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Purification of caprolactam in magnetically stabilized bed reactor

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Abstract

A magnetically stabilized bed (MSB) reactor with amorphous nickel alloy catalyst (SRNA-4) was used for purification of caprolactam. The effects of various operating conditions on the hydrogenation were investigated, and the lifetime of SRNA-4 catalyst was also examined. A mathematical model of MSB reactor for hydrogenation of caprolactam solution was established. The experiment results show that the PM number (permanganate number) of caprolactam aqueous solution can be increased from 50 s to more than 2000 s through MSB hydrogenation process, and the lifetime of SRNA-4 catalyst is more than 3200 h. The catalyst consumption is reduced by 60%, as compared with that of the slurry reactor.

Keywords: Magnetically stabilized bed; Caprolactam; Amorphous nickel alloy; Hydrogenation

1. Introduction

Caprolactam is a main raw material for producing nylon-6. The crude caprolactam products include caprolactam and some unsaturated compounds, such as 1,2-cyclohexanedione, 2-hydroxyclohexanone. The presence of these unsaturated compounds, which can not be removed by extraction or distillation, is disadvantageous because they can impair the physical–mechanical properties of the nylon-6 made by polymerizing caprolactam. Whereas the saturated compounds formed by hydrogenation of these unsaturated compounds are easily removed from caprolactam by distillation [1,2]. So, the purification of caprolactam is a main process for producing caprolactam. In conventional technology, the hydrogenation of caprolactam aqueous solution is completed in the presence of Raney nickel catalyst in slurry reactor. But this process has some disadvantages, such as the low hydrogenating efficiency and the large catalyst consumption. Therefore, it is necessary to develop a new hydrogenation process for the purification of caprolactam.

Magnetically stabilized bed (MSB), a fluidized bed of magnetizable particles by applying a spatially uniform and time-invariant magnetic field oriented axially relative to the fluidizing fluid flow, has many advantages such as the low pressure drop and the high mass transfer efficiency [3–5]. However, magnetically stabilized bed reactor has not yet been used commercially in petroleum processing or chemical industry because most industrial catalysts are not magnetizable and the reaction temperature is too high. Recently, a novel amorphous nickel alloy catalyst (SRNA-4) for hydrogenation was developed at Research Institute of Petroleum Processing, SINOPEC [6]. This catalyst is ferromagnetic, and it has a high hydrogenation activity at lower temperature. Therefore, this catalyst is suitable for using in magnetically stabilized bed. In this paper, we try to combine the advantages of MSB

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Nomenclature

A	free-exponential factor
c	constant
C	reactant concentration (mol/m^3)
C_0	reactant concentration in feed (mol/m^3)
E_a	apparent activation energy (J/mol)
LHSV	liquid hourly space velocity (h^{-1})
P	hydrogen saturation pressure (MPa)
PM	PM number (s)
PM_0	PM number in feed (s)
r	reaction rate (mol/m^3 s)
T	temperature (K)
V	volume of bed (m^3)
V_L	liquid flow rate (m^3/s)
ε_s	holdup of solid phase

and amorphous nickel alloy catalyst, and develop an MSB reactor for purification of caprolactam.

2. Experiment

2.1. Apparatus and flow scheme

The flow scheme of the MSB hydrogenation process is depicted in Fig. 1. The key section of this process is the MSB reactor, which consists of a reactor and six coils outside the reactor. The reactor is 300 mm in diameter and 4 m in height. The feed caprolactam aqueous solution contacts with hydrogen in a mixer, in which hydrogen dissolves in the caprolactam aqueous solution, then the gaseous hydrogen is separated from

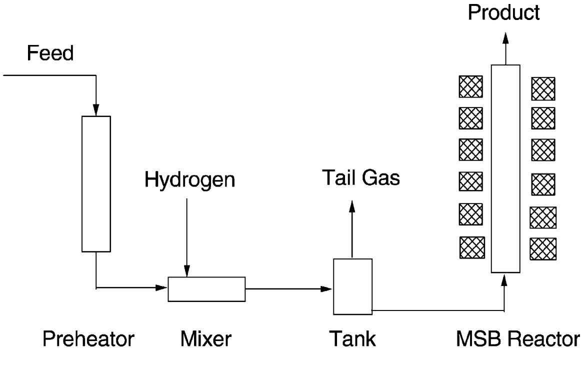

Fig. 1. Flow scheme of the reaction system.

