

# Adsorption Equilibrium of Volatile in Condensed Mode Polyethylene Process

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**Abstract** In this paper *n*-hexane is chosen as typical volatile in condensed mode polymerization process, and the adsorption equilibrium of volatile in polyethylene particles is studied through experiments at different temperatures, pressures and particle diameters. It is found that more adsorbed quantity of volatile at equilibrium can be obtained with lower temperature, higher pressure and smaller particle diameter. Under polymerization conditions, the adsorbed quantity at equilibrium is more strongly affected by temperature than by pressure, and if the diameter distribution of particles is very wide the effect of diameter on the adsorbed quantity must be taken into consideration. With theoretical analyses a model is proposed for calculating the adsorbed quantity of volatile at equilibrium.

**Keywords** adsorption equilibrium, adsorption model, polyethylene process, condensed mode

## 1 INTRODUCTION

In polyethylene process the adsorbed quantity of volatile under different polymerization conditions must be known clearly especially after the introduction of condensed mode technology<sup>[1,2]</sup>. The determination of this quantity not only affects the prediction of devolatilization rate and holding capacity of resins in degassing bin, but also influences the working load of compressor and heat exchanger in recycling system. Besides, the volatile introducing rate as condensate is directly influenced by the adsorbed quantity of volatile in particles. Hence, a reliable model must be built up to predict the adsorbed quantity accurately.

Most studies in the past centered on the adsorption equilibrium of monomer or comonomer in particles, and very limited work has been done on the adsorption of hydrocarbon that is used as condensate for heat removal. The determination of this adsorption equilibrium is a new problem arisen from the condensed mode technology, which does not exist in the conventional mode. Henry model<sup>[3]</sup> is tried by the United Carbide Corporation to calculate the adsorbed quantity of the condensable hydrocarbon, however, the prediction by this model is so unsatisfactory that the deviation between the predicted data and the actual data is even up to 100%. Therefore, in this paper a new model with some physical significance is proposed through

experimental studies and theoretical analyses, and for condensed mode process the quantity of the volatile adsorbed in particles can be predicted with more accuracy.

## 2 EXPERIMENTAL APPARATUS AND PROCESS

The experimental apparatus and process are similar to those figures in Ref. [4], about which the presentation will be terse in this paper. In this experiment the desorption column is replaced by an adsorption bottle. While pure nitrogen passes through a volatile liquid *n*-hexane which is kept at a given temperature by a super isothermic vessel, gas mixture with certain amount of *n*-hexane (as adsorbate) is obtained. Then the gas mixture passes through the adsorption bottle and after some time the particles in the bottle will be saturated with *n*-hexane. If the chromatograph detector shows that the outlet concentration of the bottle has kept constant for a long time, then it is known that the adsorption equilibrium is established. The adsorption quantity can be calculated by subtracting the quantity in the void among particles from the weight increment of the bottle. Three types of resins are chosen in our experiments and some of their characteristic parameters are listed in Table 1.

Table 1 Some characteristic parameters of polyethylene in experiments

| Resins  | $d_p \times 10^{-3}$ , m | $\rho_s$ , kg·m <sup>-3</sup> | $\rho_p$ , kg·m <sup>-3</sup> | MI, g·(10 min) <sup>-1</sup> | Source of resins  |
|---------|--------------------------|-------------------------------|-------------------------------|------------------------------|-------------------|
| PE150   | 1.0                      | 932                           | 900                           | 0.75                         | Qilu P&C Corp.    |
| PE105   | 0.5                      | 932                           | 900                           | 0.75                         | Qilu P&C Corp.    |
| DGM1810 | 0.7                      | 918                           | 900                           | 1.00                         | Maoming P&C Corp. |

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### 3 MATHEMATICAL MODEL

Barry's work<sup>[5]</sup> indicated that those models similar to Langmuir type were good for describing the adsorption behavior of *n*-hexane on molecular sieves, and David<sup>[6]</sup> found this type of models also fitted well to the adsorption of benzene on active carbon particles. Our experiments show that this type of models are satisfactory in describing the adsorption equilibrium of *n*-hexane on polyethylene particles, that is

$$q = q_{\infty} \frac{B p_v}{1 + B p_v} \quad (1)$$

where  $q$  is the adsorbed quantity at equilibrium,  $q_{\infty}$  is the theoretical limiting value of  $q$ ,  $p_v$  is the partial pressure of volatile in gas mixture, and  $B$  is a model parameter.

