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Pyrolysis Characteristics and Heat Transfer for Oil Shale and Oil Sand Retorting

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Abstract: ***In this paper, the properties of oil shale and oil sand were evaluated, including Fischer assay, proximate analysis, heat value, ultimate analysis, composition of retorting gas, et al.The pyrolysis experiments on Indonesia oil sand, Estonia and Longkou oil shale, were performed using the differential scanning calorimetry (DSC) and the thermogravimetric analyzer (TGA) at different heating rates of 15, 20, 25 and 30℃/min. The kinetic parameters (apparent activation energy E and frequency factor A) were determined using Friedman procedure, parallel pyrolysis reaction model and maximum pyrolysis rate method, respectively. It is found that the activation energy increases with the increasing conversion. The calculated results using parallel pyrolysis reaction model are shown to be in good agreement with experimental results. More than 50% reactions were carried out corresponding to the activation energy of 167～210 kJ·mol-1. The apparent activation energy in maximum pyrolysis rate was obtained, which is closed to the result of Friedman method corresponding to about conversion of 50%. It is also shown that the plot of lnA vs. E for oil sand and oil shale pyrolysis becomes a linear line.***

Keywords: Oil shale, Oil sand, Heat transfer, Coefficient of heat conductivity, Kinetics.

1. NATURE AND RESOURCE DISTRIBUTION OF OIL SHALE

1.1 Oil Shale Definition and Characteristics

Oil shale (Oil Shale) is also known as oil shale. Oil shale is defined as [1]: oil shale is a sedimentary rock containing solid organic matter in its mineral skeleton, its organic matter content is usually 10-35 per cent, the organic matter is mainly oleaginous (casein), insoluble in common solvents.Oil shale is a solid fossil fuel (Solid Fossil Fuel). As a source of energy, oil shale is heated and the oil matrix is pyrolysed to produce shale oil.

1.2 Oil Shale Distribution in the World

According to the United States Geological Survey in 2011, oil shale reserves in the United States totalled about 4.3 trillion barrels of shale oil, mainly in southwestern Wyoming, northwestern Colorado and the northeastern basin of Utah. In Russia, more than 80 oil shale deposits have been discovered, with different levels of exploration. In summary, the United States has the largest oil shale resources in the world, followed by Russia, Zaire, Brazil, Jordan, Morocco, Australia, China and Estonia.

2. 2.OIL SAND (MINING)

2.1 Nature of Oil Sands and the Distribution of Domestic and Foreign Resources

2.1.1 Oil sand properties

Oil sands are a mixture of sand and minerals encapsulated with bitumen, oil sands are also known as "tar sands", oil sands are essentially a mixture of bitumen, sand, mineral-rich clay, and water, and oil sands thick oil is a kind of asphalt oil with high density, viscosity, and hydrogen-carbon ratio.

2.1.2 Main oil sand resources

The world's oil sands-rich countries include Canada, Venezuela, the United States, Russia and China, with oil sands reserves of about 1.7 trillion barrels of crude oil.Foreign countries have a long history of exploiting oil sands, and 85 per cent of the world's proven reserves of oil sands resources are distributed in the northern region of Alberta, Canada, which is equivalent to about 2.9×10^{12} barrels of oil sands oil, mainly concentrated in the oil sands areas of Ashabasca, Cold Lake and Peace River, with an area of 4.3 million hectares, 729,000 hectares and 976,000 hectares, respectively.

2.2 Oil sand Processing Process

Usually heavy oil hydrogenation can be divided into fixed bed, moving bed, suspended bed, boiling bed four different reactors, and so far relatively more mature and widely used technology is the fixed bed and boiling bed reactor, but the oil sands extracted asphalt is heavier and more viscous than heavy oil, so the general deep processing of the use of residue boiling bed hydrocracking process, such as the LC-Fining process and so on.

2.3 Oil Sand Distillation Technology

The dry distillation method is now widely used in the field of oil shale, and various processing furnaces have been developed at home and abroad. The method is to make the organic matter decompose by heating to produce oil and gas, and the oil obtained is lighter, which is a better method to treat oily oil sands. After the dry distillation method, the sand and gravel, to the deposit area of water and rock body of the environmental pollution is small, and can be used as paving materials. The Oil Sands Technical Authority of Alberta, Canada, has proposed the use of the Aostar Taciuk Process, or ATP, which runs through granular oil shale.

