux ratio is over 3.5. As it can be seen in Figure 6, the energy consumption is proportional to the reflux ratio. The preferred reflux ratio for the azeotropic distillation column is 3.5.

Stage number. Stage number is another important factor for distillation column. The recovery of MAL and the water content in MAL product were calculated under stage number ranging from 10 to 17 and the results were shown in Figure 7. The recovery of MAL and water content in MAL product are sensitive to the stage number. The recovery of MAL increases greatly when the stage number is from 10 to 14, whereas the water content in MAL product decreases straightly with the stage number increasing from 10 to 16. The change slows down when the stage number further increases. The stage determines the energy required for the reboiler. With the increase of the stage number, the capital costs upgrade. Thus, the preferred stage number of azeotropic distillation column is 16.

Contrast of simulation and experimental results. Under the above preferred conditions, the simulation and experimental results were obtained and listed in Table 2.

As it can be seen in Table 2, under the conditions of the reflux ratio 3.5 and column stage 16, the recovery of MAL is over 99% with the water content in MAL product below 0.01%. The MAL content in the bottom water is lower than 0.01%. Also the simulated results are in good agreement with the experimental results in the top product except the content of $CO_2$, CO, IB, etc. The content of $CO_2$, CO, IB, etc. in experimental results is much lower than that in simulated results. Presumably, $CO_2$, CO, and IB are very easy to volatilize from the liquid mixture when they were added into the azeotropic distillation column. Thus, in the tower bottoms, the content of methanol and MAL of experimental results is higher than that of simulated results. That may be due to the fact that the separating effect of the azeotropic distillation column is not as good as the designed value.

### *IL Green Process*

#### ***Absorber column***

Solvent capacity. In this process, MAL was absorbed in absorber column under the solvent capacity ranging from 2600 kg/h to 3600 kg/h. As it can be seen in Figure 8, the absorbility of MAL increases with the capacity of solvent increasing, and the total energy consumption of this process increases straightly. When the capacity of solvent is over 3200 kg/h, insignificant increase in absorbility of MAL is observed, whereas the energy consumption still increases straightly. A preferred capacity of solvent is 3200 kg/h.

Stage number. The stage of the absorber column varying from 9 to 13 results in a continuously increasing absorbility of MAL. When the column stage is more than 13 stages, the absorbility of MAL is affected insignificantly, as seen in Figure 9. Therefore, the stage number of 13 would be preferred.

Contrast of simulation and experimental results. Under the above preferred conditions, the simulation and experimental results were obtained and listed in Table 3.

As it can be seen in Table 3, the results of simulation were in good agreement with the experimental results of the top product except the content of methanol. The content of

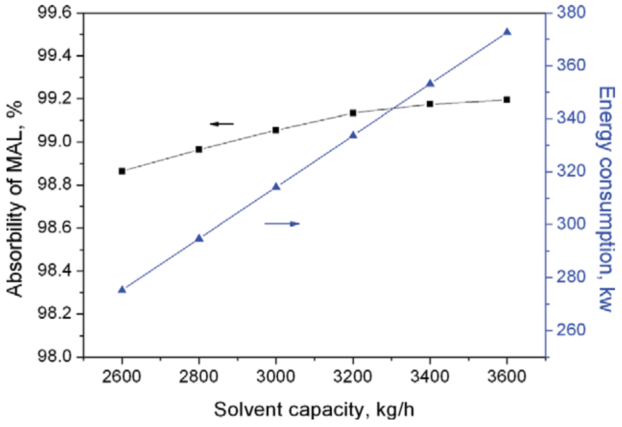

**Figure 8. Effect of solvent capacity on the absorbility of MAL and energy consumption.**

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

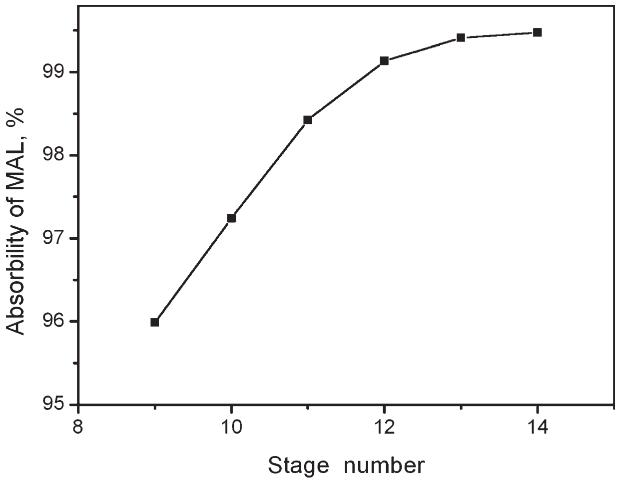

**Figure 9. Effect of stage number on the absorbility of MAL.**

Table 3. Comparison of Simulation and Experimental Results of Absorber Column in the IL Green Process

