



Full Length Article

Modeling study on effects of intraparticle mass transfer and secondary reactions on oil shale pyrolysis



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ABSTRACT

A comprehensive model accounting for intraparticle heat and mass transport phenomena, primary and secondary reaction processes was developed. Mass loss history, particle surface temperature history, and volatile product distribution of oil shale particles at different pyrolysis temperatures were favorably compared with experimental data. Particle size and reactor temperature would affect temperature and residue solid density distribution in oil shale particle. It was proved by the model that the increase of pore surface area in smaller oil shale particle may not be the main reason causing the decrease in oil yield and the increase in gas yield. Neglecting the variation of the residue solid density at different particle sizes, the model showed that with the increase of particle radius, the oil yield decreased and the gas yield increased. The effects of heating rate on the volatile product distribution might depend on intraparticle mass transport resistance.

1. Introduction

Oil shale, one of the most promising energy resources, has gained much attentions with conventional fossil fuels decreasing [1]. Oil shale is employed to yield shale oil through pyrolysis process because of its high organic matter content in some countries [2]. For the optimal design and operation of chemical reactors, it is quite useful to understand how product distribution depends on oil shale properties and pyrolysis process conditions.

During the pyrolysis process, oil shale will be heated to a certain temperature, meanwhile the organic matter within oil shale, which is called the kerogen, will decompose to shale oil (defined as the condensable hydrocarbons and other organic compounds escaping from oil shale particle), shale gas (defined as the noncondensable vapors escaping from oil shale particle) and coke (defined as the benzene-insoluble portion of the kerogen remaining in the spent shale). The decomposed products of kerogen may also react with each other and solid residue when they releases out of oil shale particle, modifying the final volatile product (shale oil and shale gas) distribution of oil shale pyrolysis [3]. In addition, there exists internal temperature gradients, non-uniform temperature distribution, within oil shale particle in the industrial rotating drum and vertical cylindrical retorts [4,5]. The role of heat and mass transfer in the pyrolysis process has been highlighted by Weitkamp and Gutberlet [6]. They suggested that the pyrolysis process may be a diffusion limited process controlled by heat and product

diffusion. The various process parameters have been investigated, such as reactor temperature [7–17], heating rate [13,18], oil shale particle size [10,15,19,20], residence time [15] and atmosphere [17,21].

However, there is some disagreement in the literature regarding the effect of particle size on the oil yield from oil shale. Wallman [22], Rubel [23], and Mclendon [20] found higher oil yields for smaller oil shale particles compared to larger oil shale particles. But other researchers showed that there was a decrease in oil yield for smaller oil shale particles, such as Sohn [24] and Coburn [25]. In addition, Campbell [26] showed that there were no significant effects of particle size on oil yield for a range of sizes in their experiments.

In order to better understand oil shale pyrolysis process, some mathematical models on oil shale particle pyrolysis were developed in last decades. Granoff et al. [27] developed a non-isothermal shrinking-core model considering the kinetics of oil shale pyrolysis and heat transfer effects, which could describe the observed pyrolysis process well at high temperature. Shih and Sohn [4] developed a model incorporating the intrinsic kinetics of the decomposition of kerogen and carbonate minerals, and the internal as well as external heat-transfer effects, which described the pyrolysis of oil shale more accurately than the shrinking-core model or the uniform-temperature model. Han et al. [28] developed a thin rectangle heat transfer model incorporating the pyrolytic heat as an internal heat sink, to analyze the thermal behavior within oil shale particle in pyrolysis process, which predicted the central temperature history and heating time of oil shale particles of

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different sizes. Gerasimov and Volkov [5] developed an elaborated model of pyrolysis reactor including motion of bulk solids in reactor, heat transfer between heat carrier and fuel, thermal decomposition of kerogen and the secondary chemical reactions, to give good prediction on the shale oil yield in industrial pyrolysis reactor.

However, most mathematical models were limited to one-step reaction mechanisms and assigned proportions of different volatile products empirically, without considering volatile product distribution. And few models take account of the secondary reactions of primary pyrolysis volatile products, which occurs when primary ones are releasing out of oil shale particles. So most mathematical models of oil shale particle pyrolysis cannot predict the pyrolysis volatile product distribution well under various operating conditions. Furthermore, few mathematical models can reflect the effects of particle size on the volatile product distribution.

In this study, a comprehensive model of oil shale particle pyrolysis was developed, including a kinetic model taking account of the secondary reactions, heat and mass transfer processes within oil shale particle. And this model was validated by comparing model predictions with experimental data in literatures. This model predicted mass loss history, particle surface temperature history of oil shale particle and pyrolysis volatile product distribution well, providing a further understanding on effects of intraparticle heat and mass transfer on the volatile product distribution. The effects of particle size on the volatile product distribution were investigated by this model.

