Kinetics of thermal decomposition of phospholipids obtained from phosphate rock

Jale Naktiyok *, Hatice Bayrakçeken, A. Kadir Özer, M. Şahin Gülaboğlu

Department of Chemical Engineering, Atatürk University, 25240 Erzurum, Turkey

ABSTRACT

The soluble organic matter in the phosphate rock was extracted with n-hexane. Its structure was analyzed by using ^{1}H NMR, ^{13}C NMR and FTIR. ^{1}H NMR and ^{13}C NMR studies indicated that it has rather aliphatic nature. FTIR results showed that the bands obtained from organic matter exhibit a phospholipids characteristic. The kinetics of thermal decomposition of phospholipids obtained from phosphate rock was studied by means of thermal analysis techniques (TG/DTG) in nitrogen atmosphere at heating rates of 2.5, 5, 10, and 20 K min^{-1}. TG and DTG measurements indicated that thermal behavior of phospholipids has two-stage degradation. Kinetic parameters were determined from the TG and DTG curves for the stages I and II by using two model-free methods, i.e. Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose. The kinetic triplets consisting of E_a, A and $g(\alpha)$ models of the materials were determined. The average activation energies (E_a) obtained from both models for the decomposition of phospholipids are 64.15 kJ/mol and 122.3 kJ/mol and the pre-exponential factors ln(A) were 15.8 and 20.4 for stages I and II, respectively. The decomposition of phospholipids proceeds by two-dimensional diffusion (D_2) for stage I, followed by three-dimensional diffusion (D_5) for stage II.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Phosphate rocks are used in large quantities in agricultural and other industries. Phosphate rock is composed mainly of calcium phosphate and silica, iron and aluminum oxide, organic matters, carbonates, and clayey matter as impurities [1]. The phosphate rocks consist of complex organic material which is finely distributed in an inorganic matrix [2]. This organic matter releases volatile compounds that are harmful to the environment and lead to the formation of foam that complicate the process of filtering in the phosphoric acid production, known as wet process. In order to minimize all these problems, the phosphate rock is calcined around 700 °C before its commercialization [3].

Organic matter within phosphate rocks is divided into two operational fractions: 1) The bitumen (free lipids) can be directly extracted from the phosphate rock with an organic solvent and is routinely analyzed for biomarkers in petroleum geochemistry, 2) Kerogen (bound lipids) is extractable only after acid destruction of the mineral matter and usually disregarded in biomarker studies due to analytical difficulties [4,5].

Lipid biomarkers are fossil biochemical detected in the geological record whose basic skeletal features have been sufficiently well-preserved to allow unambiguous links to known, contemporary natural product precursors. Biomarkers can give valuable information about the source of the organisms, the thermal maturity of the host organic

matter and the paleoenvironmental conditions at the sediment surface which prevailed during deposition. The most useful biomarker molecules (lipids) are those that are thermodynamically stable, with a limited number of well-defined biological sources [6]. The lipid compounds often contain the basic skeletal structure and functional group details of the original source [7]. Therefore, the investigation of lipid compositions in various recent depositional environments can provide much information about the source and diagnetic processes of organic matter [8,9].

We are aimed to observe the thermal decomposition of the lipid biomarkers obtained from phosphate rock at higher temperatures with TGA method. The TG–DTG analysis of the lipid biomarkers offers the possibility of correlating the kinetic parameters of non-isothermal degradation. There are different methods to analyze the non-isothermal kinetic data from TGA. According to the mathematical model, there are two possible approaches: model-fitting and model-free (isoconversional) methods [10–16]. Model fitting methods use different models in order to choose a model that provides the best statistical approximation during the calculation of the kinetic parameters. Model-free, non-isothermal methods require several kinetic curves to perform the analysis. Calculations from several curves at different heating rates are performed on the same value of conversion, which allows calculating the activation energy for each conversion point. The advantage of the model-free analysis is found on its simplicity and on the avoidance of errors connected with the choice of a kinetic model [17]. In non-isothermal kinetics (model-free analysis), Kissinger–Akahira–Sunose (KAS) [18,19], Flynn–Wall–Ozawa (FWO) [20,21] methods are the most popular

---

representatives of the isoconversional methods. Several studies have shown that non-isothermal thermogravimetry (TG) is a powerful tool for characterizing the thermal behavior of polymers, different materials and various types of biomass [22–26].

The thermal analysis of phospholipids was mostly given with DSC and there are fewer studies with DTA in the literature. The phase transition at the phospholipids is quite rapid and this process must be recorded at moderate scan rates by using DSC [27].

In the present paper, the structure of phospholipids obtained from phosphate rock was analyzed by using ^{1}H NMR, ^{13}C NMR and FTIR techniques and the decomposition kinetics was investigated by using the TGA apparatus at different heating rates and the activation energy (Ea) is calculated by non-isothermal and isoconversional methods. KAS and FWO are used to evaluate the value of Ea at different values of α. The kinetic parameters determined by both models were compared and the mechanisms for the decomposition reactions were predicted by the method suggested by Ortega [28].