| | $N_2$ | | $O_2$ | | MAL | | $H_2O$ | | $CO_2$ | | $CH_4O$ | | ILs | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. |
| Top product (wt %) | 86.34 | 87.53 | 6.15 | 6.61 | 820 ppm | 0.07 | 5 ppm | 0 | 4.85 | 4.92 | 2.64 | 0.87 | 0 | 0 |
| Tower bottoms (wt %) | 281 ppm | 0 | 22 ppm | 0 | 9.68 | 10.82 | 0.25 | 0.33 | 340 ppm | 0 | 12.56 | 12.47 | 77.50 | 76.38 |

methanol in experimental results is much lower than that in simulated results, which may be due to the combining effect of methanol and $BmimBF_4$ under the experimental conditions. In the tower bottoms, the results of simulation were in good agreement with those of experiments. Under the conditions of solvent capacity 3200 kg/h and stage number 13, the absorbility of MAL was over 99.1%.

### *Flash tank*

Desorption temperature. The MAL was desorbed from $BmimBF_4$ solvent in a flash tank. The recovery of MAL was investigated under temperature ranging from 403.15 K to 418.15 K, as seen in Figure 10. At low temperature, the recovery of MAL and energy required for flash are low. With the increase of temperature, the recovery of MAL and energy consumption for flash both increase. When the desorption temperature is over 413.15 K, the recovery of MAL increases insignificantly, while the energy required increases obviously. Therefore, the preferred desorption temperature is about 413.15 K.

Contrast of simulation and experimental results. Under the above preferred conditions, the simulation and experimental results were obtained and listed in Table 4.

As it can be seen in Table 4, the results of simulation and experiments were close to each other. Therefore, the parameters from simulation can be used in actual production. Under the conditions of desorption temperature at 413.15 K, the recovery of MAL was over 95.5%.

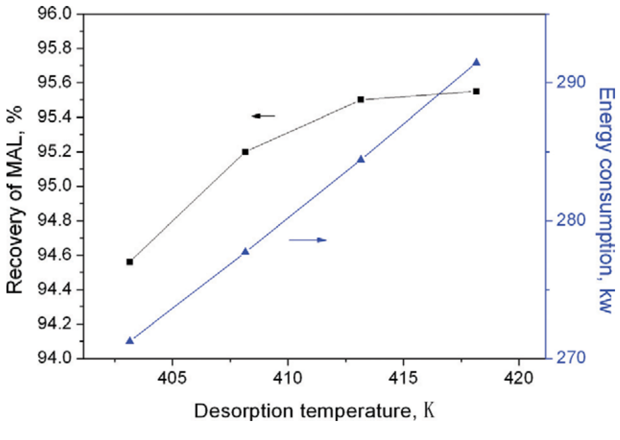

**Figure 10. Effect of desorption temperature on the recovery of MAL and energy consumption.**

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

### *Comparison of MAL absorption*

The solubility of MAL in $BmimBF_4$ is much higher than that in water. The absorption pressure in the azeotropic distillation process is 500 kPa, whereas in the IL green process MAL is absorbed by $BmimBF_4$ at normal pressure. High pressure means that more electric power is necessary for the absorption process. The high pressure will also result in increase of the equipment cost.

More water would be required due to the lower solubility of MAL in it. In the azeotropic distillation process, the solvent capacity is 5300 kg/h, whereas that in the IL green process is 3200 kg/h. More solvent increases the running expense. Much more energy consumption and cost will be needed for the absorption in the IL green process.

Because MAL is easier to be absorbed in $BmimBF_4$ than in water, the stage of absorption column in the IL green process (13) is smaller than that in the azeotropic distillation (18). That is to say, absorption in the IL green process needs less contact area, which results in the decrease of the column height and cost.

### *Comparison of MAL recovery*

In the azeotropic distillation process, it needs a column to separate MAL from water through azeotropic distillation. In the IL green process, MAL can be easily flashed off by a flash tank, which makes the recovery process simple and economic.

### *Comparison of economic analysis*

Under the optimized operating conditions, the comparison of economic analysis of the two processes is obtained. As it can be seen in Figure 11, in the azeotropic distillation process, the cost of equipment and the solvent are low. The cost of solvent can be even ignored because water is a cheap substance. In the IL green process, the cost of both equipment and solvent are low, too. The cost of energy consumption occupies most of the total cost in the two processes.

The equipment cost of the azeotropic distillation process is higher than that of the IL green process, whereas the

Table 4. Comparison of Simulation and Experimental Results of Flash Tank in the IL Green Process

| | Methanol | | MAL | | ILs | | $H_2O$ | | $CO_2$, CO, IB, etc. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. |
| Top product (wt %) | 52.80 | 53.41 | 40.20 | 41.50 | – | – | 0.49 | 0.51 | 6.51 | 4.59 |
| Tower bottoms (wt %) | 0.55 | 0.53 | 0.48 | 0.52 | 98.90 | 98.72 | 145 ppm | – | – | – |

