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Thermogravimetric study on the pyrolysis kinetics of apple pomace as waste biomass

M. R. Baray Guerrero [a], M. Marques da Silva Paula [b], M. Meléndez Zaragoza [a], J. Salinas Gutiérrez [a], V. Guzmán Velderrain [a], A. López Ortiz [a], V. Collins-Martínez [a,*]

[a] Departamento de Materiales Nanoestructurados, Centro de Investigación en Materiales Avanzados, S.C., Miguel de Cervantes 120, Chihuahua, Chih. 31109, Mexico

[b] Laboratory of Synthesis of Multifunctional Complexes, PPGCS, Universidade do Extremo Sul Catarinense, 88806-000 Criciúma, SC, Brazil

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ABSTRACT

Biomass waste-to-energy is an attractive alternative to fossil feedstocks because of essentially zero net CO_2 impact. A viable option consists in an integrated process, in which biomass is partly used to produce valuable chemicals with residual fractions employed for hydrogen production. One example of a biomass waste is the apple pomace, which is the residue generated in the process of extraction of apple juice. In this research, a kinetic study of the pyrolysis of apple pomace biomass (APB) was performed by TGA aiming its liquid and gaseous products be utilized for the production of valuable chemicals and hydrogen. Characterization of APB consisted in calorific value, compositional, proximal and elemental analyzes. Kinetics were evaluated using three iso-conversional TGA models at 5, 10, 15 and 20 °C/min. Activation energy values of 213.0 and 201.7 kJ/mol were within the range for hemicellulose and cellulose, respectively, which are the main components of biomass.

Introduction

The current global economic development is based on the trade and processing of oil, however, depletion is expected during the first quarter of this century, which poses both economic and energy supply problems because energy demand is met mainly from fossil fuels [1]. Biomass as a renewable source not only allows to partially replace fossil fuels, but also to reduce concentrations of gaseous pollutants (carbon oxides) emitted into the atmosphere [2]. Agro-industrial residues represent a renewable source of energy, as obtained in large quantities as a result of industrial processing of fruits and vegetables and are a cheap raw material for conversion to biofuels [3].

Moreover the use of renewable energy technologies such as wind, geothermal, hydro, solar, hydrogen and those obtained from biomass are alternatives in the medium and long-term for the replacement of fossil fuels [4]. Today hydrogen is generated mostly from fossil fuels with a consequent, release of CO_2

* Corresponding author. Tel.: +52 6144391129.
E-mail address: virginia.collins@cimav.edu.mx (V. Collins-Martínez).
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during its production stage. While, biomass waste-to-energy is an attractive alternative to fossil feedstocks because of essentially zero net CO_2 impact. A viable economical option consists in an integrated process, in which biomass is partly used to produce valuable materials or chemicals with residual fractions employed for hydrogen production. Therefore, the transformation of waste biomass into energy valued compounds (i. e. H_2) is a research field that is considered of great importance in the present due to the current energy crisis and environmental pollution issues [2]. Furthermore, biofuels produced from various lignocellulosic materials such as wood, agricultural or forest residues, have the potential to be a valuable substitute (or supplement to gasoline biofuels) to liquid or gaseous fuels for the transport sector [4].

One specific example of a biomass waste is the apple pomace, which is the residue generated in the process of extraction of apple juice. This apple pomace, is formed by a complex mixture of shell, seed kernel, calyx, stem and soft tissue, which is representative of the pomace, and this contains mainly cellulose, hemicellulose, lignin and pectin.

The processing of biomass is grouped into three major groups: biochemical, thermochemical and physicochemical. Basically three types of thermochemical processes are distinguished: pyrolysis, gasification and combustion. The term pyrolysis refers to the incomplete thermal degradation which leads to the production of coal tars and condensable liquids and gases. In its strictest sense, pyrolysis must be performed in complete absence of oxygen, however, this term is now used in a broader connotation, to describe the chemical changes caused by the action of heat [5].

