Kinetic Analysis of Tar’s Separation from Lump Coal

Qihang LIU,1,2)* Keng WU,1) Ruiling DU,1) Yuan SHE1,2) and Xiao LIU1)

1) State Key Laboratory of Advanced Metallurgy, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing, 100083 China. 2) School of Metallurgical Engineering, Xi’an University of Architecture and Technology, 13 Yanta Road, Xi’an, Shaanxi, 710055 China.

(Received on November 5, 2014; accepted on January 19, 2015)

The tar separated out from the lump coal has an important effect on COREX process. In this paper, a designed experimental method is used to study the kinetics of tar’s separation from lump coal. The weight percent gain of the tar was defined as the tar’s separation conversion using the weight-loss ratio in TGA for reference, and then the isothermal and non-isothermal kinetic models were used to analyze the dynamics mechanism of tar’s generation. Based on the characteristic of tar’s generation, we suppose that the shrinking core model is suited to the early heating process of lump coal, and the mid-term and later stage of tar’s generation are respectively controlled by the coal pyrolysis and the spread of the tar molecule. Thus, the equation of non-isothermal unreacted core model, the first order reaction model and the Anti-Jander diffusion equation are respectively established to describe the tar’s generation. The fitting results of these three models showed a good linear dependence relation illustrating that the experimental method and the hypothetical models in this paper are reliable. What’s more, a way is provided to study the tar’s or other substances’ dynamic separation through the experiment method.

KEY WORDS: tar generation separation; dynamics; COREX; kinetic models.

1. Introduction

Lump coal, ore and some low quality coke were used in Baosteel’s COREX C3000 which is a new technology to produce hot metal. Different from blast furnace, the coking and sintering process were not needed for COREX, and it was an environmentally friendly process with little pollution.1–4) Lump coals were added to the top of COREX melter gasifier, then the fast pyrolysis of lump coal occurred in the high temperature surroundings. The tar was separated fast from the lump coal, and lots of the separated tar could not be decomposed within a short time in melter gasifier. What’s more, the separated tar would be easily condensed and bonded in the gas pipeline, which leads to the blockage of gas pipeline, then the cycle of device maintenance was shortened. The reduction process would also be influenced by the precipitated tar.5,6) Lots of research about the catalytic cracking and gasification kinetics of the coal char has been done in the Lab,7–10) and TGA (Thermogravimetric Analysis) is a common method to analyze the dynamic characteristics.11–13) However, the conventional ways including TGA are not suitable for the analysis of tar’s separation. Thus, we designed an experiment to dynamically record the weight of separated tar, and then define the tar’s separation conversion using the defined conversion in TGA for reference.

Considering the conditions of the simulation experiment (the reactor equipped with coal samples was not put into furnace until the furnace reached the setting temperature), the lump coal would take a certain period of time to be heated to the setting temperature due to the large thermal resistance,14) and the heating process before the lump coal reached the setting temperature is non-isothermal. At this non-isothermal process, coal tar would also be separated fast out from the lump coal. After the center of coal reached the setting temperature, the tar was separated fast under constant temperature. Sometime later, the surface reaction of lump coal was completed, and the tar was only separated out from the interior of the coal which needs the diffusion through lump coal to reach the tar condensing unit. Based on the characteristic of tar precipitation, we suppose that the non-isothermal retract model is suitable for the early tar precipitation, and the medium-term and later tar precipitation rate are respectively controlled by pyrolytic reaction and molecular diffusion.

2. Experiment

2.1. Test Method

Table 1 shows the analysis of lump coal used in COREX. As shown in Table 1, FCd is fixed carbon, Ad is ash content, Vd is volatile, St,d is sulfur content, Mad is moisture, and GR,I is caking index.

Table 1. Analysis of the lump coal [wt%].

<table>
<thead>
<tr>
<th>FCd</th>
<th>Ad</th>
<th>Vd</th>
<th>St,d</th>
<th>Mad</th>
<th>GR,I</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.35</td>
<td>7.71</td>
<td>31.94</td>
<td>0.46</td>
<td>2.84</td>
<td>55</td>
</tr>
</tbody>
</table>

* Corresponding author: E-mail: liuqihang2@126.com
DOI: http://dx.doi.org/10.2355/isijinternational.55.947
was put in the high temperature reactor, then N₂ was injected into the reactor to eliminate the air. In order to simulate the fast heating process in COREX, an empty muffle furnace was first heated to 873 K, then the sealed reactor which is collected to a tar collecting device was quickly put into the furnace, and the door of the furnace closed to avoid any temperature drop. The coal in the reactor was suddenly heated to the high temperature, and a large number of tar generated in the reactor. The tar escaped from the reactor was absorbed by the tar collecting device, and the yield of tar is recorded in the computer through electronic balance. The test process above was performed respectively under the setting temperature of 973 K, 1073 K, 1173 K or 1273 K.

