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Research Status of Oil Shale Pyrolysis Mechanism

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Abstract

Oil shale is an important mineral energy with huge resources. It is an important alternative energy for oil and natural gas. Pyrolysis is an important technology of oil shale utilization. The oil shale pyrolysis mechanism is of great significance to improve the yield and quality of shale oil and shale gas products, the research status of which is introduced in this paper in terms of the kinetics and products distribution characteristics. Finally, some suggestions and opinions about oil shale pyrolysis mechanism are put forward.

Keywords

Oil Shale Pyrolysis; Mechanism; Kinetics; Simulation.

1. Introduction

Oil shale (also known as kerogen) is a kind of solid combustible mineral with ash content of more than 40 wt.% and oil content of 3.5 wt.% - 30 wt.%, in which the contents of inorganic minerals and organic components are about 50 wt.% - 85 wt.% and 15 wt.% - 50 wt.% [1], respectively. Shale oil and combustible gas can be extracted by heating oil shale to 400 ºC ~ 500 ºC (i.e. retorting, low-temperature retorting or pyrolysis) without air or oxygen. The atomic hydrogen and carbon ratio of shale oil is similar to that of natural oil, which can be directly used as fuel oil or further processed to produce other oil products [2].

Pyrolysis is one of the thermochemical conversion technologies for oil shale, which is generally the initial chemical step in all oil shale gasification and combustion processes. The oil shale pyrolysis mechanism is quite complex, including a series of serial and parallel reactions [3]. The research on pyrolysis mechanism of oil shale is very important for the design and operation of reactor, the optimization of pyrolysis conditions, the prediction and control of pyrolysis products, and the simulation of experimental process. It is also of great significance to evaluate the economy of pyrolysis process.

So far, oil shale pyrolysis mechanism mainly focuses on the research of oil shale pyrolysis kinetics as well as the formation pathway and distribution characteristics of pyrolysis products, among which the pyrolysis kinetics is one of the basic theories of oil shale pyrolysis. Therefore, this paper will introduce the research status of oil shale pyrolysis mechanism in terms of pyrolysis kinetics and pyrolysis product distribution characteristics. It will provide a new method for further study of oil shale pyrolysis mechanism.

2. Pyrolysis kinetics of oil shale

Thermogravimetric analysis (TGA) is the most commonly used test method to study the pyrolysis kinetics of oil shale. Oil shale pyrolysis can be carried out under isothermal and non-isothermal