Moreover, pyrolysis is typically studied based on hypothetical models [6], where it is considered that the overall performance of pyrolysis is the combination of the behavior of each individual component [6,7]. Therefore, the determination of the kinetic parameters provides key information of the processes that take place, as well as the structure and composition of its constituents [6]. Furthermore, the analysis of the thermal degradation volatile products, identifies the gaseous species emitted by the biomass, and thus provides insights to the processes through which such decomposition occurs. The determination of the decomposition kinetics of lignocellulosic biomass involves the knowledge of the reaction mechanisms. However, the number of reactions occurring simultaneously in the simplest pyrolysis process is so great that prevents to develop a kinetic model that takes into account all these reactions. A kinetic study aims to reveal how the thermal decomposition takes place (whether one or more processes and what range of conversions occur) through the characteristic kinetic constants provided by the kinetic models. This last is critical to the design, construction and operation on a large-scale reactor for the pyrolysis of apple pomace subject to study, for the use of valued chemicals that may be generated or for the production of hydrogen from gaseous products or simply to get rid of certain wastes in a clean way [6]. The kinetic analysis of the thermal decomposition of biomass is generally based on the rate equation of decomposition of solids [8].

The present research is aimed to perform a basic characterization of apple pomace (from the region of Cuauhtemoc, Chihuahua, Mexico), the determination of the kinetic parameters (activation energy and pre-exponential factor) of the pyrolysis reaction under a nitrogen atmosphere using differential and integral non-isothermal iso-conversional models. Furthermore, the models employed in the present research were: the differential Friedman and two integral Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) models on TGA data for the apple pomace biomass (APB).

Experimental

Sample characterization

Apple pomace samples were collected from the northern state of Chihuahua (Cuauhtémoc, Chihuahua) and subjected to a drying process, crushed, grounded and sieved to achieve a particle size of 150 μm.

The elemental and proximal analyzes for the apple pomace sample were performed using a Carlo Erba EA-1110 elemental analyzer and an atomic emission spectrometer coupled with ICP (ICP Thermo Jarrell Ash IRIS/AP DUO), calorific power was determined through an adiabatic bomb calorimeter (Parr-1341 Oxygen Bomb Calorimeter) following the standard test method ASTM D-2015-96.

Lignin, cellulose, hemicellulose and pectin content from the pomace were determined using gravimetric techniques, described in ASTM (E 1756-95, D1106-95) and ASTM (D1103-60). Moisture, volatiles and ash content was determined according to the procedure described in ASTM E (871-82), ASTM (872-82) and ASTM (1755–1795), respectively. In order to determine the particle size (dp), samples were analyzed with dimensions: dp < 150 μm (150 μm), 150 < dp < 180 μm (180 μm), 180 < dp < 250 μm (250 μm), and 250 < dp < 450 μm (450 μm) under 100 cm^3/min N_2 flow and heating from room temperature to 800 °C at a rate of 10 °C/min. To verify the effect of the heating rate on the generation of volatiles and to obtain the kinetic parameters, the pomace sample was used with the same particle size, which was subjected to different heating rates of 5, 10, 15 and 20 °C/min.

Thermogravimetric analysis

TGA tests were carried out under an inert atmosphere (N_2) using a TGA-Q-500, TA Instruments equipment. Heating rates (β) were controlled at 5, 10, 15 and 20 °C/min. Experiments were performed under a nitrogen atmosphere with a flowrate of 100 cm^3/min and by duplicate. In all TGA tests between 20 and 30 mg of apple pomace biomass (APB) sample with a specific particle size were deposited on the crucible of the thermo balance. Then this sample was the subjected to a specific heating rate from room temperature to 800 °C.

Kinetic models

During the pyrolysis primary reactions occur, so that the kinetic study of these are of paramount importance with TGA being a very powerful tool. The determination of decomposition kinetics of lignocellulosic materials involves the knowledge of the reaction mechanisms. However, the number of reactions occurring simultaneously during a simple pyrolysis process is so great that prevents the development of a kinetic