



Full Length Article

Thermal oxidation study of Moroccan oil shale: A new approach to non-isothermal kinetics based on deconvolution procedure



Ely Cheikh Moine, Mariam Tangarfa, Mariam Khachani, Adnane El Hamidi, Mohammed Halim, Said Arsalane*

Laboratory of Materials, Catalysis and Environment (CNRST-URAC 26), University of Mohammed V, Faculty of Sciences, Avenue Ibn Battouta, BP: 1014, 10000 Rabat, Morocco

HIGHLIGHTS

- Kinetics of complex oxidation behavior of Moroccan oil shale was investigated.
- Multi-stage parallel reaction approach was used to model organic matter oxidation.
- The Fraser–Suzuki algorithm allowed a separation of two independent processes.
- The first and second process followed RO(n) model with $n > 1$ using Model Free.
- The first process is more energetic due to the composition of organic matter.

ARTICLE INFO

Article history:

Received 26 May 2015

Received in revised form 15 April 2016

Accepted 19 April 2016

Available online 22 April 2016

Keywords:

Timahdit oil shale

Oxidation kinetics

Non-isothermal analysis

Peak-deconvolution

ABSTRACT

In this paper, we have employed multi-stage parallel reaction approach and Fraser–Suzuki distribution method to fit the non-isothermal TG/DTG curves resulting from oxidation of Moroccan Timahdit (X-layer) oil shale. The kinetic study was conducted to overcome the insufficiencies of the previous works, which oversimplified the oxidation processing having complex behaviors. The differential curves (DTG) of thermal oxidation of Timahdit organic matter were separated into two independent reactions. Based on the results of the deconvolution method, the kinetic mechanism was obtained using Malek's procedure, followed by the determination of the apparent activation energy E_x using isoconversional model free methods of Friedman, Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS). The obtained values of E_x show that the first oxidation process is more energetic than the second. This behavior is correlated to nature of organic matter including in Timahdit oil shale. The kinetic modeling results for each individual peak showed that the thermal oxidation process is controlled by n th order reaction mechanism with $n > 1$, unlike to simple first order mechanism predicted by fitting methods.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Oil shale is an organic-rich, carbonaceous fine-grained sedimentary rock containing significant portions of kerogen and small amounts of bitumen, linked dispersedly within a mineral matrix [1]. It can be converted upon pyrolysis into solid coke, liquid and gaseous hydrocarbon compounds or burned directly as a low-grade fuel for power generation and heating purposes. The world's resources of oil shale are vast and represent an enormous potential larger than proven for conventional crude oil [2]. The use of oil shale as alternative fuel source and the development of unconventional oil production technology constitute the great challenges to

meet the growing global energy demands in the short and medium term.

The thermo-oxidation analysis represents one of convenient way to investigate the kinetic parameters of oil shale and optimize the conversion process. Several thermal oxidation kinetics of various oil shale, from different regions of the world, by means of isothermal and non-isothermal conditions have been conducted by using Thermogravimetric/Derivative Thermogravimetric analysis (TG/DTG) [3,4], Differential Thermal Analysis (DTA) [5,6] and Differential Scanning Calorimetry (DSC) [7,8]. However, due to heterogeneous composition and complicated nature of kerogen, consisting of organic macromolecules with three-dimensional structure and which is insoluble in usual solvent [9], the oxidation processing of oil shale, as pyrolysis is considered one of the complex processes which involve a series of reactive parallel reactions

* Corresponding author.

E-mail address: Pr.saidarsalane@gmail.com (S. Arsalane).

[10,11]. Most of the thermo-oxidation studies of oil shale reported in the literature show the presence of overlapping peaks in TG/DTG curves characterized by a complex behavior [12,13]. On the basis of simplifying assumptions, different kinetics models, consisting of model fitting methods with simple first order or n th order reactions are mostly used to fit the kinetic results [14–17]. The model fitting methods could lead, especially for complicated reactions, to the uncertainty in estimating the activation energy which primarily originates from the uncertainty of choosing the reaction models; hence the applicability of fitting methods to raw data curves for such materials is not appropriate. Therefore, it becomes required to deepen studies on the oxidation complex processes of oil shale using other mathematical approaches for kinetics data processing.

In solid-state reactions which involve several overlapping processes, the International Confederation for Thermal Analysis and Calorimetry (ICTAC) committee recommended that it is better to separate the observed multi-steps entirely and analyze their kinetic individually [18]. The separation method constitutes an interesting alternative for the kinetic analysis of complex processes. It consists of a peak deconvolution from the overall derivative thermogravimetric (DTG) curves, using statistical functions to gain insights into reaction mechanisms and for a complete kinetic description. Different deconvolution functions have been proposed for the separation of the individual processes in thermal analysis of oil shale, the Lorentz and Gauss distributions and their logistic mixture models [19–21] being the most popular because the experimental DTG curves and those reconstructed from these functions are practically similar. Other alternative functions such as Weibull and Fraser–Suzuki models have been also used, mainly for fitting the asymmetrical behaviors [22–24]. But these studies remain scarce and limited only to a few recent oil shale investigations.