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conditions. Because the non-isothermal method needs a shorter test time to determine the kinetic data, and can avoid the error resulting in the difficulty of accounting for the reactions taking place during the initial heat-up period that cannot be ignored by the isothermal method, most studies are carried out under non-isothermal conditions. The experimental data can be analyzed to determine the kinetic parameters of the pyrolysis process using various methods, such as integral method, differential method, direct Arrhenius plot method, Coats Redfern analyses method, Friedman procedure, maximum rate model, distributed activation energy model (DAEM) and parallel first-order reaction model, etc. At present, many researchers in the world have put forward serval mechanisms and kinetics models of oil shale pyrolysis related to the fuel and reactor types, but there is no generalized mechanisms and kinetics model. Most researches indicate that the pyrolysis process of oil shale and kerogen can adequately be described by means of first-order kinetics equation [4-7]. In addition, some studies suggest that bitumen and carbon residue are formed firstly from kerogen during thermal decomposition of oil shale, followed by further decomposition of bitumen. Pyrolysis bitumen is used as an intermediate product during oil shale pyrolysis, and its kinetics can be described by parallel first-order reaction [8-10]. Torels et al. [8] considered that aliphatic kerogen mainly generates liquid hydrocarbons, while aromatic kerogen is relatively stable and mainly forms carbon residue. In addition, when Charlesworth et al. [11] used the isothermal method to study oil shale pyrolysis kinetics, it was found that a single rate law could not be used to describe oil shale pyrolysis process below 500 ^{o}C, and the interpretation of data is complicated by the delay in achieving thermal equilibrium above 500 ^{o}C before appreciable reaction occurs. The solid-phase decomposition mechanism of oil shale progresses from a diffusion-controlled reaction to a nucleation and growth-controlled reaction through a phase boundary process. However, the kinetics can be adequately described by a simple first-order rate expression, together with the appropriate time-temperature transformation in the case of non-isothermal measurements. Demineralization does not change the reaction mechanism, but increases the reaction rate. Weitkamp et al. [12] indicated that pyrolysis of shale appears to be described by a diffusion-limited first-order reaction whose kinetics are complicated by the possibility of more than one bond-breaking step in the conversion of kerogen to gas, oil, and coke. Diffusion control diminishes as the shale changes from impervious rock to highly porous ash, but increases as temperatures are increased, because products are generated faster than they can diffuse out of the pores. Oil shale pyrolysis under hydrogen or deuterium pressure gives increased yields of lighter products and much less coke. The pattern of deuterium distribution in normally gaseous hydrocarbons is consistent with a thermal free-radical mechanism such that the radicals may be stabilized by the gain of a deuterium atom or the loss of hydrogen or, depending on the extent of diffusion control, may condense to form larger molecules. Aboulkas et al. [13, 14] considered that the pyrolysis process of oil shale kerogen from Moroccan Tarfaya deposits agrees with diffusion model (D4 mechanism), but after demineralization, it can be described by first-order reaction model (F1 mechanism). Demineralization will affect the kerogen pyrolysis kinetics and reduce the activation energy of kerogen pyrolysis. Al-Ayed et al. [15, 16] suggested that the formation rate of shale oil obtained from El-lajjun oil shale pyrolysis can be fitted by a second-order reaction rate equation.

3. Products distribution characteristics of oil shale pyrolysis

Pyrolysis of oil shale is a process affected by heat transfer, mass transfer and chemical reactions. It goes through multi-step reactions, involving hundreds of chemical reactions and intermediate products. It is affected by the physical and chemical characteristics of oil shale (particle size, chemical composition and mineral content of oil shale) and the operating conditions of pyrolysis process (retorting temperature, residence time, heating rate, retorting medium and reaction temperature) [17-22]. Under different conditions, the yield distribution and characteristics of oil shale pyrolysis products are significantly different. By investigating the effects of different reaction conditions on the yield distribution and characteristics of oil shale pyrolysis products, the pyrolysis process of oil shale can be optimized to maximize the energy utilization of oil shale. In view of the complexity of

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the experiment, we need to use mathematical model or simulation software to simplify the experiment properly, so as to grasp the pyrolysis characteristics of oil shale more conveniently and quickly.

