Development of a novel catalytic distillation column

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Abstract

A new type of catalytic distillation column has been developed for catalytic distillation processes. The catalysts are loaded loosely in the downcomer of the new column, so that they can be replaced easily. A new type of column plate structure has also been proposed to accommodate the new distillation column. Experimental results show that the new column and plate structure have much improved performance, with high plate efficiency, low pressure drops across the plate and very good operation flexibility. The novel catalytic distillation columns could be employed to many catalytic distillation processes. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Coupling processes of chemical reaction and separation together can overcome the thermodynamic limitation of a reversible chemical reaction, to obtain a higher reaction conversion, even up to 100%, than the equilibrium conversion. The most successful application of this process coupling technique in the chemical industry is the reactive distillation process [1]. Systematic investigations [10] carried out in the past show that catalytic distillation technology has various advantages, such as high selectivity, high yield, energy saving, simple operation and so on. Its most important benefit is the reduction in investment and energy consumption, due to reduction in the amount of equipment required, and separation costs. Since the industrialization of a catalytic distillation process for synthesis of methyl tert-butyl ether (MTBE) by CR & L Co. in 1981 [4], the development of catalytic distillation technology has received more and more attention in the field of chemical engineering.

In the last two decades, research on catalytic distillation has been extended to various industrial processes, such as hydrolysis of methyl acetate [6], alkylation, etherification and so on [7]. In this period, a number of significant investigations [2,8] have been carried out, which are helpful in the development of catalytic distillation technology. However, the problem of how to arrange catalysts expediently in distillation columns, and at the same time to make the distillation columns have high efficiency in mass transfer, has not been solved satisfactorily until now. Usually, in industry, catalysts are loaded into distillation columns in the form of catalyst bundles [2], as reported by Smith in 1980 [3], Smith and Huddleston in 1982 [4] and DeGarmo et al. in 1992 [1]. This form of catalyst loading has the advantages of lower pressure drop and no catalyst leakage, but it also has some disadvantages. On the one hand, it is very complicated [5], for example, to prepare the catalytic distillation elements, and inconvenient for catalyst replacement. On the other hand, the catalyst efficiency of this form of catalyst loading is relatively low, because there exists an external diffusion resistance to mass transfer across the meshy catalyst bags. Therefore, it is important to develop new catalytic distillation columns for industrial applications.

In this work, a novel catalytic distillation column has been developed for the industrial processing of catalytic distillation systems. This newly-designed column can be filled loosely with catalyst, making catalyst replacement convenient. In addition, a special design has been adopted for the new column to avoid catalyst leakage. Two new types of column plate have been proposed by the authors to suit the characteristics of the new catalytic distillation column. The hydrodynamics of the distillation columns and the mass transfer behavior of
the column plates have also been studied experimentally.

2. Column configuration

The configuration of the novel catalytic distillation column is shown in Fig. 1a. The column consists of rectifying section, a catalytic reactive section and a stripping section. The rectifying section and the stripping section can be of any type of plate column or packed column used in reactive distillation processes. The only difference in the new column is in the structure of the catalytic reactive section.

The main structure of the catalytic reactive section is shown in Fig. 1b. It is designed as a normal plate column with an accessional annular space in which the catalysts are loaded loosely in the form of a fixed bed. The reactive section is constructed from two concentric cylinders of different diameters, and separated into several stages cross-sectionally by separating plates. Each reactive stage corresponds to one of the distillation plates. An arched downcomer is located on one side of the plate and an arched upspout on the opposite side. The downcomer is connected to the entrance of the reactive stage, and the upspout to the exit of the reactive stage. During operation, the liquid phase first flows through the downcomer to the upside, i.e. the entrance, of the catalytic bed, where the catalytic reaction takes place, and then, after the reaction, effuses from the bottom of the catalyst bed to the upspout. The liquid phase now flows onto the distillation plate, where mass and heat transfer with the cross-flowing gas phase are conducted, and then it runs further to the next stage. The height of the catalyst bed should not be much higher than the level of the liquid phase on the column plate, so that the catalysts are always submerged in the liquid phase. In addition, glass beads or screen meshes can be located underneath the catalyst bed to avoid catalyst leakage. This column structure needs a larger space between the consecutive column plates, because there is a necessary loading amount of catalyst. Therefore, the original column plates do not suit the new structure and new types of plates have had to be developed to fit the new design of reactive distillation columns.