3. OIL SHALE AND OIL SAND

3.1 Pyrolysis Kinetics of Oil Shale and Oil Sands

The chemical kinetic method is mainly based on the theory of late pyrolytic hydrocarbon production by casein, i.e., the hydrocarbon parent material of hydrocarbon production is casein, which undergoes a series of thermal degradation reactions to produce hydrocarbons under the effect of thermodynamics and kinetics. The chemical kinetics is mainly to select a suitable kinetic model to deal with the experimental data, and calculate the kinetic parameters such as apparent activation energy, apparent frequency factor and number of reaction stages.

3.2 Current Status and Content of Chemical Dynamics Research

The research began in the 1960s, and the research in this area absorbed to a considerable extent the results of pyrolysis kinetics of coal and oil shale, which had been studied abroad in the 1920s. Since then, some scholars have successively proposed various kinetic models, including the lumped reaction model, parallel reaction model, tandem reaction model, and cascade reaction model with bitumen as the intermediate product.

Chemical kinetics is the study of not only the rate of a chemical reaction and how various factors (concentration, pressure, temperature, catalyst, etc.) affect the rate of the reaction, but also the steps that a chemical reaction goes through when it actually takes place, i.e., the chemical reaction mechanism.

The study of chemical kinetics begins with the rate of a chemical reaction, which refers to the degree to which a reaction proceeds quickly or slowly. However, this intuitive concept does not satisfy the requirements of quantitative science, as a clear definition must be given. It is usually defined as the decrease in the concentration of reactants or the increase in the concentration of products per unit time. Then comes the rate equation for a chemical reaction.

3.3 Current Status of Pyrolysis Dynamics

The research on the pyrolysis dynamics of oil sands started late at home and abroad, but the pyrolysis process of oil sands distillation is similar to that of coal and oil shale. Therefore, the research results of coal and oil shale can be referred to, and there are a lot of reports and research results at home and abroad.

4. BASIC STUDIES OF HEAT TRANSFER

4.1 The Basic Concept of Heat Transfer

Heat transfer occurs because of the transfer of heat due to the presence of a temperature difference. The process of heat transfer can be classified into three types of modes, namely conduction, convection and thermal radiation.Heat transfer that occurs in different parts of an object as a result of a temperature difference, or between two objects of different temperatures as a result of direct contact, is conduction.

4.2 Heat Transfer of Oil Shale

It was found by thermal difference one thermogravimetric experiments that oil shale is a pore-fracture developed material, and the casein root is endowed in the pore-fracture of oil shale in the form of solids, and the laminations inside the oil shale are tiny, and are in the state of closure in the subsurface.

After pyrolysis, the caseous roots of oil shale form many pores, and the formation and connectivity of these pores can further improve the permeability of oil shale.

4.3 Heat Transfer of Oil Sand

There are few domestic and international studies on heat transfer from oil sands, and only the process of heat transfer with the furnace wall during the dry distillation of oil sands has been analysed. Since the rest of the methods are not industrialised except for the Canadian water washing method.

4.4 Fixed-bed Reactor Heat Transfer and Model

The effect of temperature on the conversion rate during heat transfer was found to be related to the magnitude of the change in the effective heat transfer parameter. Factors affecting the heat transfer parameters of a fixed-bed reactor include: reactor structure, ratio of bed diameter to filled particle diameter, pressure, temperature, fluid properties, particle shape, particle material, and so on.

The thermal conductivity of the upright furnace was modelled without considering the effect of chemical reactions and assuming zero heat of dry distillation, as shown in equation (1).

$$\frac{a\tau}{R^2} = 3.84\left(\frac{\lambda_c \cdot R}{\lambda \cdot \sigma}\right)^{-0.43} \cdot \left(\frac{t_k - t_0}{t_c - t_0}\right)^2 \tag{1}$$

Based on the parameters of the heat transfer process in the coal charge of the upright furnace, an empirical formula for the heat transfer coefficient was summarised.

5. ANALYSIS OF THE BASIC PROPERTIES OF OIL SHALE, OIL SANDS AND RELATED PRODUCTS

5.1 Basic Nature Analysis

Oil shale and oil sands are relatively similar in nature, the thermal decomposition of the oil matrix produces hydrocarbons, which are basically no longer produced when heated to about 500°C and constant for a certain period of time. In addition to the pyrolysis method, oil sands can also be solvent extraction method, the use of organic solvents to dissolve the bitumen in the oil sands, the process is a physical separation process, unlike the pyrolysis process occurs in the chemical reaction of the molecular bond breaking process. To study the heat transfer process of oil shale and oil sands, it is first necessary to determine the oil content, specific gravity and other basic properties, and then based on the determination of the basic parameters and then combined with the experimental data of heat transfer to establish a heat transfer model for calculation.