3.1 Numerical calculation method

The kinetic characteristics of oil shale pyrolysis are the basis for the calculation and study of oil shale pyrolysis characteristics. Kök and Pamir [23] studied the pyrolysis process of oil shale by thermogravimetric (TG / DTG) analysis under non-isothermal conditions, and obtained the pyrolysis characteristics and kinetic parameters of oil shale. They have developed a general computer program to determine the kinetics of thermal decomposition of oil shale. The accuracy and simplicity of five reaction kinetic methods were compared. Do [24] has conducted a theoretical study on the pyrolysis of large oil shale particles in an isothermal fluidized bed retort using a two-step model. The two-step model considers that after oil shale is kept at 500 ºC for one minute, the kerogen first decomposes into light oil, bitumen and water vapour. This bitumen further undergoes two parallel reactions. One reaction occurs after keeping 15 minutes at 500 ºC and mainly produce heavy oil, which is far slower than the decomposition rate of kerogen. And the other reaction can produce gas and coke in the ratio of 1:4. Lastly, the light oil and heavy oil are further cracked to give gas and light oils, respectively. In the two-step model, only the pore diffusion resistance is considered, and the film resistance at the solid-liquid interface is neglected because of high sweeping of the inert gas and perfect mixing of the fluidized bed. In addition, the effects of particle size, pore size, porosity of oil shale and temperature are also considered. Isothermal conditions can be assumed in the fluidized bed and the intraparticle temperature can be assumed to be equal to the surface temperature. With these assumptions, the model can predict the evolution of light and heavy oils, the evolution of gas and the coke distribution. Based on the information of the final production distribution and the dynamic response, the model solutions give guidance in selecting an appropriate temperature to operate the fluidized bed retort for the oil shale with a given particle size. Dung et al. [25] established a comprehensive two-dimensional model to describe fluidized bed reactor system, which is composed of four distinct groups of equations, namely partial differential equation describing mass and enthalpy balances and boundary conditions, the stoichiometries and kinetics of chemical reaction involved; equations describing reactor characteristics (fluidization dynamics, heat transfer and mass transfer) and correlations and data for the thermal and physical properties of compounds involved in process operation. The model can be used to simulate fluidized bed retort and combustor. The reactions incorporated in the retort model include pyrolysis of oil shale kerogen, thermal cracking and coking of oil vapour on shale ash. In addition, the mixing of different kinds if solid streams and the increase in the volumetric flow of gaseous products generated from retorting are also considered. The combustor model considers only the combustion of organic carbon in spent shale particles. The models are being used not only in process variable studies of full scale plants, but also to test the generality of kinetic data obtained from other studies within the oil shale programme The combustion of residual carbon is considered in the burner model. In order to assess the reliability of these kinetic data for scale-up purposes, some experiments have been carried out in a 150 mm diameter process development unit (PDU). The PDU fluidized bed retort and combustor are both dense phase fluidized bed reactors. The detailed reactor model predictions for the PDU retort are remarkably close to the actual performance measured on the PDU. Although performance of the PDU combustor is less well predicted, this is probably due to a significant production of carbon monoxide within the bed, particularly when operating at low oxygen concentrations. Further experimental work is required to confirm that this is the case. However, indications are that the kinetic data can be confidently scaled up to reactor systems at the PDU scale. This is to a large extent the result of the reliability of the correlations used for fluidization dynamics at the PDU scale, as indicated by the good prediction of solid residence times for both retort and combustor. Although these studies were performed in fluidized beds, the kinetic data are non-process specific. While the large scale reactors are in fact fluidized bed reactors, this does not imply that such units are regarded as the optimal for oil shale processing, and the data could equally well be applied to any reactor system (packed bed, back-mix, plug flow) which might be selected as the most suitable. And then Dung et al. [26] also established a mathematical model for a moving packed bed retort, and

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developed the corresponding calculation program. The model is composed of different equations describing the relevant heat and mass balances. The convective gas-solid heat transfer is considered as the main heat transfer mechanism between the recycled shale and the raw shale. In order to obtain the accurate solids temperature profiles along the retort, the heat loss / gain of solid particles should be considered. The input data required by the model include stoichiometric factors, rate constant for the reactions considered, flow rates, temperatures, moisture contents of raw and recycled shales, and temperatures of retort wall. The simulation results include product yields, organic carbon conversion to oil, gas and char, temperature profiles (raw and recycled shales, gas) and oil vapour concentration. The simulation results can guide the design of retort and the planning of experiments.

