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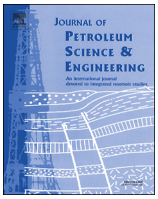

The kinetic modeling of the non-isothermal pyrolysis of Brazilian oil shale: Application of the Weibull probability mixture model

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ABSTRACT

The detailed kinetic analysis of the non-isothermal pyrolysis of Brazilian oil shale was carried out using thermogravimetric analysis (TGA) and the derivative thermogravimetry (DTG). The investigated process was modeled using a statistical Weibull 2-component mixture model. By using different kinetic methods, it was found that the investigated process is very complex. Application of the differential and the integral isoconversional methods showed that the pyrolysis of Brazilian oil shale takes place through three reaction steps. It was found, that the third reaction step of the investigated pyrolysis process cannot be modeled by the simple first order reaction kinetics. It was established that the third reaction step can be described with the n-th order ($n \neq 1$) kinetics, including $f(\alpha)=(1-\alpha)^{1.23}$ mechanism function. The kinetic compensation effect (KCE) was identified for observed oil shale pyrolysis. Based on the behavior of the shape parameter (θ) in complex statistical model under the consideration, it was determined that no change in the rate-limiting step occurs for the investigated pyrolysis process.

1. Introduction

World reserves of conventional fossil fuels such as petroleum, natural gas and coal are finite. The supply of energy has become a worldwide problem in recent decades. Many countries have attempted to diversify their potential energy sources in order to cope with oil price increases and their effect on the economy. So, there are a plenty of researches into alternative sources of conventional fossil fuels. Oil shale represents an enormous potential as a substitute. Oil shales are broadly defined as petroleum source rocks containing sufficiently high contents of organic matter to make utilization a possibility. Like coal, the world's resources of oil shales are vast, being many times larger than those proven for crude oil (Sari and Aliyev, 2006). Oil shale utilization has attracted renewed attention as a source of transport fuels and chemical feed stocks due to the long-term uncertainties over crude oil supplies.

The thermal decomposition of oil shale is the only recommended way to obtain liquid oil from the insoluble organic matter (kerogen). Kerogen in oil shale is such a complicated heterogeneous mixture of organic compounds (Kamali and Mirshady, 2004) that the pyrolysis kinetics studied is undoubtedly a sum of many different reactions that give the oil product. For the energy potential of oil shale to be maximized, the conversion processes of oil shale to the oil should be studied varying conditions of the process, such as the heating rate, final temperature and the particle size, for obtaining the optimal ones (Shen et al., 1991; Ahmad and Williams, 1998; Nazzal, 2008). It is necessary to study the mechanism of pyrolysis and to determine the rate of decomposition. In order to predict the course of thermal decomposition of oil shale, the accurate kinetic triplet (the kinetic parameters, the apparent activation energy (E_a) and the pre-exponential factor (A)) and function of reaction mechanism ($f(\alpha)$) of decomposition is required. Several key investigations have been carried out on the kinetics of kerogen decomposition in oil shales (Hubbard and Robinson, 1950; Allred, 1966; Braun and Rothman, 1975; Campbell et al., 1978; Nazzal, 2002; Li and Yue, 2003; Aboulkas and El Harfi, 2009; Al-Ayed et al., 2010). Applying the isothermal conditions, Hubbard and Robinson (1950) used the mechanism of two-step first order reactions to describe the decomposition of kerogen to bitumen and subsequently to the oil. Braun and Rothman (1975) showed that the oil production kinetics could be explained more accurately by taking into account, an initial thermal induction period. The apparent activation energies and the pre-exponential factors for each step of the proposed two-step reaction mechanism were obtained. The kinetic characteristics in pyrolysis process of Huadian oil shale's using the isoconversional method were investigated by Wang et al. (2007). They have found that the decomposition process of Huadian oil shale involves three stages. The results were shown that the apparent activation energy is not a constant throughout the reaction process, but in the conversion (α) range of 0.1–0.9, the apparent activation energy changes slightly. The authors have used the Šesták–Berggren complex kinetic mechanism for modeling the

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Nomenclature

E_a	the apparent activation energy (kJ mol^{-1})
A	the pre-exponential factor (min^{-1})
n	the reaction order
R	the universal gas constant (8.314 J K^{-1} mol^{-1})
T	the absolute temperature (K)
T_p	the peak temperature (°C)
β	the linear heating rate (°C min^{-1})
x	the reduced apparent activation energy
$\pi(x)$	the analytical expression for the temperature integral
X	the random variable
w_i	the relative abundance of the i-th component
$f(T,\psi)$	the three-parameter Weibull density function
θ	the shape parameter
η	the scale parameter (min)
T_o	the location parameter (°C)
$f(T,\zeta)$	the probability density function of the mixture distribution model
$F(T,\zeta)$	the cumulative distribution function of the mixture distribution model
Δt_{FWHM}	the full width at half maximum of the peak on the conversion rate curve
T_{iso}	the isokinetic temperature (°C)

Acronyms

SI	the shape index
ROn	the reaction order model
TGA	thermogravimetric analysis
DTA	differential thermal analysis
DTG	derivative thermogravimetry
IKR	the isokinetic relationship
KCE	the kinetic compensation effect

process, where the results showed that oil shale pyrolysis is not a simple first order reaction. The considered pyrolytic mechanism is complex and mainly attributes to the nuclear mechanism (Wang et al., 2007).