The larger the specific area, that is, the ratio of the total interfacial area available for adsorption to the volume of particles, the larger the limiting value  $q_{\infty}$  will be. Supposing that the adsorbing ability at each point of the solid surface is the same, then the adsorbed quantity must be proportional to the specific area

$$q_{\infty} \propto a_p \quad (2)$$

where  $a_p$  is the specific area of particles. The following equation is tentatively assumed<sup>[4]</sup>

$$a_p \propto d_p^I \quad (3)$$

then we have

$$q_{\infty} \propto d_p^I \quad (4)$$

The volatile molecules adsorbed on the internal wall of particle pores and dissolved in the crystalline matrix will possess more kinetic energy to overcome the solid bonds if temperature increases, therefore in this paper it is supposed that  $q_{\infty}$  is reversely proportional to the mean molecular speed. According to the classical theory the mean molecular speed  $u_m$  can be expressed as follows

$$u_m = \sqrt{\frac{8KT}{\pi m}} \quad (5)$$

where  $K$  is Boltzmann constant and  $m$  is the mass of a molecule, then we have

$$q_{\infty} \propto \frac{1}{\sqrt{T}} \quad (6)$$

for  $q_{\infty}$  is independent of pressure, the following equation can be obtained

$$q_{\infty} = \frac{q_0 d_p^I}{\sqrt{T}} \quad (7)$$

where  $q_0$  is a model parameter, probably implying the effect of particle structure and molecular kinetic energy.

Assuming the following equation<sup>[6]</sup> for parameter  $B$

$$B = B_0 \sqrt{T} \exp\left(\frac{E_d}{RT}\right) \quad (8)$$

where  $B_0$  is a model parameter and  $E_d$  is activation energy of adsorption, then from Eqs. (1), (7) and (8) we have

$$q = \frac{q_0 d_p^I}{\sqrt{T}} \cdot \frac{B_0 \sqrt{T} \exp\left(\frac{E_d}{RT}\right) p_v}{1 + B_0 \sqrt{T} \exp\left(\frac{E_d}{RT}\right) p_v} \quad (9)$$

If the parameters in Eq. (9) can be determined through experimental data, then a model will be obtained for calculating the adsorbed quantity at equilibrium.

## 4 RESULTS AND DISCUSSION

### 4.1 Experimental results

The parameters in Eq. (9) can be calculated by Gauss-Newton method if these parameters are regarded as the regression coefficients. The average deviation between the experimental data and the predicted results by Eq. (9) for the adsorbed quantity is 5.6% and the maximum is 13%. The results can be expressed as follows when the parameters in Eqs. (7)–(9) are given

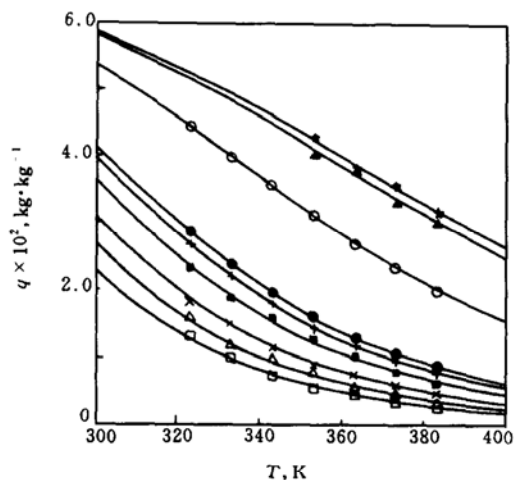
$$q_{\infty} = \frac{q_0 d_p^I}{\sqrt{T}} = \frac{220 d_p^{-0.21}}{\sqrt{T}} \quad (10)$$

$$B = B_0 \sqrt{T} \exp\left(\frac{E_d}{RT}\right) = 1.33 \times 10^{-10} \sqrt{T} \exp\left(\frac{2.82 \times 10^4}{RT}\right) \quad (11)$$

$$q = \frac{220 d_p^{-0.21}}{\sqrt{T}} \cdot \frac{1.33 \times 10^{-10} \sqrt{T} \exp\left(\frac{2.82 \times 10^4}{RT}\right) p_v}{1 + 1.33 \times 10^{-10} \sqrt{T} \exp\left(\frac{2.82 \times 10^4}{RT}\right) p_v} \quad (12)$$