The tar is collected by the device as Fig. 1. The coal gases first go through a high-temperature filter device which is made of glass fiber, then the absorption bottles equipped with CH₂Cl₂ are used to extract the tar from the filtered coal gases. The first absorption bottle is placed in the ice water mixture (273 K), and the second is placed in the acetone-dry ice mixture (198 K) to assure the sufficient absorption of the tar. After any experiment, the absorption bottles are cleaned and the filter device is also changed.

2.2. Test Results
Through the above experiment, the weight of separated tar was recorded in the computer. Here, we define the tar’s separation conversion as \( \alpha = m_t/m_f \), \( m_t \) refers to the weight of separated tar at the moment \( t \), \( m_f \) refers to the total weight of separated tar at a certain experimental conditions. Thus, the changes of tar’s separation conversion over time at different temperature are obtained as Fig. 2.

3. Kinetic Analysis of Tar’s Separation

3.1. Non-isothermal Kinetic Analysis of Tar’s Early Separation
Under the test conditions, the surface of lump coal is first reached to the setting temperature, and the heat is transmitted from the surface into the center of lump coal. Thus, we suppose that the tar is first formed on the coal’s surface, and then extends gradually to the inner. Then the shrinking core model is adopted to describe the characteristic of early tar separation. For this non-isothermal process, the following kinetic equation is used:

\[
\frac{d\alpha}{dt} = kf(\alpha) \quad \text{or} \quad G(\alpha) = kt \quad \text{............... (1)}
\]

\[
G(\alpha) = \int^{\alpha} \frac{da}{f(\alpha)} \quad \text{............... (2)}
\]

Where, \( t \) is the tar separation time, \( k \) is the speed constant of tar separation, \( f(\alpha) \) and \( G(\alpha) \) are the differential form and integral form of mechanism function controlling the tar’s separation.

The heat conductivity coefficient of lump coal is regarded as a constant in the early tar separation, and the temperature distribution of lump coal is linear, that is the heating rate \( \beta \) of lump coal is a constant. Therefore, Eq. (1) could be expressed as:

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT)f(\alpha) \quad \text{............... (3)}
\]

According to the derivation and simplification of Eqs. (2) and (3), the Coats-Redfern integral equation is obtained:

\[
\ln[G(\alpha)/T^2] = \ln \left( \frac{AR}{\beta E} \right) + \frac{E}{RT} \quad \text{............... (4)}
\]

Where, \( A \) is pre-exponential factor, \( E \) is activation energy of tar generation, kJ/mol, \( T \) is temperature.

According to the characteristic of early tar separation, the kinetic model function \( G(\alpha) = 3[1-(1-\alpha)^{1/3}] \) is used for data-fitting.\(^{18}\) The heating rate \( \beta = (T_f - T_0)/t_f \), \( T_0 \) is the start temperature of tar’s separation, and \( t_f \) is the heating time of lump coal from \( T_0 \) to \( T_f \). The data of early tar separation conversion are used in Eq. (4) for fitting, and \( 1/T \) as abscissa, with \( \ln(G(\alpha)/T^2) \) as the ordinate. Then the fitting results is as shown in Fig. 3. In order to estimate the heating time of lump coal from the room temperature to the setting temperature, the point of the maximum rate change (the value of \( d^2\alpha/dt^2 \) is largest) is used as the demarcation point between the different stages.

By the slope and intercept of fitting results, the activation energy \( E \) and pre-exponential factor \( A \) could be obtained as Table 2. The related fitting results of this non-isothermal stage is as shown in Table 3.

![Fig. 1. Schematic diagram of tar collection device. 1-gas pipe connected to the reactor, 2-filter material made of glass fiber, 3-insulated cabinet, 4-absorption bottle with CH₂Cl₂ in ice water (273 K), 5-absorption bottle with CH₂Cl₂ in acetone-dry ice (198 K), 6-electronic balance, 7-computer 8-gas analyzer.](image)

![Fig. 2. The relationship between \( \alpha \) and \( t \).](image)
3.2. Kinetic Analysis of Mid-term Tar Separation

After the center of lump coal reached to the setting temperature, the tar’s separation from lump coal is going on under the constant temperature. Thus, an isothermal model based on the shape and characteristic of lump coal is established to describe the process of tar’s separation.