In addition, Diaz et al. [27] have developed a computer model to simulate a hot-solid recycle retorting process consisting of a staged fluidized bed pyrolyzed and a lift-pipe combustor. The retort is modeled by a series of stirred batch reactors, and the combustor is simulated by a lumped-parameter model of the finite difference elements. The whole system meets the mass and heat balance. The model calculates the steady-state operating conditions for the retorting system, taking into account the chemical and physical processes occurring in the two reactors and auxiliary equipment. The calculation results include the stream flow rates, temperatures and pressures, bed dimensions and heater, cooling and compressor power requirements. Finally, the model is used to simulate a hypothetical commercial operation to produce an oil-plus-gas equivalent of 50 000 bbl / day, using 30 gal / ton shale. Although data for model validation are not yet available, the calculated results of the simulation appear reasonable. In 1989, Camp et al. [28**]** used this mathematical model to study the influence of key process parameters on commercial-scale plant with the raw shale feed rate of 63,100 tons/d based on the research of Diaz et al [27]. The model can be run in various modes: a design mode in which the model calculates the reactor dimensions needed to obtain a desired kerogen conversion or recycle-shale temperature; an operation mode in which the model calculates the kerogen conversion and recycle temperature, given the reactor dimensions; and mode variations that allow different combinations of independent and dependent variables. The staged fluidized-bed pyrolyzer submodel includes calculations of fluidization behavior such as pressure drop and minimum fluidization velocity as a function of particle size distribution and densities. It also includes bound water release and kinetic calculations of kerogen pyrolysis and thermal cracking of oil in the reactor headspace. The solids are assumed to have a uniform residence time within each stage and within the whole pyrolyzer. The lift-pipe-combustor model allows four particle-size classes of newly spent shale (one of which is the fines) and three particle-size classes of recycled shale. The velocity, temperature, and composition of each are individually calculated and tracked. The chemical aspects of the lift-pipe model include combustion of char, kerogen, and pyrrhotite. The retarding effects of oxygen diffusion and mass transfer are included as are the intrinsic combustion kinetics. In the surge bin, rates of dolomite and calcite decomposition are calculated. A simple energy balance relates the extent of this decomposition to the temperature decrease in the bin. Wang et al. [29] utilized the FLASHCHAIN model to simulate the formation process of pyrolysis products considering the cluster chemical structure parameters in the oil shales determined by ^{13}C solid-state NMR. The model consists of four devolatilization reactions, namely bond-breaking reactions, spontaneous condensation reactions, bimolecular recombining and removal of peripheral functional groups, which can be used to simulate the pyrolysis process of oil shale, and provides theoretical support for the future development and comprehensive utilization of oil shale.

3.2 Simulation method

The above numerical calculation method have built different retort models for different types of reactors. Generally speaking, they all take into account the pyrolysis kinetics, heat transfer and mass transfer and other properties. However, these models involve reactor structure parameters, which are difficult to apply to different reactors. Moreover, they still include many characteristic equations with higher calculation difficulty, which can be simplified by the reactor model built in the chemical engineering process simulation software. Aspen Plus software, as large-scale chemical simulation

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software developed by the Massachusetts Institute of Technology, is a chemical engineering process modeling tool for steady state simulation, design, performance monitoring, optimization and business planning, and is used in the material and energy balance calculations. It can simulate a unit or the whole process by establishing an accurate model and using strict and scientific calculation method, so as to realize the optimization of the existing process conditions and the design and transformation of the process unit [30]. Based on the principle of mass and energy balance, Nguyen et al. [31] have attempted to model oil shale conversion processes using a combination of detailed process unit models and Aspen process flowsheeting. The model only integrates the key process, such as drying / preheating and pyrolysis of raw shale, combustion of shale char and sensible heat recovery of shale ash. Aspen in conjunction with detailed process unit models has been used to achieve mass and energy balances around the process. Performance data for individual process units were generated using detailed reactor models developed previously. The results show that this process modeling approach is very useful in assessing process schemes. The simulation procedure, which is complicated at this stage, will be greatly simplified once the data generated by the detailed process unit models have been transformed into performance equations which can be directly incorporated into ASPEN flowsheet models. Chen et al. [32] have developed a simple calculation model for a simple two-vessel fluidized-bed oil shale retorting process using Aspen process simulation software and economic evaluation system. In this process, fresh shale is pyrolyzed in a fluidized-bed retort, and the residual char on the shale is burned in a fluidized-bed combustor to provide process heat. Heat is transferred to the retort by recycled solids between the combustor and the retort. This paper is concerned with an evaluation of the overall energy balance and the impact of the decomposition of calcite ($CaCO_3$) minerals in the shale on the energy balance of such a retorting arrangement. Under some operating conditions, a large amount of carbonate decomposes, and the heat required for decomposition will affect the temperature distribution of the reactor. Bai et al. [33] simulated the low-temperature retorting process of Huadian oil shale under the Fischer assay experimental conditions by Aspen Plus, and compared the product yields obtained under the simulated and experimental conditions, which provided reference data for the comprehensive utilization of oil shale. Han et al. [34] have suggested a comprehensive utilization system of oil shale by combining fluidized bed retort with semicoke circulating fluidized bed boiler. Based on this system, a comprehensive process flow was developed and an optimization calculation was conducted to achieve mass and energy balance of the whole system by Aspen. The sensitivity of various operating parameters on the performance of the process was also discussed to optimize the comprehensive utilization system of oil shale. Wang et al. [35] also presented a novel comprehensive utilization system of Huadian oil shale involving retort subsystem, combustion subsystem, power generation subsystem and ash processing subsystem. Based on the principle of minimum Gibbs free energy obtained as system achieves equilibrium, the effects of different parameters on the comprehensive utilization system performance were investigated by using Aspen software. The simulation results provided a reference for developing the new comprehensive utilization technology of oil shale.