A new type of passette, named Type B, has been developed for the column plates in this work, based on the sieve plate by Xu et al. [9], in order to make use of the large space above the column plates adequately and achieve a high efficiency in the mass transfer process. The typical upstanding sieve cap, named Type A, has been studied experimentally to make a convective comparison. The structure of the two passette types is illustrated in Fig. 1c. Type A is a stubbier cap, with orifices located only on the top. The total holed area is

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Fig. 1. Configuration of the reactive distillation column; (a) global structure; (b) structure of single plate; (c) two types of passette structure.
Fig. 2. Scheme of the experimental apparatus; 1. cylinder for O₂; 2. rotary flowmeter; 3. tank of water; 4. pump; 5. absorption column; 6. gas-liquid separator; 7. column; 8. sampling line; 9. collector of weeping; 10. U-barometer; 11. compressor; 12. Liquid collector.

3. Experimental

3.1. Experimental set-up

In order to investigate the hydrodynamics and mass transfer behavior of the catalytic distillation column developed as described in this paper, an experimental apparatus is set up as shown schematically in Fig. 2. The apparatus consists mainly of a distillation column, an absorption column, a gas–liquid separator, air and water supplying systems and a sampling system. The distillation column is built from Plexiglas. The diameter of the internal cylinder of the column is 140 mm and the diameter of the external cylinder is 300 mm. The annular channel formed between the two cylinders as downcomer is filled with an ion exchange resin of 0.6 mm particle diameter, as a catalyst. In the experiments, a 10 mm layer of glass beads of 2 mm diameter were loaded under the resin catalyst, with a 50 mm layer of 3.5 mm diameter glass beads beneath these, in order to avoid maldistribution of the liquid phase flow in the downcomer. The column has three plates, separated by a space of 1000 mm, on which gas nozzles with a hole diameter of 38 mm and a height of 15 mm are located. The middle plate is used to determine the plate efficiency for mass transfer and the pressure drop through the plate. The upper plate is used to determine the amount of entrained droplets, while the plate below is used to determine the weeping velocity.

A liquid collector is used to measure the amount of liquid entrained to the above plate by the gas phase. A U-shaped differential pressure meter is mounted to record the pressure drop across the column plate. A weeping collector is mounted on the bottom of the column to indicate the weeping velocity.

3.2. Methods and procedures

The experiment is carried out under ambient temperature and pressure. Air and oxygen-rich water are used as experimental system. The volumetric flow rate of air from the compressor is measured by a rotameter, and then the air flows into the distillation column at the bottom. Oxygen from an O₂ cylinder, whose flow rate is controlled by a pressure regulator, and water from a
water tank (3), together enter the absorption column. The oxygen-rich water can be obtained after absorption, and then the water is fed into the distillation column at the entrance of the downcomer for the upper column plate. The oxygen-rich water comes into contact with the cross-flowing air on the middle column plate, where mass transfer proceeds between the gas and liquid phases. Thereafter, the liquid phase leaves the column through the downcomer into the water reservoir. During the experiments, liquid samples are drawn from both the entrance and exit of the middle column plate. The plate efficiency is calculated after the oxygen content of the samples is determined.

4. Results and discussion

4.1. Plate efficiency

The plate efficiency of the catalytic distillation column is measured using the oxygen desorption method. The oxygen concentration in the liquid phase is analyzed by means of an oxygen-absorptiometer (Model Jenway 9070). The measured results of the plate efficiency are illustrated in Fig. 3, in which it can be seen that the plate efficiency of the typical upstanding bubbling cap, Type A, can be maintained at a level of 93% in the case of the relatively small liquid load of 6.496 m$^3$/m$^2$/hr. However, it decreases swiftly with the increased flow rate of the gas phase, under the condition of high liquid load. Compared with Type A, the Type B bubbling cap has a much better performance in mass transfer. The bubbling cap Type B can achieve a substantially higher plate efficiency, nearly 100%, than Type A, for a large range of the gas flux and under the condition of low liquid load. Even in the case of high liquid load, the plate efficiency can also be very high for a certain range of the gas flux.

The high plate efficiency of the new type of bubbling cap can be explained by the fact that the new type bubbling cap can utilize the large space between the column plates efficiently. The bubbling cap is so designed that the mixture of gas and liquid can be sprayed much higher to make use of the large space. It can extend the contact time of gas and liquid if the gas–liquid mixture travels a longer distance. Therefore, mass transfer can be improved when the new type of bubbling cap is utilized.