2. Material and methods

2.1. Preparation of samples

Phosphate rock used in this study was provided from the Mazıdağı phosphate deposits. The sample was crushed, ground and then sieved to obtain a fraction of 100 μm. A detailed mineralogical study on the phosphate rock can be found elsewhere [29].

100 g of dried phosphate sample having particle sizes of 100 μm was extracted with *n*-hexane in Soxhlet for 48 h. After the extraction, the extract was distilled on the Rotavapor to remove *n*-hexane. Then, the organic matter obtained was dried and its structure was analyzed by using FTIR and ^{1}H NMR and ^{13}C NMR.

2.2. Analysis

The ^{1}H NMR spectra were recorded on an advance 200 MHz Varian NMR spectrometer. The chemical shifts are given with respect to tetramethyllesilane (TMS) taken as an internal reference.

Solid state ^{13}C NMR spectra of the organic matter were obtained with a Varian spectrometer operating at 50 MHz and equipped with cross-polarization and magic angle spinning (CPMAS). The chemical shifts were calibrated with respect to tetramethyllesilane (TMS).

FTIR spectra of the organic matter were recorded in the range of 4000–400 cm^{-1} on a Perkin Elmer spectrometer.

The experiments were performed using thermogravimetric analyzer NETZSCH STA 409 PC Luxx of which the balance and temperature control system can accurately record weight loss of 0.001 mg and temperature of 0.1 K to characterize the thermal decomposition of organic matter obtained from the extraction. A given amount of sample (approximately 15–20 mg) was put into a platinum crucible. The calcined α-Al$_2$O$_3$ powder as the standard reference was used. The experiments were carried out in the temperature ranges of 298–873 K at 2.5, 5, 10, 20 K min^{-1} heating rates in nitrogen atmosphere as the purge gas and repeatable results were obtained. The data obtained from TG–DTG curves were used to analyze the decomposition kinetics.

2.3. Theoretical models

The main idea of the data processing strategy was to use the simplest, but commonly used methods, of course by taking into account the ICTAC-2000 Protocol [12]. The "model free" methods were preferred, in both differential and integral variants. These methods allow the evaluation of Arrhenius parameters without choosing the reaction model. An important step in the kinetic analysis is the knowledge of the dependence of activation energy, E, versus the conversion

degree, α. This allows the detection of multistep processes and gives information about the reaction mechanism.

In thermogravimetric measurements, the degree of decomposition (conversion) can be calculated as follows:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} \tag{1}$$

where, α is extent of decomposition; W_0, W_t, and W_∞ are the initial, actual, and final mass of the sample, respectively.

The rate of reaction of a substance is usually expressed as

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

where α represents the fraction of substance reacted at time t, f(α) is a function depending on the reaction mechanism, and k is the specific rate constant given by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where A is the pre-exponential factor in min^{-1}, E is the activation energy (kJ/mol), R is the universal gas constant (J/mol/K), and T is the absolute temperature (K). For a non-isothermal system, a constant heating rate β is applied where

$$\frac{dT}{dt} = \beta \tag{4}$$

From Eq. (2), we get

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dT}\right) \cdot \left(\frac{dT}{dt}\right) = kf(\alpha) \tag{5}$$

Substituting value of dT/dt from Eq. (4) and the value of K from Eq. (3) into Eq. (5) and rearranging, we get

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) \cdot dT \tag{6}$$

Ordinarily, at low temperatures, the rate of the reaction is assumed to be low enough to be neglected, and thus the left and right-hand sides of Eq. (6) may be integrated from 0 to α and from 0 to T:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \int_0^T \exp\left(-\frac{E}{RT}\right) dT \tag{7}$$

where $g(\alpha)$ is a new function and $\int_0^T \exp\left(-\frac{E}{RT}\right) dT$ on the right-hand side of Eq. (7) is called the temperature integral, which does not have an analytical solution.

If it is assumed that x = E/RT, then $\int_0^T \exp\left(-\frac{E}{RT}\right) dT$ reduces to $\frac{E}{R}\int_x^\infty \frac{e^{-x}}{x^2} dx = \left(\frac{E}{R}\right)P(x)$ where $P(x)$ is an infinite function of x. Hence, substituting the values of temperature integral ($P(x)$) in Eq. (7) gives:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{EAP(x)}{R\beta} \tag{8}$$

As the value of E/R is constant; the evaluation of $\int_0^\alpha \frac{d\alpha}{f(\alpha)}$ is dependent on evaluating the function $P(x)$. Doyle [30] has evaluated $P(x)$ and suggested its value to be log($P(x)$) = $-2.315 - 0.4567\times$ over the range of $20 \leq \times \leq 60$.