5.2 Oil Shale Compared with the Oil Sands

Firstly, the geological causes of the two are different. Oil sands are formed as a result of tectonic movements, where hydrocarbons are transported into shallow strata or basin margins to form oil sands mines. Oil shale has a lamellar shape, while oil sands are made of thick oil wrapped around sandstone particles, or limestone, or other sedimentary rocks, and are soluble in common organic solvents. Analysis of the basic properties shows that the pyrolysis processes of oil shale and oil sands are essentially the same, but the dry distillation of oil sands yields semi-coke with lower fixed carbon and calorific value, and higher calorific value of dry distillate gas. In contrast to shale oil, the pyrolysis product oil from oil sands is denser and has a high amount of residual carbon.

6. STUDY ON THE HEAT TRANSFER PROCESS OF OIL SHALE AND OIL SANDS

6.1 Comparison of Oil Shale Heat Transfer Experiment

Heat transfer experiments were carried out on two oil shales in a fixed-bed reactor to investigate the effect of heat transfer on the dry distillation process in three different heating rates, and three conclusions were drawn: 1) With the increase of heating rate, the difference between internal and external temperatures becomes larger, and the time required for constant temperature at the final temperature becomes longer. 2) With the increase of temperature, the thermal movement of the solid molecules of the oil shale increases, and the thermal conductivity of the air in the voids and pore space also increases, the The heat transfer coefficient gradually increases. 3) Normally the heat transfer coefficient is related to the composition structure of the material, density, moisture content, temperature, particle size, particle size distribution and other factors.

6.2 Comparison of the Heat Transfer Experiments in Oil Sands

Heat transfer experiments were carried out on Indonesian oil sands in a fixed-bed reactor to examine the effect of heat transfer on the dry distillation process at three different rates of temperature increase, and in addition to the three conclusions that are the same as those for oil shale one difference between the two was made: oil sands are less dense than oil shale and have well-developed pore space with a porosity significantly greater than that of oil shale.

7. CONCLUSION

This paper analyses and compares the basic properties of Longkou and Estonian oil shale and Indonesian oil sands, and the basic properties of the products of pyrolysis and extraction of oil sands, respectively, and compares the similarities and differences between oil shale and oil sands. The following conclusions were mainly drawn:

1) The average oil content of the oil shale in the North Soap area of Longkou, Shandong Province, is 7.43%, with a relatively low oil content. The average oil content rate of Estonian oil shale is about 20%, and its grade is significantly higher than that of China. The oil sands of Buton Island in Indonesia have an oil content rate of more than 20%, which is the highest compared with domestic and foreign oil shales. 2) The geological causes of oil shale and oil sands are different, oil shale has a lamellar shape, and its oil mother substance is an organic polymer three-dimensional polymer, which is not soluble in common organic solvents. The oil sands is thick oil parcel sandstone particles, or limestone, or other it accumulated rock and become, and can be dissolved in ordinary organic solvents. Oil shale and oil sands pyrolysis process is basically the same. 3) Lungkou shale oil has small density, low viscosity, high condensation point, solidification at room temperature, poor fluidity, high flash point, high mechanical impurity content; Estonian shale oil has low condensation point, low flash point, low mechanical impurity content, high density, high viscosity; Indonesian oil sands pyrolysis oil has low condensation point, low flash point, can be ignited at room temperature, high density, high viscosity, Mechanical impurity content is higher, and sulphur content is high. 4) After organic matter is thermally decomposed to release oil, hydrogen content decreases significantly, sulphur in inorganic minerals is enriched in semi-coke, and oxygen is transferred to the gaseous or liquid products. 5) Oil shale and oil sands are poor heat conductors and both have small heat transfer coefficients. 6) Calculations by Friedman's method show that the activation energy gradually increases with increasing conversion. 7) Calculations by six parallel one-stage reaction models show that the activation energy required for the pyrolysis reactions is mainly in the range of 167-210 kJ-mol-1, and that more than 50 per cent of the reactions occurring in that range The linear regression coefficient of Friedman method is high, and the activation energy gradually increases with the increase of conversion rate; the conversion rate calculated by the parallel one-stage reaction model agrees well with the measured conversion rate, in which more than 50% of the reactions occur within the range of 167-210 kJ-mol-1 of the apparent activation energy, and the above two methods are able to explain the complex pyrolysis process of oil sands and oil shale better.

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