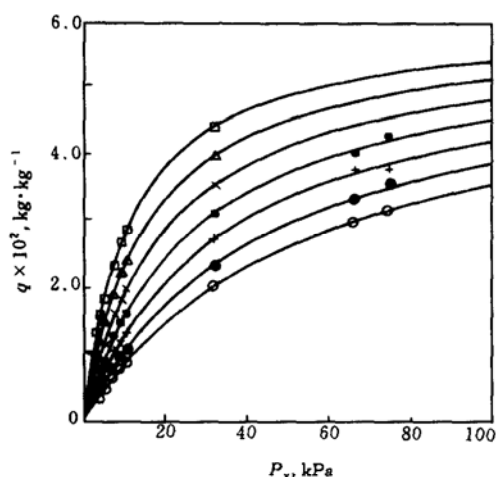
The experimental data and predicted results are presented schematically in Figs. 1–5. Fig. 1 shows the dependence of the adsorbed quantity of volatile on temperature, where both the fraction of volatile and the total pressure are given for an overall understanding. Fig. 2 exhibits the dependence of the adsorbed quantity on partial pressure. In Fig. 1 and Fig. 2 the diameter of  $5 \times 10^{-4}$  m is taken as typical particle size and in this paper the figures of other diameters are omitted because the relationships shown in these figures are similar to those shown in Fig. 1 and Fig. 2. The dependence of the theoretical limiting

value on temperature and particle diameter is respectively shown in Fig. 3 and Fig. 4, and the dependence of parameter B on temperature is shown in Fig. 5.



**Figure 1 Adsorbed quantity vs. temperature**  
(resin: PE105;  $d_p = 0.5 \times 10^{-3}$ m) — predicted data;  
□ △ × ■ + ● ○ ▲ ★ experimental data

|                      |      |      |      |      |      |      |       |       |       |
|----------------------|------|------|------|------|------|------|-------|-------|-------|
|                      | □    | △    | ×    | ■    | +    | ●    | ○     | ▲     | ★     |
| $x_v \times 10^2$    | 3.09 | 3.09 | 3.09 | 3.09 | 5.43 | 6.14 | 18.59 | 3.09  | 3.09  |
| $p \times 10^5$ , Pa | 1.01 | 1.32 | 1.72 | 2.43 | 1.72 | 1.72 | 1.72  | 21.48 | 24.12 |

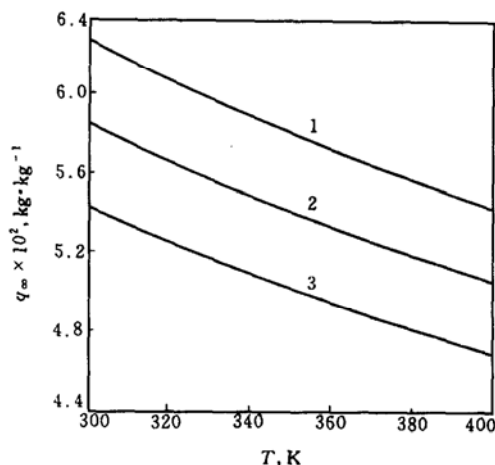


**Figure 2 Adsorbed quantity vs. partial pressure**  
(resin: PE105;  $d_p = 0.5 \times 10^{-3}$ m) — predicted data;  
□ △ × ■ + ● ○ experimental data  
T, K: □ 323.15; △ 333.15; × 343.15; ■ 353.15;  
+ 363.15; ● 373.15; ○ 383.15

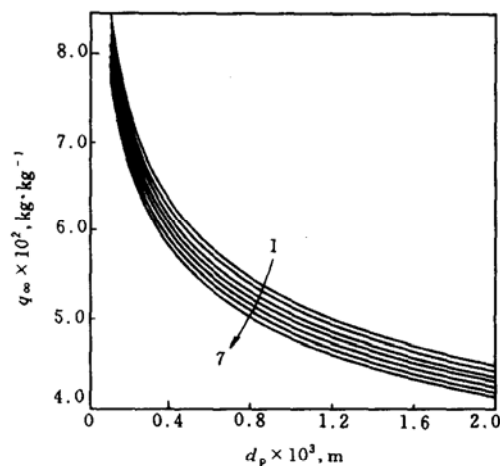
## 4.2 Results analyses and discussion

### 4.2.1 Effects of temperature on the adsorbed quantity of volatile

Fig. 1 shows that the adsorbed quantity at equilibrium decreases with the increase of temperature, and at the same temperature if the partial pressure of volatile is not the same the curve slope will be different. In the polymerization temperature range (353 K—383 K), the higher the partial pressure, the



**Figure 3 Theoretical limiting value of adsorbed quantity vs. temperature**  
 $d_p \times 10^3$ , m: 1—0.5; 2—0.7; 3—1.0



**Figure 4 Theoretical limiting value of adsorbed quantity vs. partial pressure**  
T, K: 1—323.15; 2—333.15; 3—343.15; 4—353.15;  
5—363.15; 6—373.15; 7—383.15

larger the curve slope will be, which means the adsorbed quantity is more sensitive to temperature under the condition of high partial pressure. These findings are very important for condensed mode technology, especially for super condensed mode, in which the partial pressure of volatile is generally much higher than that in routine mode. For example, under the conditions that the mole fraction of condensable hydrocarbon in gas phase is 3.09% and the total pressure for polymerization is 2.4 MPa, the adsorbed quantity will decrease by about 20% if temperature increases from 353 K to 363 K. This decrement is considerable.