The objective of the present paper is to undertake the investigation of the thermal oxidative behavior of Timahdit oil shale from Morocco. A new procedure based on the multi-peak fitting methods, taking into account the properties of thermograms, has been applied to separate the overlapping processes. Due to the asymmetric nature and properties of DTG curves, the Fraser–Suzuki function was selected to better fit the oil shale oxidation processes. The activation energy for each discrete stage was estimated by Friedman, Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) isoconversional methods and the most probable models describing the observed processes were rightly established using Malek's procedure without any assumption about the reaction model function. The procedures and methods presented herein could be extended to numerous energetic materials presenting similar kinetic behaviors.

2. Material and methods

2.1. Materials

The shales used in this study were obtained from the Timahdit deposit, which is located in the Middle Atlas Mountains of Central Morocco. The Timahdit oil shale deposit is one of three major Moroccan deposits, consisting of four layers containing variable amounts of organic matter, named T, Y, X and M and mineral matrix constituted essentially by carbonates. Several geochemical and physicochemical characterizations have previously been carried out on Timahdit oil shale [25,26]. Here, the thermal oxidation kinetic study is focused on X-layer of Timahdit oil shale. The thermo-chemical composition of oil shale samples is given in Table 1. According to ASTM standard (E11) and ICTAC recommendations, the samples were crushed and sieved to less than 80

Table 1
Mineralogical characteristic of Moroccan Timahdit oil shale.

Composition (%)	Martins et al. [27]	Sadiki et al. [28]	This work (X-layer)
Kerogen	21.9	24.1	17
Carbonate minerals	34.6	35.5	38
Inert matter	43.5	40.5	45

meshes in average particle diameter to reduce the effects of heat and mass transfers during kinetic studies and finally kept in a desiccator for further use.

2.2. Thermal analysis

The simultaneous TG/DTG/DTA analyses were carried out using a Labsys TM Evo (1F) Setaram apparatus. ICTAC kinetics committee recommendations for collecting experimental data [29] and performing kinetics computations [18] were followed to evaluate the kinetic parameters. Before experiments, the thermal analysis system was firstly calibrated for temperature reading with copper sulfate pentahydrate. It was essential to calibrate and balance for buoyancy effects to allow quantitative estimation of weight changes. The materials chosen for investigating such effect were silver and gold, which have the melting points of 960.8 °C and 1064 °C respectively. The experiments were conducted under non-isothermal conditions in air flow atmosphere of 40 ml min⁻¹ from room temperature up to 900 °C, at various heating rates (2.5, 5, 10 and 15 °C min⁻¹). Before tests, the samples were placed in an oven at 100 °C for 2 h to remove the adsorbed moisture. The measurements were repeated three times in order to ensure the reproducibility. An initial mass of sample; about 10.0 ± 0.2 mg; was placed in an alumina pan. The sample was well dispersed with negligible depth to minimize heat and mass transfers.

3. Kinetic studies

3.1. Activation energy

The rate of a solid-state reaction can be generally described by:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad \text{ou} \quad \frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where $d\alpha/dt$ is the conversion rate of reaction. k is the rate constant that obeys the Arrhenius correlation ($k = A \cdot \exp(-E/RT)$). $f(\alpha)$ is the kinetic model function, as can be seen in Table 3. A is the pre-exponent factor (min⁻¹), and E is the activation energy (kJ mol⁻¹). β is the heating rate (dT/dt) expressed by (°C min⁻¹). R is the universal gas constant (8.314 J mol⁻¹ K⁻¹). T is the reaction temperature (K) and α is the conversion fraction of solid.

The dependence of the apparent activation energy E_x on the reacted fraction α can be determined from isoconversional methods without any assumption about kinetic reaction model $f(\alpha)$. The advantage of these methods is they are able to predict the most complicated reaction even at a different range of temperature provided that the mechanism of reaction does not change with temperature and heating rate. Combined with multi heating rate model free method, the general kinetic equation (Eq. (1)) can be rearranged to allow the calculation of kinetic parameters. Table 2 includes the different equations of kinetic models applied in this study. At a constant value of α and for different heating rates, the activation energy (E_x) is determined from the slope of different plots of Y versus X .

The differential equation proposed by Friedman is one of the most extensively used isoconversional method that provides accu-

Download English Version:

<https://daneshyari.com/en/article/6633829>

Download Persian Version:

<https://daneshyari.com/article/6633829>

[Daneshyari.com](https://daneshyari.com)