2. Mathematical model

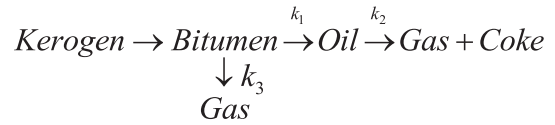
2.1. Model assumptions

In this study, the spherical oil shale particle is in inert and high temperature environment. The one-dimensional reacting medium is modeled as a solid matrix, where the void volume, formed by pores, is initially filled by an inert gas. With the temperature increasing to a certain extent, a solid residue is formed, and volatile species are produced and then transported out of the particle. In addition, the following assumptions are made in the modeling of oil shale particle pyrolysis process:

- (1) Solid matrix and gaseous species are locally in thermal equilibrium.
- (2) No particle shrinkage, swelling or breakage occurs in the pyrolysis reactions.
- (3) Enthalpy flux due to gaseous species convection and diffusion is ignored.
- (4) Body forces of all species are ignored.
- (5) No secondary reactions occur outside of the particle due to dilution by inert atmosphere.

2.2. Kinetic model

In order to predict the volatile product distribution of oil shale in the pyrolysis process well, the pyrolysis reaction mechanism had to be coupled with intraparticle heat and mass transfer. However, due to the one-step global reaction mechanism [29–36], most existing kinetic models of oil shale pyrolysis were not suitable for this study. The main disadvantages of these kinetic models were that they do not classify volatile products, or estimate a constant ratio of each species to the total yield [37–40]. Only a few models took account of the secondary reactions of the primary volatile products [5,41,42]. Thus, most kinetic models could not predict effects of pyrolysis conditions, such as reactor temperature, heating rate and particle size, on the volatile product distribution. In this study, pyrolysis reaction was described based on the kinetic model proposed by Volkov and et al. [41], in which the species in volatile products were simplified, and kinetic parameters were adjusted based on the properties of oil shale investigated:



where k_1 is the decomposition rate constant of bitumen into oil, k_2 is the decomposition rate constant of coke, and k_3 is the decomposition rate constant of bitumen into gas. In this kinetic model, it was assumed that the kerogen transformed into a plastic state, defined as the bitumen, as soon as pyrolysis reaction takes place. Upon additional heating, further decomposition of the bitumen formed oil and gas. Oil would also decompose into gas and coke in the intraparticle pores when transported out of the oil shale particle, which described the secondary reactions. Decomposition of all species was assumed as individual first-order chemical process.

2.3. Mathematical formulation

The core of this model was that the heat and mass transfer are coupled with the kinetic model, which took account of the secondary reactions, to predict volatile product distribution within a spherical oil shale particle.

Assuming that primary reaction rate is proportional to the mass of unreacted kerogen, mass balance for kerogen (K) (bitumen) was written as the following:

$$\frac{\partial \rho_K}{\partial t} = -(k_1 + k_3)\rho_K \quad (1)$$

where ρ_K is the density of kerogen, t is the reaction time. In the calculation, the mass fraction of kerogen was assigned to the total mass loss of oil shale particles after pyrolysis.

It was assumed that gaseous species could be transported by advection and diffusion through the intraparticle pores. Darcy's law, which expressed the conversation of momentum, was included to describe velocity and pressure profiles of gaseous species within the particle. Neglecting the contribution of the inert atmosphere initially presented within the particle, the conservation equation for gaseous species, including oil and gas, could be written as the following:

$$\frac{\partial(\varepsilon\rho_V)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r}(r^2\varepsilon\rho_V U) = \omega_V^m \quad (2)$$

$$\omega_V^m = (k_1 + k_3)\rho_K - (1-\alpha)k_2\rho_V Y_O \quad (3)$$

$$U = -\frac{K}{\mu} \frac{\partial p}{\partial r} \quad (4)$$

$$p = \frac{\rho_V RT}{MW} \quad (5)$$

where ε is the porosity of oil shale particle, ρ_V is the density of the total gaseous species including oil and gas, U is the convective velocity of the gaseous species, ω_V^m is the net generation rate of gaseous species, $\alpha = k_{2,gas}/(k_{2,gas} + k_{2,coke}) = 0.4$, the Y_O is the mass fraction of oil, K is the permeability of oil shale particle, μ is the viscosity of gaseous species, p is the pressure of gaseous species, R is the universal gas constant, MW is the mean molecular weight of the gaseous species.

Considering the advection and diffusion of oil within the particle, the transport of oil could be written as the following:

$$\frac{\partial(\varepsilon\rho_V Y_O)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r}(r^2\varepsilon\rho_V U Y_O) = \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2\varepsilon\rho_V D_{e,o} \frac{\partial Y_O}{\partial r}\right) + \omega_o^m \quad (6)$$

$$\frac{\partial(\varepsilon\rho_V Y_g)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r}(r^2\varepsilon\rho_V U Y_g) = \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2\varepsilon\rho_V D_{e,g} \frac{\partial Y_g}{\partial r}\right) + \omega_g^m \quad (7)$$

$$\omega_o^m = k_1\rho_K - k_2\rho_V Y_O \quad (8)$$

$$\omega_g^m = k_3\rho_K + \alpha k_2\rho_V Y_O \quad (9)$$

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