From Eq. (9) it can be seen that two parameters,  $q_\infty$  and  $B$ , reflect the effect of temperature on the adsorbed quantity, hence it is necessary to discuss the dependence of both  $q_\infty$  and  $B$  on temperature. First discussion goes to  $q_\infty$ . Fig. 3 shows that the curve slopes are nearly same to different particle diameters,

that is, the change tendency of  $q_\infty$  with temperature is hardly influenced by particle diameter. And in Fig. 4, the curves are densely located, which indicates that the dependence of  $q_\infty$  on particle diameter is not affected much by temperature although Fig. 3 shows the decrease of  $q_\infty$  with the increase of temperature. The explanation for Fig. 3 is that at high temperature, more adsorbed molecules can obtain enough kinetic energy to break solid bonds for escape, while the influence of temperature on kinetic energy is similar as shown in Eq. (7). The similarity of particle structure may account for the phenomena in Fig. 4. To be specific,  $q_\infty$  is mainly determined by particle structure, system properties and adsorption temperature. For the adsorption system in our experiments, the particle structure can be regarded as a good duplication of the catalyst structure<sup>[8,9]</sup>, this results in the similarity of particle structure though the diameters are different. Similar particle structure implies similar adsorption ability for per unit adsorbing area. Thus it is concluded that similar effects of particle structure and temperature correspond to similar adsorbing behavior for a given system. Therefore, to some extent,  $q_\infty$  can be regarded as the reflection of particle structure and properties of the adsorption systems at a given temperature.

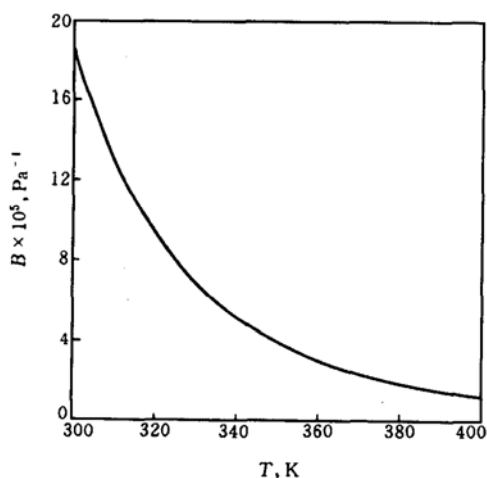


Figure 5 The value of parameter B vs. temperature

From Fig. 5 it is found that parameter B decreases with the increase of temperature, and this change is obvious. Generally the value of B is very small, and if the partial pressure of volatile is not too high, the following equation will stand

$$1 + Bp_v \approx 1 \quad (13)$$

thus Eq. (9) is simplified to a linear one, which will be discussed in the next section. Here it is worth mentioning that the value of parameter  $E_d$  in Eq. (8) lies in the same order of the latent heat for liquidation,

which implies the physical significance of parameter B, probably reflecting the properties of adsorption system, especially the adsorbate. From Ref. [4] it is noted that the activation energy of desorption is also close to this latent heat.

#### 4.2.2 Effects of pressure on the adsorbed quantity of volatile

Fig. 2 shows that the adsorbed quantity of volatile in particles increases with the increase of partial pressure of volatile and there is a limiting value, *i.e.*  $q_\infty$ , to the adsorbed quantity at a given temperature. As mentioned above, an approximately linear relationship will exist if the partial pressure of volatile is not too high (generally below 10 kPa)

$$q \approx q_\infty B p_v = 2.93 \times 10^{-8} d_p^{-0.21} \exp\left(\frac{2.82 \times 10^4}{RT}\right) p_v \quad (14)$$

In polyethylene process the total pressure of degassing bin is at about 0.1 MPa, which results in the low partial pressure of volatile, thus the adsorbed quantity in particles at the entrance of degassing bin can be simply calculated by Eq. (14). However, while the resins are discharged from the fluidized bed, Eq. (12) must be used because the total pressure of discharging vessel is only slightly lower than that of reactor, that is, 2.4 MPa or so. From Ref. [4] it can be seen that the linear relationship presented in Eq. (14) is helpful in solving the desorption rate model.