Table 1
Properties of the catalyst

Catalyst	BET area (m^2/g)	Pore volume (ml/g)	Size (μm)	Shape
SRNA-4	145	0.10	70–120	Spheric

caprolactam aqueous solution, and subsequently, this hydrogen-containing caprolactam aqueous solution is introduced into the MSB reactor from the bottom. The unsaturated impurities in caprolactam aqueous solution are turned into saturated ones by hydrogenation in magnetically stabilized bed.

2.2. Catalyst

Amorphous nickel alloy catalyst (SRNA-4) is used as the hydrogenation catalyst. Table 1 gives the properties of the catalyst.

2.3. Feed

The feed is caprolactam aqueous solution with 30% caprolactam by weight. The purity of caprolactam aqueous solution is expressed by the PM number (permanganate number). The PM number is a measure of the oxidizability. A higher PM number means that a smaller amount of oxidizable impurities (unsaturated compounds) is present. The PM number is defined as the number of seconds elapsing after the addition of 1 ml of potassium permanganate 0.002 mol/l to 100 ml of caprolactam solution (3 g/100 ml) at 20 °C until the moment at which the color of this solution becomes equal to the color of a standard solution [1]. The PM number of the feed caprolactam aqueous solution is about 50 s.

3. Results and discussion

3.1. Method of mixing hydrogen and caprolactam aqueous solution

The content of unsaturated compounds in the feed caprolactam aqueous solution is generally very little, so the quantity of hydrogen that can dissolve in the reaction mixture under the reaction conditions is sufficient to purify the caprolactam aqueous solution. In this paper, hydrogen is dissolved into the caprolactam aqueous solution in a static mixer or in a stirred tank, then this hydrogen-containing caprolactam aqueous solution is introduced into the reactor. The experiment results show that both static mixer and stirred tank have high efficiency of mixing hydrogen and caprolactam aqueous solution. When a static mixer or a stirred tank is used to mix hydrogen and caprolactam aqueous solution, the PM number of product can increase to more than 2000 s through MSB hydrogenation process. The static mixer has the advantages of smaller volume, less investment, and no consumption of power. So, the static mixer is the better equipment for mixing hydrogen and caprolactam aqueous solution. Table 2 shows the effect of hydrogen/caprolactam aqueous solution ratio (V_{H_2}/V_L) on the PM number of product. It can be seen that hydrogen/caprolactam aqueous solution ratio just has an insignificant effect on the quality of the product. In MSB process, high hydrogenation efficiency can be achieved even when the hydrogen/caprolactam aqueous solution ratio is as low as 0.7 (v/v). The lower hydrogen/caprolactam aqueous solution ratio will result in a lower operating cost. The suitable hydrogen/caprolactam aqueous solution ratio is in a range of 0.7–1.5 (v/v).

3.2. Effect of reaction conditions

In the study on the application of MSB reactor in the purification of caprolactam, the effects of various operating conditions including magnetic field intensity (H), temperature (T), pressure (P), and liquid hourly

Table 2
Effect of hydrogen/caprolactam aqueous solution ratio on the reaction[a]

Mixer	Rotational speed (rpm)	V_{H_2}/V_L (v/v)	PM of product (s)
Static mixer	–	0.4	2100
	–	0.7	2650
	–	1.0	2810
	–	1.3	2830
	–	1.7	2850
Stirred tank	100	1.0	2750
	200	1.0	2780
	300	1.0	2780

[a] Mixing conditions: temperature 90 °C, pressure 1.0 MPa. Reaction conditions: temperature 90 °C, pressure 0.7 MPa, liquid hourly space velocity 30 h^{-1}, magnetic field intensity 25.6 kA/m.

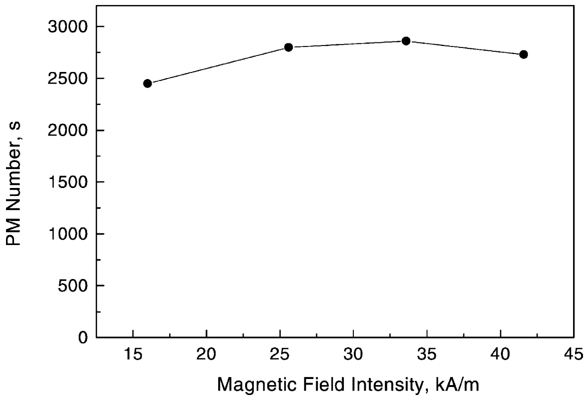

Fig. 2. Effect of magnetic field intensity on the reaction ($T = 90\,°C$, $P = 0.7$ MPa, LHSV = 30 h^{-1}).

space velocity (LHSV) on the hydrogenation were investigated. In the following experiments, a static mixer is used to mix hydrogen and caprolactam aqueous solution, with the hydrogen/caprolactam aqueous solution ratio of 1.0 (v/v).

