

Model-free kinetics applied to sugarcane bagasse combustion

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Abstract

Vyazovkin's model-free kinetic algorithms were applied to determine conversion, isoconversion and apparent activation energy to both dehydration and combustion of sugarcane bagasse. Three different steps were detected with apparent activation energies of 76.1 ± 1.7 , 333.3 ± 15.0 and 220.1 ± 4.0 kJ/mol in the conversion range of 2–5%, 15–60% and 70–90%, respectively. The first step is associated with the endothermic process of drying and release of water. The others correspond to the combustion (and carbonization) of organic matter (mainly cellulose, hemicellulose and lignin) and the combustion of the products of pyrolysis.

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1. Introduction

In the tropics, sugarcane constitutes a major raw material for the production of sugar and alcohol. Brazil is one of the world's largest producers of sugarcane. During processing, however, a number of by-products are generated. These substrates include molasses, filter mud and sugarcane bagasse. Vinasse is regarded as a secondary by-product [1]. Sugarcane bagasse, the residual fibre, is obtained after the pressing of the sugarcane. Bagasse is usually burned to supply electric energy and steam for the process. However, 10% surplus bagasse still remains. Due to its high content in xylose, it can be used for the production of furfural. Furthermore, a few results about the production of active carbon from bagasse have also been reported [2].

The characterization of the properties of bagasse allows both their appropriate use as well as their increased use as an energy source. Thermal analysis methods are widely employed in the characterization of many materials. Among the methods of thermal analysis, differential scanning calorimetry (DSC) and thermogravimetry (TG) are significantly prominent, the common advantage of both techniques being the simplicity of sam-

ple preparation. Thermogravimetric analysis (TGA) techniques have a number of advantages that are relevant to the study of any reaction in which there is a weight loss or gain, the temperature can be controlled more accurately than by almost any other technique and, most importantly for rate studies, the chosen reaction temperature may be reached very quickly [3]. Kinetic investigations are nowadays one of the most important applications of thermal analysis. Knowledge of kinetic parameters, such as the reaction rate and activation energy, is one of the keys to determining reaction mechanisms in solid phases. Solid-state kinetic data are of major and growing interest in many technological processes. These processes include, for instance, thermal decomposition of crystalline solids and energetic materials, thermal oxidation and decomposition of polymers and coal, crystallization of glasses and polymers, and pyrolysis and combustion of biomass resources. There are numerous papers in the literature that include these kinetic studies in which these techniques are applied [3–19]. The aim of the present study is to determine the kinetic parameters for bagasse oxidation using Vyazovkin's model-free kinetics methodology.

2. Experimental

The cane bagasse sample used in this study was obtained from the Cruz Alta mill in Olimpia, São Paulo State, Brazil. It

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Nomenclature

A	pre-exponential factor
E	activation energy
$f(\alpha)$	reaction model
$g(\alpha)$	integrated reaction model
$k(T)$	temperature-dependent constant
R	gas constant
t	time
T	temperature

Greek symbols

α	extent of reaction
β	heating rate

was placed in a sealed sample box to avoid contamination and then dried in an oven at a temperature of 105 °C for 3 h, close to the moisture equilibrium value of bagasse in contact with ambient air. The bagasse sample was subsequently classified into two fractions: fibres and powder [20,21]; the sample was screened for 30 min, after which it was separated into fibres and powder bagasse types. The sample used in the analyses was the powder-type cane bagasse. Its elemental chemical composition, obtained via three repetitions in a C–H–N Perkin-Elmer model 2400B elemental analyzer was: C, 45.4%; H, 5.3%; N, 1.5%.

A Mettler-Toledo TGA/SDTA851^e and a DSC822^e were used for the thermal analyses in oxygen (or nitrogen) dynamic atmosphere (50 ml/min) at a heating rate of 10 °C/min. For the kinetics measurements, the TG experiments were carried out in an oxygen atmosphere at heating rates of 5, 10 and 20 °C/min. In all cases, 1–2 mg of powder sugarcane bagasse sample was thermally treated. In TGA tests under oxygen, a Pfeiffer Vacuum ThermoStarTM GSD301T mass spectrometer was used to determine the evacuated vapours. The masses 18 (H₂O), 44 (CO₂) and 46 (NO₂) were tested by using a detector C-SEM, operating at 1400 V, with a time constant of 0.5 s.

2.1. Determination of kinetic parameters and modelling

The rate of heterogeneous solid-state reactions can generally be described by:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where t is time, $k(T)$ the temperature-dependent constant and $f(\alpha)$ a function called the reaction model, which describes the dependence of the reaction rate on the extent of reaction, α .

The temperature dependence of the rate constant is described by the Arrhenius equation. Thus, the rate of a solid-state reaction can generally be described by:

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \quad (2)$$

where A is the pre-exponential factor, E the activation energy and R the gas constant.

The above rate expression can be transformed into non-isothermal rate expressions describing reaction rates as a func-

tion of temperature at a constant heating rate, β :

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (3)$$

Kinetics analysis is traditionally expected to produce an adequate kinetic description of the process in terms of the reaction model and the Arrhenius parameters. These three components ($f(\alpha)$, E , and A) are sometimes called the “kinetic triplet”.

There are many methods for analysing solid-state kinetic data [22]. These methods may be classified according to the experimental conditions selected and the mathematical analysis performed. Experimentally, either isothermal or non-isothermal methods are employed. The mathematical approaches employed can be divided into model-fitting and isoconversional (free model) methods.

The earliest kinetics studies were performed under isothermal conditions [22,23] the concepts of solid-state kinetics being established on the basis of these experiments. A major problem of the isothermal experiment is that a sample requires some time to reach the experimental temperature. The situation is especially aggravated by the fact that, under isothermal conditions, a typical solid-state process has its maximum reaction rate at the beginning of the transformation. However, the advantages of the non-thermal experimental technique are at least partially compensated by serious computational difficulties associated with the kinetic analysis.

In the model-fitting method, the $f(\alpha)$ term is determined by fitting various reaction models to experimental data. Subsequently, the $k(T)$ can be evaluated by the chosen form of $f(\alpha)$. Historically speaking, model-fitting methods were the first and most popular methods, especially for isothermal experiments. They were widely used because of their capacity to directly determine the kinetic triplet. However, these methods suffer from several problems, among which two are of particular importance. The first is that non-isothermal experiments provide information on both $k(T)$ and $f(\alpha)$, but not in a separate form. Thus, almost any $f(\alpha)$ can satisfactorily fit data at the cost of drastic variations in the Arrhenius parameters that compensate for the difference between the assumed form $f(\alpha)$ and the true, but unknown kinetic model. That is to say, the method is unable to provide a unique reaction model. The second problem is that only a single pair of Arrhenius parameters results from each application of the model-fitting method. The majority of solid-state reactions are not simple one-step processes, and thus a combination of serial and parallel elementary steps should result in an activation energy that changes during the course of the reaction. Consequently, the popularity of these methods has recently declined in favour of isoconversional methods, which can compute kinetic parameters without modelling assumptions [24–26].

Model-free isoconversional methods allow the activation energy to be estimated as a function of α without choosing the reaction model. The basic assumption of these methods is that the reaction rate for a constant extent of conversion, α , depends only on the temperature [27–30]. Hence, constant E values may be expected in the case of single-state decomposition, while a multi-step process E varies with α due to the variation in the relative contributions of the single step to the overall reaction rate.

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