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Fitting TGA data of oil sludge pyrolysis and oxidation by applying a model free approximation of the Arrhenius parameters

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Abstract

Interpreting the thermal pyrolysis data from organic substances using thermogravimetric analysis (TGA) requires assuming certain formal kinetic models to be a priori for parametric fitting. The form of the assumed model limits the accuracy of stimulating the pyrolysis data. This work demonstrates the feasibility of modeling the pyrolyzed sample as a continuous mixture, in which an Arrhenius-type kinetics is applied with activation energy, pre-exponential factor, and reaction order as continuous functions of conversion. Such a data fitting scheme is not used to identify the actual chemical kinetics involved, but rather to describe the complex chemical kinetics in a unified, “model free” manner for engineering applications.

Keywords: Thermal pyrolysis; Continuous mixture; Oil sludge; Kinetics

1. Introduction

Sludge pyrolysis provides a potential alternative method for treating petroleum refinery oil sludge. The pyrolysis process involves heating sludge in an inert atmosphere, which allows some of the organic matter to be released from the sludge and recycled [1,2], which matches resource utilization appeals. Additionally, heavy metals (except mercury and cadmium) that are going to their oxidized salts could be safely enclosed in the solid residues [3,4]. Some researchers employed a fluidized bed to investigate the pyrolysis of sewage sludge [5–7].

Thermogravimetric analysis (TGA) can provide pyrolysis kinetic data of sludge at raised temperatures. A few studies experimentally elucidated the pyrolysis kinetics of sewage sludge using the TGA test [8,9]. However, data interpretation generally encounters major difficulties in distinguishing the weight versus temperature data to yield a complex reaction scheme [10]. For engineering applications, a lump-type kinetic model is frequently adopted to correlate pyrolysis data. Dumpelmann et al. [9] devised a model for pyrolysis of sewage sludge that could forecast the maximum weight loss in a fluidized bed. Conesa et al. [11] designed a kinetic model for the pyrolysis of anaerobically digested and non-digested sewage sludge. Conesa et al. [12] employed this proposed kinetic model to interpret sewage sludge pyrolysis data.

During sludge pyrolysis various compounds would be generated and released from the sample surface, thus reducing the sample weight over time. Previous studies generally adopted a formal kinetic model to interpret the obtained TGA data, such as the parallel scheme proposed by Cosena et al. [11], and then assessed the model parameters by regressing the pyrolysis data. For example, Chu et al. [13] observed two peaks in their TGA curves for hydrolyzing activated sludge sample, and thus a kinetic scheme with two parallel reactions was proposed and found to fit. Conesa et al. [12] devised the more complicated kinetic model, containing six chemical species, during thermal pyrolysis. Nevertheless, regardless of the complexity of the proposed scheme, the fact that the actual chemical reactions involved could not be comprehensively incorporated by the formal kinetic models means they should be considered preliminary.

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Reactions involving numerous components require simplification, for example by describing components as a continuous distribution of species rather than a discrete number of components. The chemical reaction of continuous mixtures has attracted considerable research interest, including interest from Aris [14] and Amundson and Aris [15]. This approach does not consider any chemical schemes that actually occur during reaction, but uses some relevant process indices (such as the boiling point of a mixture in distillation) to characterize the reaction to assist in its application in engineering contexts. The main objective of the adopted kinetic model is to provide cracker design information for sludge pyrolysis. Wu et al. [16] thus adopted this concept for modeling the pyrolyzed wastewater sludge as a continuous mixture. The proposed continuous model has good fit to the experimental data, but since the pyrolysis kinetics is simple to handle, the formal kinetic model fits the data equally well. The use of so-called ''model free'' approach is not new, and Friedman [17], Ozawa [18], and Flynn and Wall [19] all developed similar ideas. This study applied the refined version of this scheme to emphasize its feasibility for correlating TGA data using a general framework.

The pyrolysis of certain samples reveals multiple maxima with rates that are difficult to handle using the formal kinetic model [20]. The oily sludge gathered from the petroleum refinery plant is such an example. This study demonstrated that the proposed continuous model can describe very complicated pyrolysis kinetics and thus is suitable for situations where most formal kinetic models fail. Oily sludge from a petroleum refinery plant served as the testing sample.