The above simulation is based on the minimum Gibbs free energy of the system in the thermodynamic equilibrium state to predict the amount of reactants and products in the equilibrium state of the chemical system. It is a thermodynamic model based on the thermodynamic equilibrium of the system, and has nothing to do with the structure of the reactor. In the calculation process, the kinetic parameters (reaction rate) of the chemical reaction and some unsatisfactory conditions are not considered. Simultaneously, it is not provided in the calculation that the reaction time for the reaction system achieving theoretical thermodynamic equilibrium state. The kinetic model can be introduced to study oil shale pyrolysis characteristics based on the thermodynamic equilibrium simulation in order to make the simulation process closer to the real pyrolysis process. At present, the simulation of oil shale pyrolysis kinetics in China is rarely reported, but the pyrolysis kinetics simulation has been applied to biomass pyrolysis. Yang et al. [36] have employed HSC chemistry for thermodynamic and Sandia PSR for kinetic simulations, considering the integrated effects of thermodynamic and kinetic phenomena occurring in biomass pyrolysis on the distribution of gaseous products. The

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principle of simulation applied was to extract substitutable gas phase compositions from HSC calculations, which were predicted thermodynamically. Then, the gas phase compositions were inputted into the Sandia PSR code to consider the potential constrains of kinetics involving in the pyrolysis and finally to get the distributions of gas products which should be closer the realistic situation. The combination of HSC and PSR is a powerful calculation tool for simulating biomass pyrolysis, and the evolution characteristics of gas products are well validated in conjunction with reactor structure characteristics. If the structural characteristics of oil shale are considered in the simulation, the simulation calculation will be closer to the real pyrolysis process. Ru [37] has used a variety of experimental characterization methods to study the kerogen molecular structure and physicochemical properties. The kerogen average molecular structural model was obtained by recombination of the selected fragments using Materials Studio simulation software. The correction and evaluation were carried out to make the established model be logical. This structural model can be viewed as a foundation for the theoretical study of kerogen. The microstructural parameters of the model (charge distribution, related bond length and bond order) were calculated by semi-empirical quantitative chemistry method. The forming process of pyrolysis products was speculated and this has a guiding significance on the research on oil and gas generation. Such information based on oil shale molecular structure can reflect the difference of samples.

4. Conclusions

In this paper, the research and development status of oil shale pyrolysis mechanism at home and abroad are introduced from the perspectives of pyrolysis kinetics and distribution characteristics of pyrolysis products. The pyrolysis kinetic characteristics of oil shale are closely related to the types of oil shale. The complexity of oil shale structure and composition leads to the diversification of oil shale pyrolysis kinetic models. The pyrolysis process of oil shale is complex, and it is affected by operating conditions and oil shale composition. In order to make the simulation method suitable for different pyrolysis reactors, it can be considered to introduce the kinetic model to study the pyrolysis characteristics of oil shale on the basis of thermodynamic equilibrium simulation, and also further used Molecular simulation software to study the pyrolysis characteristics of oil shale. However, many chain chemical reactions occur in the pyrolysis process of oil shale, and the reaction process is complex and staggered. The simulation calculation is also carried out under certain assumptions. Therefore, there are still many problems and difficulties in the study of pyrolysis mechanism of oil shale, and the detailed mechanism needs to be further explored.