The results of cold model experiments show that MSB has three different operating regimes depending on the intensity of magnetic field. They are particulate regime, chain regime, and magnetically condensed regime, respectively. In the particulate regime, when the MSB is operated under weaker magnetic field, the catalyst particles move freely, particles backmixing and entrainment occur, and the controllable range for stable operation is narrow. As the magnetic field intensity increased to a range of 12.8–36.5 kA/m, the MSB is operated in the chain regime. The catalyst particles are aligned themselves along the direction of magnetic field. The bed is operated in a stable state with uniform voidage. In the magnetically condensed bed, when the magnetic field intensity is increased to higher than 36.5 kA/m, bypassing occurs and the catalyst surface is not fully available to the reaction.

Fig. 2 shows the effect of the magnetic field intensity on the reaction (Table 3). The results indicate that the

Table 3
The original data of Fig. 2

Magnetic field intensity (kA/m)	PM (s)
16.0	2450
25.6	2800
33.6	2860
41.6	2730

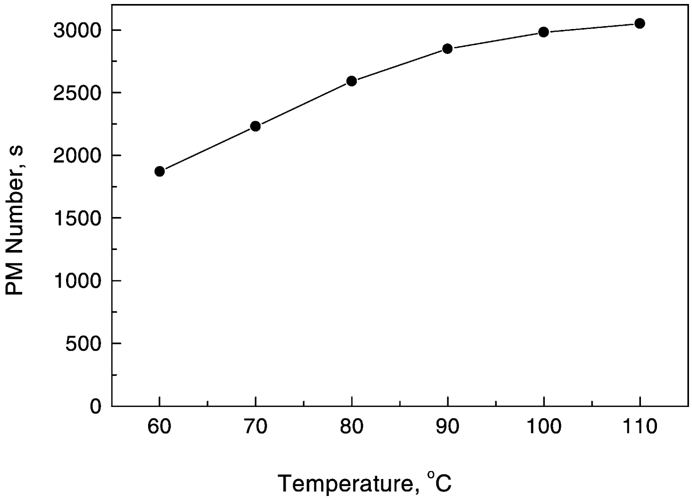

Fig. 3. Effect of temperature on the reaction ($P = 0.7$ MPa, LHSV $= 30\,h^{-1}$, $H = 25.6$ kA/m).

best result is obtained at the magnetic field intensity of 15–35 kA/m, so the chain regime is the optimum state for the reaction. Higher intensity is not favorable for purification of caprolactam in magnetically stabilized bed reactor.

Fig. 3 shows the results of hydrogenation carried out at different temperatures (Table 4). From the results in Fig. 3, it can be seen that the PM number of product increases with the increase of temperature. As temperature higher than 90 °C, the PM number of product increases slowly with the increase of temperature. Temperature has an influence on the rate of the surface reaction. The reaction rate increases with the increase of temperature. Temperature also has an influence on the solubility of hydrogen in the caprolactam solution. The solubility of hydrogen in the caprolactam solution decreases with increase of temperature.

Fig. 4 shows the results of hydrogenation carried out at different pressures (Table 5). From the results in Fig. 4, it can be seen that the PM number of product increases with the increase of pressure. When pressure is lower than 0.5 MPa, the PM number of product increases obviously with the increase of pressure, and only slight effect can be observed when the pressure is higher than 1.0 MPa.

In this process, hydrogen gas is introduced into the liquid phase by mechanical mixing outside the MSB reactor to make the hydrogen dissolved in the liquid. The solubility of hydrogen in the caprolactam solution increases with increasing hydrogen pressure according to the Henry's law. During the reactions in the MSB reactor, the higher the operation pressure is, the higher the hydrogen concentration at the surface of the catalyst particle is, as a result, the reaction rate is high. But when the pressure is high enough, the reactions are controlled by kinetics, and the effect of the pressure on the reaction rate becomes slight.