2. Sample data

The oil sludge was taken from a petroleum refinery plant in northern Taiwan. The thermal analyzer (SETARAM, 77A-92) was used to record the thermographs using nitrogen and different volume concentrations of oxygen as the carrying gas. The sludge was first dried at 378 K for 24 h. The cell was at a temperature that increased at 5.2 K/min from 380 to 1123 K. The carrier gas was nitrogen mixed with various quantities of oxygen (0%, 4.83%, 8.52% and 12.35% oxygen, respectively). Following this stage, the operation was repeated at heating rates of 12.8 and 21.8 K/min. The weight–time $(w-t)$ data represent the TGA curve.

The lab-scale experimental apparatus and detailed description of the operating procedures for oil sludge pyrolysis are the same as in previous studies [21,22]. CAHN 1000 ELECTROBALANCE (C-1000) was used for thermogravimetric analysis. Some balance specifications included: capacity of 100 g, sensitivity of 1 μg, and ultimate repeatability of 1.5 μg. A sample with known mass (8 ± 0.5 mg) was placed on a small quartz disk, with diameter 2 cm and thickness 1 mm. The sample was spread as widely as possible on the disk to create a thickness of less than 0.1 mm. This arrangement minimized the possible internal resistances of heat and mass transfer from the sample to the air. The disk was hung on the extension wire, which was a nichrome wire with diameter 0.1 mm and weight 0.68 mg/cm, of the electrobalance. The disk and wire were enclosed in a quartz shell and tube reactor. The outer shell was 92 cm long and 3.5 cm inside diameter. The inner tube had length 20 cm long and internal diameter 1.2 cm. The reactor was placed in the heating furnace (HAS 100/250G and 7000 W). A K-type thermocouple was inserted into the reactor to measure the temperature, and placed 5 mm below the center of the disk. Nitrogen gas at a specific flow rate was introduced into the electrobalance and reactor for at least 8 h for purging. The flow rate was then adjusted to the desired value, say 50 cm^3/min under 101.3 kPa (1 atm) and 293 K, and was controlled via a Cole-Parmer N062-01 rotameter. Following approximately 1 h, the control unit (Eurotherm 815 S, Eurotherm International Ltd.) of the furnace was set to a specific heating rate (5.2, 12.8 and 21.8 K/min). Meanwhile, the data acquisition unit (IBM PC-486 DX33 with 4.5 digit DVM card and RS232 interface), with a sampling interval of 15 s, logged the measurement results. The system was operated at atmospheric pressure. The effluent gas was cold-trapped at 298 K and then vented to a fume hood. Upon completion of the run, the flow of nitrogen gas was maintained until the system temperature was below 373 K.

3. Model fitting

Define the pyrolysis conversion as the ratio $\alpha = \frac{w_\mathrm{i}-w}{w_\mathrm{i}-w_\mathrm{f}}$, where w, w_i and w_f, denote the sample weights at time t, time zero, and the end of the test, respectively. Fig. 1 illustrates the $\mathrm{d}\alpha/\mathrm{d}t$ versus T data of the four samples at three different heating rates. Pyrolysis reaction of the sludge is significant during 450–850 K. At least three to four major maxima, together with numerous small peaks, can be identified in Fig. 1. The presence of 4.8–8.6% O_2 causes reactions to shift to higher temperatures with decreasing reaction rates at specific temperatures. At 12.6% O_2 the pyrolysis curves resemble those without O_2. The detailed reaction scheme should be complex. A formal kinetic model with four or more parallel reactions might be required to fit the present data set. However, a practical difficulty in establishing the formal kinetic model is the observation that some peaks identified at one heating rate might fail to be identified at other heating rates. For example, in the 0% O_2 test (Fig. 1a) the peak at the 690 K and 0.36 K/s heating rates cannot be identified via the 0.09 and 0.21 K/s tests. Another example is that the 790 K peak identified in 8.6% O_2 test at both the 0.09 and 0.21 K/s heating rates cannot be identified at the 0.36 K/s heating rate (Fig. 1c). The traditional approach adopted in the literature thus has difficulty in satisfactorily describing the noted kinetics. The following briefly summarizes the continuous mixture model designed by Wu et al. [16] and demonstrates the superiority of this scheme compared to the traditional approach for describing the oily sludge pyrolysis.

Assuming that the kinetics follows the Arrhenius-type expression:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(\frac{-E}{RT}\right)(1-\alpha)^n \tag{1}$$