4.2. Hydrodynamic behavior of the gas phase

The pressure drop across the column plate, and the upper and lower limits of the velocity of the ascending gas stream, are two important design and operating parameters. The pressure drop, foam entrainment and weeping behavior have been tested experimentally for the newly-developed column plate, in order to evaluate the performance of the new type of bubbling cap. Fig. 4 shows the measurements of the pressure drop for the cases of dry and wet plate, respectively. The pressure drop across the plate with the newly designed bubbling cap, whether dry plate or wet plate, is remarkably smaller than the typical upstanding bubbling cap. The experimental results of the pressure drop for the dry plate depend mainly on the gas velocity through the nozzles, and can be described by the following expressions:

$$\Delta P_d = 1.672 \frac{\rho G^2.166}{2} \text{ Pa} \ (9 \text{ m/s} \leq \omega \leq 39 \text{ m/s})$$

Fig. 3. Influence of gas flux on the plate efficiency under different liquid loads.

Fig. 4. Pressure drop versus gas phase flux.
Type B: $\Delta P_d = \frac{4.112 \rho_w \omega^{1.706}}{2}$ Pa (10 m/s ≤ $\omega$ ≤ 25 m/s)

The pressure drop across the dry plate is caused by energy loss due to the shrinkage, expansion and direction change of the air stream through the nozzle and the gaps of the bubbling caps. If there is liquid on the plate, i.e. in the case of the wet plate, the flow of gas through the nozzle and the cap gaps may cause extra pressure drop, due to liquid entrainment. In addition, the liquid height on the plates can also cause an extra pressure drop, hence the pressure drop for the wet plate is larger than that for the dry plate. This extra pressure drop is dependent on the depth of the liquid on the plate and therefore the pressure drop across the wet plate can be described by

Type A: $\Delta P_w = 1.672 \frac{\rho_w \omega^{2.166}}{2} + 9.174 h \rho_w$ Pa (9 m/s ≤ $\omega$ ≤ 30 m/s)

Type B: $\Delta P_w = 4.112 \frac{\rho_w \omega^{1.706}}{2} + 9.045 h \rho_w$ Pa (10 m/s ≤ $\omega$ ≤ 25 m/s)

where $h$ is the liquid height above the nozzles and the water density takes the value of 1000 kg/m$^3$.

The liquid level difference between the in- and outside of the bubbling caps is the driving force for liquid flow into the bubbling caps, and the pressure difference caused by the gas stream flowing through the gaps of the bubbling caps is a resistance to the liquid flow into the bubbling caps. The pressure difference across the bubbling caps increases with gas velocity. The gas will flow out of the bottom of the bubbling caps, if the pressure difference is larger than the liquid level difference. At this point the pressure drop of the column plate will experience a sudden decrease, which corresponds to the turning point in Fig. 4. If the gas flux exceeds the value of the turning point, the gas–liquid contact, or the mass transfer, will deteriorate. Therefore we can take this point as the upper operating limit of the gas velocity.

The lower operating limit of the gas velocity may be defined as the point by which the liquid weeping rate reaches a value of 10% of the whole liquid phase flow rate, which gives the lowest gas flow rate for normal operation of the distillation column. The upper and lower operating limits for gas velocity have been measured and the results are shown in Fig. 5. The lower operating limit of the gas velocity depends only on the liquid load, and decreases slightly with the liquid load. The lower limits are the same for the bubbling caps of both Type A and Type B, because they have equal diameter. The upper limit for the column plate of Type A is higher than that of Type B, but the mass transfer efficiency of Type A is relatively small for the case of high gas flux. It can also be seen that the upper limit is independent of the liquid load.

4.3. Hydrodynamic behavior of the liquid phase

In order to evaluate the hydrodynamic behavior of the catalyst bed in the column downcomer, the liquid flux and the flowing resistance through the catalyst bed have been investigated experimentally. In the experiment an ion exchange resin with mean diameter of 0.6 mm (DOWEX G-26H, produced in the USA) is used to fill the catalyst bed. Under the resin catalyst is loaded a 10 mm layer of glass beads of 2 mm diameter, and below this a 50 mm layer of glass beads of 3.5 mm diameter. This filling mode can decrease the resistance of the catalyst bed and efficiently avoid maldistribution of the liquid across the catalyst bed. The experimental results, as shown in Fig. 6, demonstrate that the resistance of the whole catalyst bed has a linear relationship with the superficial liquid velocity, and the height of the resin bed affects the slope of the bed resistance curves. According to the analysis and treatment of the experimental results, a relationship between the resistance of the catalyst bed and the superficial liquid velocity and the catalyst height can be obtained:

$$\Delta R = (6.83 \times 10^9 \eta_L H_{cat} + 5.10 \times 10^7 \eta_L) u_L$$

where the first term represents the resistance of the resin layer, and the second term the local resistance at the catalyst bed bottom, caused mainly by the glass beads.