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References

[1] Qian J.l., Wang J.Q., Li S.Y. Utilization and development trend of oil shale resources in the world. Journal of Jilin University (Earth Science Edition), 2006, 36(6):877-887. (in Chinese)

[2] Lin L.X., Lai D.G., Guo E.W., et al. Oil shale pyrolysis in indirectly heated fixed bed with metallic plates of heating enhancement. Fuel, 2016, 163:48-55.

[3] Gai R.H., Jin L.J., Zhang J.B., et al. Effect of inherent and additional pyrite on the pyrolysis behavior of oil Shale. Journal of Analytical and Applied Pyrolysis, 2014, 105:342-347.

[4] Williams P.T., Ahmad N. Investigation of oil-shale pyrolysis processing conditions using thermogravimetric analysis. Applied Energy, 2000, 66(2):113-133.

[5] Hillier J.L. and Fletcher T.H. Pyrolysis kinetics of a green river oil shale using a pressurized TGA. Energy & Fuels, 2011, 25(1):232-239.

[6] Jaber J.O., Probert S.D. Pyrolysis and gasification kinetics of Jordanian oil-shales. Applied Energy, 1999, 63(4): 269-286.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202107_7(7).0044

[7] Yan J.W., Jiang X.M., and Han X.X. Study on the characteristics of the oil shale and shale char mixture pyrolysis. Energy & Fuels, 2009, 23(12):5792-5797.

[8] Torels N., Veryklos X.E., and Grossmann E. Catalytic effects of transition metals on oil shale pyrolysis. Industrial and Engineering Chemistry, Process Design and Development, 1986, 25(2):552-557.

[9] Thakur D.S., Nuttall H.E.J. Kinetics of pyrolysis of Moroccan oil shale by thermogravimetry. Industrial & Engineering Chemistry Research, 1987, 26(7):1351-1356.

[10] Li S.Y., Yue C.T. Study of different kinetic models for oil shale pyrolysis. Fuel Processing Technology, 2003, 85(1):51-61.

[11] Charlesworth J.M. Oil Shale Pyrolysis. 2. Kinetics and Mechanism of Hydrocarbon Evolution. Industrial and Engineering Chemistry, Process Design and Development, 1985, 24(4):1125-1132.

[12] Weitkamp A.W. and Gutberlet L.C. Application of a microretort to problems in shale pyrolysis. Industrial and Engineering Chemistry, Process Design and Development, 1970, 9(3):386-395.

[13] Aboulkas A., El harfi K., Nadifiyine M., et al. Investigation on pyrolysis of Moroccan oil shale/plastic mixtures by thermogravimetric analysis. Fuel Processing Technology, 2008, 89(11):1000-1006.,

[14] Aboulkas A., El harfi K., El bouadili A. Kinetic and mechanism of Tarfaya (Morocco) oil shale and LDPE mixture pyrolysis. Journal of materials processing technology, 2008, 206(1-3):16-24.

[15] Al-Ayed O.S., Suliman M.R., Rahman N.A. inetic modeling of liquid generation from oil shale in fixed bed retort. Applied Energy, 2010, 87(7):2273-2277.,

[16] Al-Ayed O.S., Matouq M., Anbar Z., et al. Oil shale pyrolysis kinetics and variable activation energy principle. Applied Energy, 2010, 87(4):1269-1272.

[17] Han X.X., Jiang X.M., Cui Z.G. Studies of the effect of retorting factors on the yield of shale oil for a new comprehensive utilization technology of oil shale. Applied Energy, 2009, 86(11):2381-2385.