We suppose that the tar’s separation at this stage is controlled by the pyrolysis of lump coal which is regarded as a first order reaction, and the coal particles whose size remains the same in the pyrolysis process are considered as sphere. According to the relationship between radius and conversion:

\[ \alpha = \frac{R_0^3 - r^3}{R_0^3} \]

Where, \( R_0 \) is the radius of lump coal, \( 1.5 \times 10^{-2} \) m, and \( r \) is the radius of tar’s separation from lump coal at one moment, m.

The reaction cross-sectional area of single particle at one moment is:

\[ A_1 = 4 \pi r^2 = 4 \pi R_0^2 (1-\alpha)^{2/3} \]

And the number of particles of unit mass in the reaction system:

\[ N = \frac{3}{4 \rho \pi R_0^2} \]

When \( \alpha = 0 \), then:

\[ \frac{da}{dt} = k_{rea} A N (1-\alpha) = \frac{3k_{rea}}{\rho R_0^2} (1-\alpha)^{5/3} \]

Where, \( \rho \) is the density of lump coal, \( 1.28 \times 10^3 \) kg/m³, \( k_{rea} \) is the speed constant, kg/(m²·s)

When \( t=0 \), \( \alpha=0 \). Then the integral equation is obtained:

\[ 1 - (1-\alpha)^{2/3} = -\frac{2k_{rea}}{\rho R_0^2} t \]

The data of mid-term tar separation conversion are used in Eq. (4) for fitting, and \( t \) as abscissa, with \((1-\alpha)^{2/3} - 1\) as the ordinate. Then the fitting results is as shown in Fig. 4.

The related fitting results of the mid-term stage of tar’s separation are shown in Table 4.

3.3. Kinetic Analysis of Tar’s Separation at Later Stage

In the later stage of tar’s separation, the surface reaction of lump coal has almost completed while lots of tar separated out from the interior of lump coal. Then the tar needs the diffusion through lump coal to reach the tar condensing unit. In this case, the tar’s separation could be controlled by the spread of tar molecular in the lump coal. The Anti-Jander diffusion equation is established on a hypothetical model.

![Fig. 3. Fitting results of shrinking core model in the early tar separation.](image)

![Fig. 4. Fitting results of the first order reaction model in the mid-term tar separation.](image)

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Activation energy E [kJ/mol]</th>
<th>Pre exponential factor A [s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>26.57</td>
<td>2.57×10⁻⁴</td>
</tr>
<tr>
<td>973</td>
<td>26.72</td>
<td>3.94×10⁻⁴</td>
</tr>
<tr>
<td>1073</td>
<td>29.76</td>
<td>7.62×10⁻⁴</td>
</tr>
<tr>
<td>1173</td>
<td>28.48</td>
<td>1.26×10⁻³</td>
</tr>
<tr>
<td>1273</td>
<td>27.55</td>
<td>4.20×10⁻³</td>
</tr>
</tbody>
</table>

Table 2. Kinetic parameters of the early tar separation.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Starting time [s]</th>
<th>Ending time [s]</th>
<th>Ratio [%]</th>
<th>Correlation coefficient [-]</th>
<th>Slope [-]</th>
<th>Intercept [-]</th>
<th>Rate constant k [kg/(m²·s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>0</td>
<td>80</td>
<td>3.10</td>
<td>0.887</td>
<td>-3.196.5</td>
<td>-18.35</td>
<td>2.97×10⁻⁵</td>
</tr>
<tr>
<td>973</td>
<td>0</td>
<td>100</td>
<td>4.60</td>
<td>0.889</td>
<td>-3.213.3</td>
<td>-17.86</td>
<td>4.40×10⁻⁵</td>
</tr>
<tr>
<td>1073</td>
<td>0</td>
<td>120</td>
<td>3.80</td>
<td>0.916</td>
<td>-3.579.4</td>
<td>-17.28</td>
<td>6.05×10⁻⁵</td>
</tr>
<tr>
<td>1173</td>
<td>0</td>
<td>140</td>
<td>9.21</td>
<td>0.918</td>
<td>-3.425.5</td>
<td>-16.76</td>
<td>7.90×10⁻⁵</td>
</tr>
<tr>
<td>1273</td>
<td>0</td>
<td>100</td>
<td>7.94</td>
<td>0.874</td>
<td>-3.314.1</td>
<td>-15.88</td>
<td>9.87×10⁻⁵</td>
</tr>
</tbody>
</table>

Table 3. The fitting results of shrinking core model in the early stage of tar separation.
that the thickness of the product layer gradually increased outside the reacted core, which is similar to the tar's diffusion process in the lump coal. According to the Fick's law:\(^{19}\)

\[
\frac{dm}{dt} = D \left[ \frac{dc}{dx} \right]_{x=R_0} \quad \text{(6)}
\]

and

\[
\frac{dm}{dx} = \rho dx \quad \text{(7)}
\]

Where, \(m\) is the tar molecule’s volume of migration, kg, \(x\) is the tar molecule’s migration distance (0 < \(x < R_0\)), m, \(c\) is the tar’s concentration, kg/m\(^3\), \(c_0\) is the initial concentration of the tar, kg/m\(^3\). \(D\) is the diffusion coefficient, m\(^2\)/s.