Table 4
The original data of Fig. 3

Temperature (°C)	PM (s)
60	1870
70	2230
80	2590
90	2850
100	2980
110	3050

Table 5
The original data of Fig. 4

Pressure (MPa)	PM (s)
0.1	1820
0.3	2400
0.5	2700
0.7	2850
0.9	2950
1.1	3010

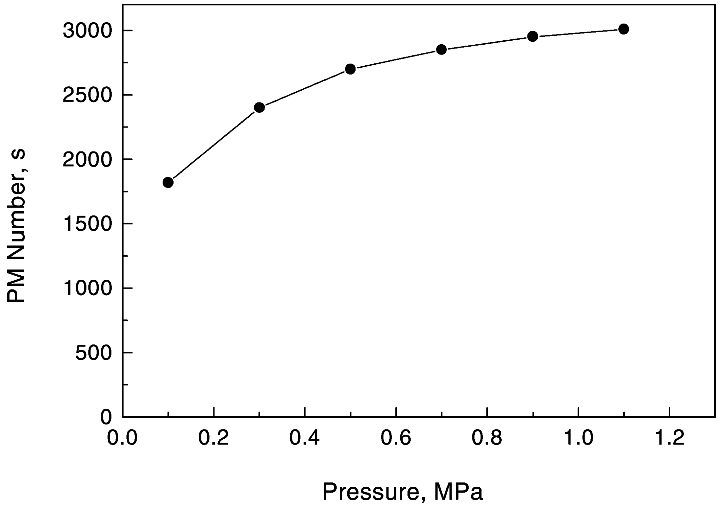

Fig. 4. Effect of pressure on the reaction ($T = 90\,^{\circ}\mathrm{C}$, LHSV $= 30\,\mathrm{h}^{-1}$, $H = 25.6\,\mathrm{kA/m}$).

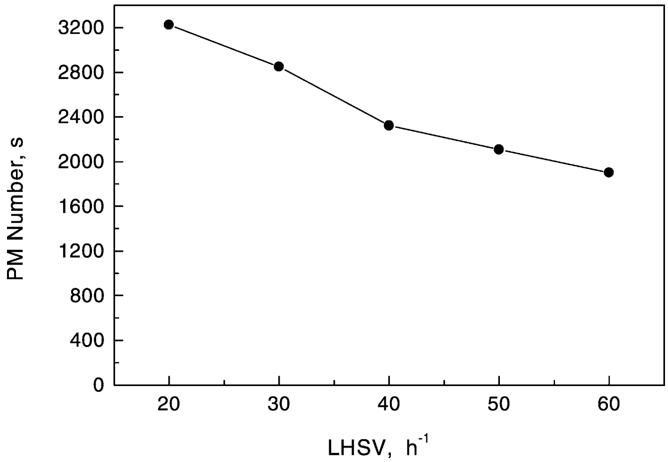

Fig. 5. Effect of LHSV on the reaction ($T = 90\,^{\circ}\mathrm{C}$, $P = 0.7\,\mathrm{MPa}$, $H = 25.6\,\mathrm{kA/m}$).

The results in Fig. 5 show the effect of liquid hourly space velocity on the reaction (Table 6). The results indicate that the PM number of product decreases from 3226 to 1902 s with the increase of LHSV from 20 to $60\,\mathrm{h}^{-1}$. The higher LHSV is helpful for increasing the capability of the reactor, but when LHSV is higher than $50\,\mathrm{h}^{-1}$, the catalyst particles entrainment occurs.

Summing up the experimental results given above, the operating conditions suitable for hydrogenation

Table 6
The original data of Fig. 5

LHSV (h^{-1})	PM (s)
20	3226
30	2850
40	2324
50	2109
60	1902

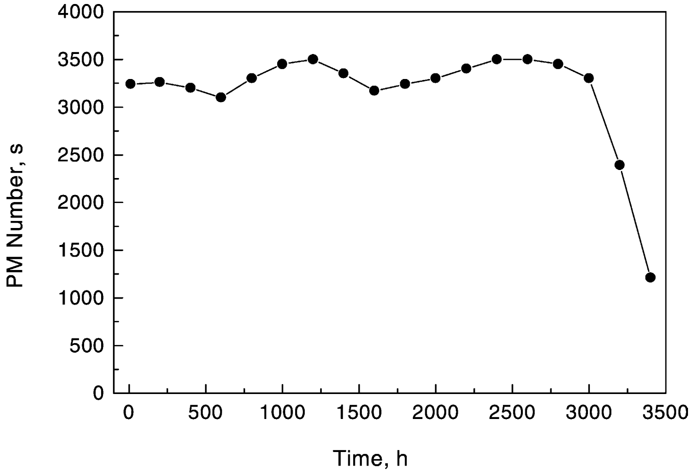

Fig. 6. Lifetime of SRNA-4 catalyst ($T = 90\,^\circ$C, $P = 0.7$ MPa, LHSV $= 30\,h^{-1}$, $H = 25.6$ kA/m).

of caprolactam aqueous solution in magnetically stabilized bed reactor are as follows: temperature 80–100 °C, pressure 0.5–1.0 MPa, LHSV 30–50 h^{-1}, magnetic field intensity 15–35 kA/m.