Another phenomenon is that if the partial pressure is low the adsorbed quantity will be more sensitive to it, therefore the partial pressure should be carefully considered when calculating the adsorbed quantity at the inlet of degassing bin. This has been supported by some practical examples<sup>[11]</sup>. In the reactor of condensed mode, however, the partial pressure of volatile is generally higher than 0.6 MPa, thus the adsorbed quantity is not sensitive to the polymerization pressure.

#### 4.2.3 Effects of particle diameter on the adsorbed quantity of volatile

Fig. 4 shows that the adsorbed quantity of volatile decreases with the increase of particle diameter, and this is mainly because the particle specific area decreases with the increase of diameter. If the diameter is small, the adsorbed quantity will be more sensitive to it, maybe this is because the change of the pore number is greater at smaller diameter than at larger one. In practical manufacturing process the diameter distribution of polyethylene particles is generally controlled in a narrow range, therefore it is acceptable in engineering field to calculate the adsorbed quantity on the basis of average diameter. However, if the diameter distribution is wide and the adsorbed quantity lies in the sensitive range, then the distribution must

be taken into account. This is especially important for condensed mode because in this mode wide diameter distribution is allowed. It is worth noting that the discussion here also fits the theoretical limiting value  $q_{\infty}$ , because according to Eq. (12) the effect of particle diameter on the theoretical limiting value is the same as that on the adsorbed quantity.

From Eqs.(3) and (10) it can be seen that the value of parameter  $I$  is  $-0.21$  which is close to those values in Ref.[4]. This consistency probably indicates that Eq. (3) can be used to calculate the specific area of polyethylene particles. Some experimental data<sup>[10]</sup> show that the specific area of polyethylene particles can be approximately calculated by a half empirical equation

$$a_m \approx \frac{1}{3} d_p^{-1/5} \quad (15)$$

## 5 CONCLUSIONS

(1) The adsorbed quantity of volatile decreases with the increase of temperature or diameter, but it will increase if the partial pressure of volatile increases.

(2) In condensed mode polyethylene process, the adsorbed quantity of volatile in fluidized bed reactor is more sensitive to temperature than to partial pressure of volatile, because the partial pressure is much higher than that of routine mode. However, the adsorbed quantity is more sensitive to partial pressure at the inlet of degassing bin, as the operating pressure lies in the atmospheric range.

(3) The effect of particle diameter on adsorbed quantity of volatile is generally less obvious than that of temperature or partial pressure, but this effect must be taken into account carefully if the distribution of particle diameter is wide.

(4) The adsorbed quantity of volatile at the inlet of degassing bin can be determined simply by a proportional relationship, while it can not be used to calculate the quantity in the discharging vessel.

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ticles and adsorption data at the polymerization pressure.

## NOMENCLATURE

|              |   |
|--------------|---|
| $a_m$        | specific area, <i>i.e.</i> , total interfacial area for adsorption per unit mass of particles, $m^2 \cdot g^{-1}$ |
| $a_p$        | specific area based on volume of particles, $m^2 \cdot m^{-3}$  |
| $B$          | model parameter in Eq. (1), $Pa^{-1}$   |
| $B_0$        | model parameter in Eq. (8), $K^{-1/2} \cdot Pa^{-1}$  |
| $d_p$        | particle diameter, m  |
| $E_d$        | activation energy of adsorption, $J \cdot mol^{-1}$   |
| $I$          | model parameter in Eq. (3)  |
| $K$          | Boltzmann constant  |
| $MI$         | melting index of resins, $g \cdot L^{-1} \cdot min^{-1}$  |
| $m$          | mass of a molecule, kg  |
| $p$          | total pressure of the system considered, Pa   |
| $p_v$        | partial pressure of volatile, Pa  |
| $q$          | adsorbed quantity of volatile at equilibrium, $kg \cdot kg^{-1}$  |
| $q_0$        | model parameter in Eq. (7)  |
| $q_{\infty}$ | theoretical limiting value of the adsorbed quantity of volatile, $kg \cdot kg^{-1}$                               |
| $T$          | temperature, K  |
| $u_m$        | mean value of the motion speed of a molecule, $m \cdot s^{-1}$  |
| $x$          | mole fraction of volatile in gas mixture  |
| $\rho_p$     | apparent density of particles, $kg \cdot m^{-3}$  |
| $\rho_s$     | actual density of particles, $kg \cdot m^{-3}$  |

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