Simultaneous Eqs. (6), (7), (8):

\[
\frac{dc}{dx} = \frac{c_0}{x} \quad \text{(8)}
\]

Based on the definition of conversion rate in the sphere:

\[
\alpha = \left( \frac{R_0 + x}{R_0} \right)^{3/2} - 1, \quad \text{that is } x = R_0[(1+\alpha)^{3/2} - 1], \text{ then substituting into Eq. (9):}
\]

\[
\left[ (1 + \alpha)^{3/2} - 1 \right]^2 = \frac{2Dc_0}{\rho R_0} t = kt \quad \text{(10)}
\]

This is the Anti-Jander diffusion equation.\(^{15}\) The data of the late tar separation conversion are used in Eq. (10) for fitting, and \(t\) as ascissa, with \([1+(1+\alpha)^{3/2} - 1]^2\) as the ordinate. Then the fitting results is as shown in Fig. 5.

The related fitting results of the later stage of tar’s separation are shown in Table 5.

According to the empirical relationship between the diffusion coefficient and the temperature:

\[
D = D_0 \exp \left( \frac{-E_0}{RT} \right) \quad \text{(11)}
\]

<table>
<thead>
<tr>
<th>Table 4. The fitting results of first order reaction model in the mid-term tar separation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [K]</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>873</td>
</tr>
<tr>
<td>973</td>
</tr>
<tr>
<td>1073</td>
</tr>
<tr>
<td>1173</td>
</tr>
<tr>
<td>1273</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5. The fitting results of Anti-Jander diffusion equation in the later tar separation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [K]</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>873</td>
</tr>
<tr>
<td>973</td>
</tr>
<tr>
<td>1073</td>
</tr>
<tr>
<td>1173</td>
</tr>
<tr>
<td>1273</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6. The activation energy of tar’s middle and later separation [kJ/mol].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy of pyrolysis</td>
</tr>
<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td>63.41</td>
</tr>
</tbody>
</table>

Fig. 5. Fitting results of the Anti-Jander diffusion equation in the later tar separation.

That is: \(\ln D = \ln D_0 - \frac{E_0}{RT}\), set \(1/T\) as ascissa, with \(\ln D\) as the ordinate, then the diffusion activation energy could be obtained by the fitting results. Set \(1/T\) as ascissa, with \(\ln k_{rea}\) as the ordinate, then the pyrolysis activation energy could also be obtained as Table 6.

As shown in Tables 2 and 6, the activation energy \(E\) of early tar’s separation is about 25–30 kJ/mol, which is much lower than the mid-term (63.41 kJ/mol) and later (84.04 kJ/mol).
stage of tar’s separation. This results could be an important support for the suggestions of preheating the lump coal before it was added to the melter gasifier of COREX C3000 to avoid the tar’s separation and the fines generation of lump coal.14)

4. Conclusions
A designed experimental method was used to analyze the kinetics of tar’s separation out from the lump coal used in COREX. Based on the characteristic of the tar’s separation in the simulation experiment, three different models were used to describe the early, mid-term and later stage of the tar’s separation. The non-isothermal unreacted core model is suited to the early tar separation which could obtain the heating time of lump coal and other dynamic parameters. The tar’s mid-term and later separation are going on under constant temperature, which are respectively controlled by the first order reaction equation and the Anti-Jander diffusion equation.

Based on the fitting results of three different models, the relevant dynamic parameters ($k_{rea}$, $D$, $E$) of tar’s separation in the early, mid-term and later stage are respectively given in this paper. The ratio of early tar separation is less than 10%, while the ratio of mid-term and later stage are about 30%–50% and 40%–60%. What’s more, the activation energy $E$ of the three stages of tar’s separation are about 25–30 kJ/mol, 63.41 kJ/mol and 84.04 kJ/mol. These results could provide a theoretical support for effectively control the tar’s generation and the fines generation of lump coal used in COREX C3000. However, more research about the influence of different kinds of coals with various heat absorption capacity, expansibility and contractibility etc. on the rate of tar’s generation are necessary to be performed in the laboratory.

Acknowledgments
The authors would like to express their thanks for the support by National Natural Science Foundation China (51274026, 51474022, 50934007), Independent research project (41603003) of State Key Laboratory of Advanced Metallurgy and the National High-Tech.

REFERENCES