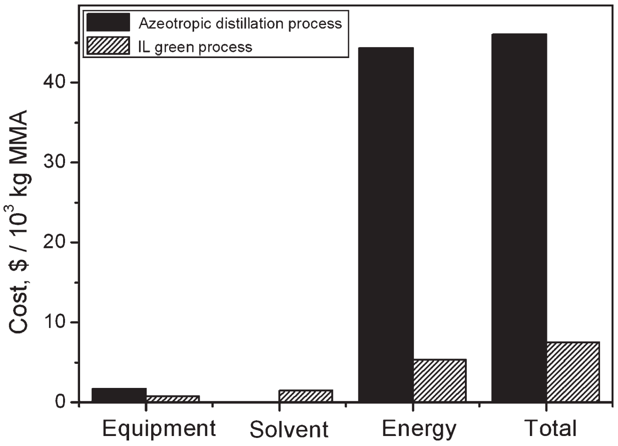

**Figure 11. Comparison of economic analysis between the azeotropic distillation process and the IL green process.**

solvent cost of the azeotropic distillation process is lower than that of the IL green process. The cost of equipment and solvent for these two processes are approximate. The cost of energy consumption for these two processes is quite different. The cost of energy consumption in the azeotropic distillation process is \$39 higher than that in the IL green process per ton MMA, which leads to a much higher total cost for the azeotropic distillation process comparing with the IL green process. That is to say, an extra cost of \$384,800 should be paid every year for the azeotropic distillation in the scale of $10^7$ kg MMA production.

### *Comparison of green degree*

Green degree includes two parts. One is the green degree of material and the other is the green degree of energy. Under the selected operating conditions, the comparison of green degree is obtained, as seen in Figure 12. Green degree of material for the IL green process is a little higher than that for the azeotropic distillation process, and the green degree of energy for the IL green process is much higher than that for the azeotropic distillation process. Therefore, the IL green process is much greener than the azeotropic distillation process.

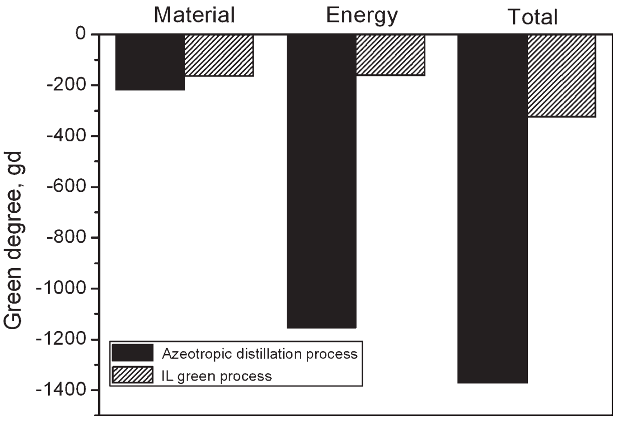

**Figure 12. Comparison of green degree between the azeotropic distillation process and the IL green process.**

## Conclusions

This research presents two processes for MAL separation. One is the azeotropic distillation process; the other is the IL green process using $BmimBF_4$ as absorbent. In the azeotropic distillation process, after absorbed by water, MAL was separated through azeotropic distillation, which made the separation process of MAL simplified. The entrainer methanol was a reactant in the next reaction, so it did not need to be separated. The water content was well controlled (below 500 ppm). The IL green process was designed using a mixture of $BmimBF_4$ and methanol as absorbent. The separation process was further simplified and the equipment investment as well as running cost was largely reduced compared with the azeotropic distillation process. The simulated results of these two process showed good agreement with the experimental results, which were obtained in a pilot plant. In addition, the economic and green degree analysis of both processes was carried out. The IL green process exhibits better economic superiority and green degree.

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## Notation

$\phi$ = tower diameter, mm
$A_i$ = unit cost of equipment, \$
$m$ = life length, year
$n$ = yearly output of MMA, kg
$S_0$ = recycle solvent capacity, kg
$S$ = annual dissipation, kg
$D$ = unit cost of solvent, \$/kg
$Co_i$ = annual cooling cost of the *i*th cooling equipment, \$
$H_j$ = annual heating cost of the *j*th heating equipment, \$
$P_k$ = annual electricity cost of the *k*th pump or compressor equipment, \$
$W_i$ = annual refrigerant consumption of the *i*th cooling equipment, kg
$D_i$ = unit cost of refrigerant, \$/kg
$S_j$ = annual steam consumption of the *j*th heating equipment, kg
$D_j$ = unit cost of steam, \$/kg
$E_k$ = annual electricity consumption of the *k*th pump or compressor, MJ
$D_k$ = unit cost of electricity, MJ/kg
$C_T$ = total operating cost in this part process, \$/$10^3$ kg MMA
$C_i$ = cost of the *i*th part, \$/$10^3$ kg MMA
$C_{Eq}$ = equipment cost in this part process, \$/$10^3$ kg MMA
$C_S$ = solvent cost in this part process, \$/$10^3$ kg MMA
$C_E$ = energy cost in this part process, \$/$10^3$ kg MMA
Cal. = data from simulation
Exp. = data from experiment
GD = green degree

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