[18] Al-Harahsheh A., Al-Ayed O., Al-Harahsheh M., et al. Heating rate effect on fractional yield and composition of oil retorted from El-lajjun oil shale. Journal of Analytical and Applied Pyrolysis, 2010, 89(2):239-243.

[19] Wang S., Jiang X.M., Han X.X., et al. Effect of retorting temperature on product yield and characteristics of non-condensable gases and shale oil obtained by retorting Huadian oil shales. Fuel Processing Technology, 2014, (121):9-15.

[20] Na J.G., Im C.H., Chung S.H., et al. Effect of oil shale retorting temperature on shale oil yield and properties. Fuel, 2012, 95:131-135.

[21] Williams P.T., Ahmad N. Influence of process conditions on the pyrolysis of Pakistani oil shales. Fuel, 1999, 78(6):653-662.

[22] Wang Q., Sun B.Z., Hu A.J., et al. Pyrolysis characteristics of Huadian oil shales. Oil Shale, 2007, 24(2):147-157.

[23] Kök M.V., Pamir M.R. Comparative pyrolysis and combustion kinetics of oil shale. Journal of Analytical and Applied Pyrolysis, 2000, 55(2):185-194.

[24] Do D.D. Modelling of oil shale pyrolysis in a fluid-bed retort. Fuel Processing Technology, 1985, 10(1):57-76.

[25] Dung N.V., Duffy G.J. and Charlton B.G. Comparison between model predictions and performance of process development units for oil shale processing. Fuel, 1990. 69(9):1158-1163.

[26] Dung N.V. and Yip V. Basis of reactor design for retorting Australian oil shales. Fuel, 1991, 70(11):1336-1341.

[27] Diaz J.C., Braun R.L. Process simulation model for a staged,fluidized-bed oil-shale retort with lift-pipe combustor. Lawrence Livemore Nat. Lab., [Rep.] UCRL-53517, 1984.

[28] Camp D.W., Braun R.L. and Diaz J.C. Results of mathematical modeling of an oil shale retort having a fluidized-bed pyrolyzer and a lift-pipe combust. Fuel Processing Technology, 1989, 21(2):135-163.

[29] Wang Q., Ren L.G., Wang R.., et al. Characterization of oil shales by 13C-NMR and the simulation of pyrolysis by FLASHCHAIN. Journal of fuel chemistry and Technology, 2014, 42(3): 303-308. (in Chinese)

ISSN: 2414-1895 DOI: 10.6919/ICJE.202107_7(7).0044

[30] Xiong L.J., Zhang Z.C. Simulation of tar removal from biomass gas using Aspen Plus. Journal of Shandong University (Engineering Science), 2008, 38(6):95-98. (in Chinese)

[31] Dung N.V., Benito R.G. Modelling of oil shale retorting block using ASPEN process simulator. Fuel, 1990, 69(9):1113-1118.

[32] Chen C.C., floess J.K., Fong L., et al. Modeling of an oil-shale fluidized-bed retorting process using ASPEN. Energy Progress, 1982, 2(3):147-150.

[33] Bai J.R., Bai Z., Wang Q., et al. Process simulation for Huadian oil shale retorting system by Aspen Plus. Journal of CIESC, 2012, 32(3):85-88. (in Chinese)

[34] Han X.X., Niu M.T., Jiang X.M. Combined fluidized bed retorting and circulating fluidized bed combustion system of oil shale: 2. Energy and economic analysis. Energy, 2014, 74(2):788-794.

[35] Wang S., Jiang X.M., Han X.X., et al. Investigation of Chinese oil shale resources comprehensive utilization performance. Energy, 2012, 42(1):224-232.

[36] Lee D.H., Yang H.P., Yan R., et al. Prediction of gaseous products from biomass pyrolysis through combined kinetic and thermodynamic simulations. Fuel, 2007, 86(3):410-417.

[37] Ru X. Study on the experiment and molecular simulation of oil shale pyrolysis. Jilin University, 2013. (in Chinese)