![Graph showing the operating limit of the gas flux as a function of the liquid load.](image)
Liquid flooding is an important criterion as to whether the distillation column works smoothly or not. Usually, it is an exclusive limiting factor to the liquid load for most reactive distillation systems. Liquid flooding will occur when the flowing resistance of the gas through column plates approaches the liquid level difference between the liquid phase in the downcomer and on the column plates. Therefore the flooding curve for the newly developed catalytic distillation column can be written as

\[ \Delta P_w + h_0 \rho_w g + \Delta R = \phi (H_{spa} + h_0) \rho_w g \]  

(6)

where \( h_0 \) is the depth of the liquid phase above the plate and \( \phi \) is a safety parameter which can take a value of 0.75 because the new column has a large space between the plates. Fig. 7 presents the simulated results in the cases of different heights of catalyst bed in the downcomer from Eq. (6). The simulated results show that different heights of catalyst bed have different flooding curves, and similar flooding curves can be obtained for different bubbling cap types on the column plates. The loading height of the catalyst bed in the downcomer remarkably affects the flooding condition, and the flooding curve will shift to the left, decreasing the maximum liquid flux, as the catalyst loading height increases. Comparing the bubbling cap of Type A with Type B, it can be concluded that Type B gives a better performance for operating flexibility.

4.4. Operating performance of column plates

According to the above experimental results, the hydrodynamic behavior of the gas phase and that of the liquid phase can be combined to obtain an operating performance diagram of both gas and liquid load for the column plate with bubbling caps of Type B, as shown in Fig. 8. Thus it can be seen in the figure that the new catalytic distillation column possesses favorable hydrodynamic performance and increased operating flexibility.

5. Conclusions

A novel catalytic distillation column has been developed in this work, by which the catalysts are loosely loaded in the column. Therefore, it is very easy to load the catalyst into the column, and catalyst replacement is very convenient. The column plates are specially designed so that catalyst leakage can be effectively avoided, and to allow a large liquid flux through the
catalyst bed, even when fine particles of ion exchange resin are employed as catalysts. The new distillation column design can be used for systems with slow or fast reaction rates, because the catalyst loading can be varied according to requirements.

In order to match the structure of the new distillation column, new types of column plate and bubbling cap on the plate have also been developed. The experimental study shows that the new column plate not only has much higher efficiency for mass transfer, but also possesses the advantages of small pressure drop and large operating flexibility. Hence, it has potential for a wide range of applications in industry.

Appendix A. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>plate efficiency (%)</td>
</tr>
<tr>
<td>h</td>
<td>liquid height above gas nozzle (m)</td>
</tr>
<tr>
<td>h₀</td>
<td>liquid height above plate (m)</td>
</tr>
<tr>
<td>Hᶜᵃᵗ</td>
<td>height of catalyst bed (m)</td>
</tr>
<tr>
<td>Hₛₚₐ</td>
<td>space between plates (m)</td>
</tr>
<tr>
<td>u</td>
<td>superficial velocity (m/s)</td>
</tr>
<tr>
<td>V</td>
<td>liquid load (m³/m²/hr)</td>
</tr>
<tr>
<td>ΔP</td>
<td>pressure drop (Pa)</td>
</tr>
<tr>
<td>ΔR</td>
<td>liquid flowing resistance (Pa)</td>
</tr>
</tbody>
</table>

Greek

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ</td>
<td>parameter</td>
</tr>
<tr>
<td>ρ</td>
<td>density (kg/m³)</td>
</tr>
<tr>
<td>η</td>
<td>viscosity (Pa·s)</td>
</tr>
<tr>
<td>ω</td>
<td>gas velocity through nozzle (m/s)</td>
</tr>
</tbody>
</table>

Subscript

- **g**: related to gas phase
- **L**: related to liquid phase
- **d**: related to dry plate
- **w**: related to wet plate

References