In addition, Khraisha (1998) studied the isothermal decomposition of Jordanian oil shales. The studied process was described by two consecutive first order reactions, and the corresponding apparent activation energies were calculated for each step. Namely, a global first order rate expression is assumed for the simplicity's case. For this reason, the apparent activation energy and the pre-exponential factor are the only "representative" kinetic values for a complicated reaction system.

Furthermore, many researchers have employed the non-isothermal thermogravimetric (TG) technique to study oil shale pyrolysis (Karabakan and Yürüm, 1998; Jaber and Probert, 2000; Al-Harahsheh et al., 2011; Syed et al., 2011). It can be pointed out that the non-isothermal pyrolysis offers certain advantages over the classical isothermal method (Lee, 1991). First, this analysis eliminates the errors caused by the thermal induction period, and second, it permits a rapid scan of the whole temperature range of interest. These facts have proved to be very important in cases considering the kinetics of biomass pyrolysis reactions (Van de Velden et al., 2008, 2010), pyrolysis of waste plastics (Brems et al., 2011) and tyres (ELTs) (Al-Salem et al., 2009).

The exploitation of oil shales represents, for many countries, a valuable potential source of liquid hydrocarbons and energy. For the energy potential of oil shale to be maximized, the conversion process of the oil shale to oil should be undertaken under optimal process conditions. A range of process conditions have been investigated in the pyrolysis of oil shale to ensure the maximum and efficient extraction of the oil. The parameters identified as being of most significance are heating rate and the range of pyrolysis temperatures (Kök, 2006). In order to predict the thermal degradation of oil shale, the accurate values of the kinetic parameters over the entire range of decomposition temperature are required. There appears a range of values of the kinetic parameters pertaining to oil shale decomposition.

Generally, the pyrolysis process is very important for the shale oil extraction. This process converts kerogen in oil shale into shale oil by pyrolysis, hydrogenation, or the thermal dissolution (TD) (TD represents a hydrogen-donor solvent refining process; it can be used for the shale oil extraction and coal liquefaction) (Gorlov, 2007; Vázquez-nava and Lawrence, 2009; Patrakov et al., 2011; Shui et al., 2013). The resultant shale oil is used as fuel oil or upgraded to meet refinery feedstock specifications by adding hydrogen and removing sulfur and nitrogen impurities. As of 2010, major long-standing extraction industries are operating in Estonia, Brazil, and China. Its economic viability usually requires a lack of locally available crude oil (Kök, 2006). National energy security issues have also played a role in its development. Critics of shale oil extraction pose questions about environmental management issues, such as waste disposal, extensive water use, waste water management, and air pollution.

The aim of this study was to investigate the effects of heating rate (β) on the Brazilian oil shale pyrolysis, and also carry out a detailed kinetic analysis, together with the derived mechanistic conclusions. In this article, mass loss/derivative mass loss (TG/DTG) data have been used for the estimation of reliable kinetic triplet, for the investigated pyrolysis process. The obtained values of kinetic parameters can be useful from the petroluem engineering standpoint of the oil shale retorting and can be used in a mathematical modeling of the considered process. Based on the complexity of investigated process, the Weibull mixture model (Cai and Liu, 2008; Cai and Chen, 2009; Janković et al., 2010) originated from statistical foundations was applied for the mathematical modeling of the differential conversion (rate) curves in the case of the Brazilian oil shale pyrolysis.

2. Experimental

2.1. Materials

The oil shale used in the present study originated from Geopark Paleoroute, located in the center of the Brazilian state of Rio Grande do Sul. Chemical analysis of the oil shale is given in Table 1. The samples were crushed and sieved to pass through a 200 mesh screen, where they obtained the particles with the mean particle size of D_p=0.075 mm. With mesh size no. 200, a good particle formulation can be evaluated in the manner of the very fine description terms (ASTM-E11, 1973). All samples were used without further treatment.

2.2. Thermogravimetric (TG) measurements

A thermogravimetric analyzer (TA Instruments SDT 2960 device capable for the simultaneous TGA–DTA analysis) was used to study the pyrolysis of Brazilian oil shale. Thermogravimetric analyzer was used to obtain the mass-loss data as a function of temperature (non-isothermal heating curves). A known mass of the sample