3.3. Lifetime of SRNA-4 catalyst

The lifetime of SRNA-4 catalyst used in the process of purification of caprolactam in magnetically stabilized bed reactor was also examined. The experiment results in Fig. 6 show that the PM number of product is still more than 2000 s after running 3200 h continuously (Table 7). While in the existing commercial process, in which a slurry reactor is adopt, the PM number of product is only 200–400 s, as the catalyst and reaction conditions are same as the MSB process. For the MSB reactor process, the catalyst consumption is only 0.06 kg/t caprolactam aqueous solution, but the catalyst consumption is about 0.2 kg/t caprolactam aqueous solution in the existing commercial slurry reactor process.

Table 7
The original data of Fig. 6

Time (h)	PM (s)	Time (h)	PM (s)
10	3240	1800	3240
200	3260	2000	3300
400	3200	2200	3400
600	3100	2400	3500
800	3300	2600	3500
1000	3450	2800	3450
1200	3500	3000	3300
1400	3350	3200	2390
1600	3170	3400	1210

3.4. MSB reactor model

The purification of caprolactam is a process involving hydrogenation of many unsaturated compounds, the reactions and flow pattern in the MSB reactor are complicated. It is difficult to establish a theoretical model for the process, however, based on the following assumptions, the process can be simulated by using a simple model: (1) the temperature is uniform in the reaction zone; (2) no concentration gradient in the radial direction of MSB reactor; (3) the reactions are controlled by kinetics; (4) the overall reaction is a first order to the unsaturated compounds; (5) no condensation and evaporation occur in the MSB reactor.

For the liquid phase, the material balance equation for the liquid–solid magnetically stabilized bed reactor can be expressed as:

$$V_L \frac{dC}{dV} + r = 0 \quad (1)$$

Where, V_L is the volume flow rate of caprolactam solution. Since the reaction order is of the first order to the unsaturated compounds, and c_1 order to the hydrogen pressure, where the reaction rate, r, can be described as:

$$-r = A\exp\left(-\frac{E_a}{RT}\right) CP^{c_1}\varepsilon_s \quad (2)$$

When the applied magnetic field is kept constant, the holdup of solid phase is a function of the space velocity:

$$\varepsilon_s = c_2(\mathrm{LHSV})^{c_3} \quad (3)$$

The concentration of unsaturated compounds in the caprolactam solution can be expressed by the PM number:

$$C = c_4(\mathrm{PM})^{c_5} \quad (4)$$

By combining the Eqs. (2)–(4) with Eq. (1), and integrating the resulted equation, the following equation is obtained:

$$\ln\frac{\mathrm{PM}}{\mathrm{PM}_0} = c_0(\mathrm{e})^{(-E_a/RT)}(P)^{c_1}(\mathrm{LHSV})^{c_2} \quad (5)$$

After inputting all experimental data into the equation, by Gauss–Newton method, the model parameters are estimated as:

$c_0 = 15.88$, $E_a = 2764$, $c_1 = 0.0521$,
$c_2 = -0.1303$

Then

$$\ln\frac{\mathrm{PM}}{\mathrm{PM}_0} = 15.88(\mathrm{e})^{(-2764/RT)}(P)^{0.0521}(\mathrm{LHSV})^{-0.1303} \quad (6)$$

The equation shows the effect of temperature, hydrogen saturation pressure and LHSV on the PM number of product in the process of MSB hydrogenation of caprolactam solution, as the applied magnetic field intensity is kept in the range of 15–35 kA/m. This model fits in with the experimental results quite well with a mean deviation of 6.8%.

4. Conclusions

It is attractive to use MSB reactor for the purification of caprolactam. The optimized reaction conditions are as follows: temperature 80–100 °C, pressure 0.5–1.0 MPa, liquid hourly space velocity 30–50 h^{-1}, hydrogen/caprolactam aqueous solution ratio 0.7–1.5 (v/v), and magnetic field intensity 15–35 kA/m. Under these conditions, the PM number of caprolactam aqueous solution can be increased from 50 s to more than 2000 s through MSB hydrogenation process. The experimental result shows that the PM number of product of MSB reactor process is increased by a factor of eight times, and the catalyst consumption is reduced by 60%, as compared with that of the existing commercial slurry reactor process.

Acknowledgements

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