



Non-isothermal pyrolysis of pectin: A thermochemical and kinetic approach



J. Aburto^a, M. Moran^a, A. Galano^b, E. Torres-García^{a,*}

^a Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte # 152, 07730 México DF, Mexico

^b Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Vicentina, Iztapalapa, CP 09340 México DF, Mexico

ARTICLE INFO

Article history:

Received 1 October 2014

Received in revised form 15 January 2015

Accepted 4 February 2015

Available online 7 February 2015

Keywords:

Hi-Res/modulated-TG

Citrus pectin

Pyrolysis

Kinetic parameters

TGA-FTIR

Autothermal reactions

ABSTRACT

The thermal degradation of pectin was investigated by simultaneous TGA-DSC/FTIR analysis and Hi-Res/modulated-TGA technique under nitrogen atmosphere. Pyrolytic degradation is a complex set of simultaneous and consecutive reactions related to: (i) dehydration at temperatures $\leq 100^\circ\text{C}$; (ii) initial depolymerization by breaking the glycosidic linkages for temperature $\leq 210^\circ\text{C}$, (iii) secondary degradation of the pectin units between 250 and 580°C , and (iv) direct gasification of char residues at temperatures $\geq 600^\circ\text{C}$. Three model-free-kinetics algorithms, Friedman (F), Kissinger–Akahira–Sunose (KAS) and modulated TGA (MTGA), were used to predict the pyrolytic cracking kinetics. The results are discussed in terms of activation energy, the most probable mechanisms, and their relationship with the structure.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

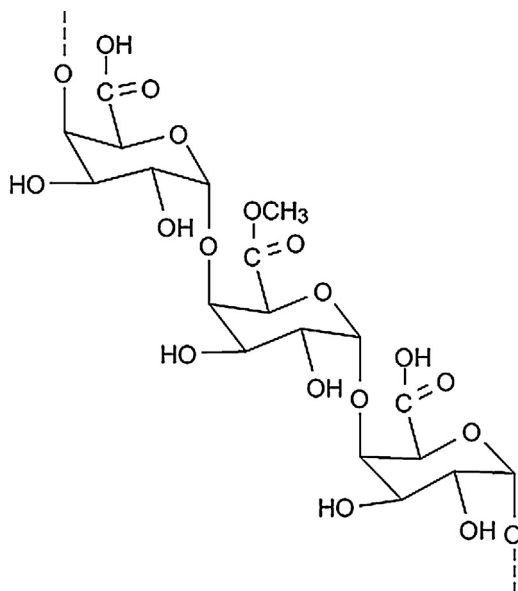
Nowadays, the imprint of human progress is not only reflected by comfort and ease of every human activity, but also by the increasing demand and consumption of energy and fuels, which has brought, as a consequence, a high environmental impact due to the increasing emissions of greenhouse gases produced by the combustion of fossil fuels. This problem has motivated the search of new options for renewable fuels, which include ligno-cellulosic biomass as raw material. Therefore, the development and optimization of new methods to convert biomass and organic residues into diverse chemical and fuel products is of high priority and urgency [1–3].

Ligno-cellulosic wastes such as citrus fruit waste, forest residues and sawdust are economically attractive by-products due to their easy accessibility and availability. Furthermore, these wastes produce visual pollution and are a source of harmful fauna and do not compete with human food production or land use. In this context, it is known that ligno-cellulosic biomass can be converted into biofuels or organic compounds through different biochemical and thermochemical processes [4,5]. Among the thermochemi-

cal methods to convert biomass wastes into biofuels, chemical products and energy, the most employed are (at least) combustion, gasification and pyrolysis [6,7]. Pyrolysis is one of the most promising thermochemical conversion routes in the biomass conversion. Nevertheless, due to the complexity and diversity of the available biomass, and also because biomass pyrolytic cracking proceeds through a complex system of reactions, the content and classification of ligno-cellulosic biomass fuel is very important [4,8,9].

The orange world production was raised to 68.2 million tons in 2012 and the main producers are Mediterranean countries, California and Florida in USA, Brazil, Mexico and China [10]. Moreover, 50–60% becomes citrus peel waste containing about 40% of citrus pectin from which only ca. 14% may be recoverable through conventional extraction procedures [11]. Citrus pectin is a particularly abundant hydrocolloid found in the by-products of the citrus processing industry. It is also found in most plants, being its major sources the peels of apples, citrus fruits, and plums. Citrus pectin is widely used in the food industry, in the production of cosmetics and as an ingredient in some anti-diarrhea medicines [12]. Pectin is a complex heteropolysaccharide mainly composed by alternating galacturonic acid and rhamnose residues and some arabinan and/or galactan side chains [13]. Nevertheless, their main building blocks are α -D-galactopyranosyl acid units and its methyl ester derivative (Scheme 1), in that order of abundance.

* Corresponding author. Tel.: +52 55 91758430; fax: +52 55 91756429.
E-mail addresses: eneliot@yahoo.es, etorresg@imp.mx (E. Torres-García).



Scheme 1. Chemical structure of pectin.

Hence, understanding pyrolysis kinetics of individual and representative components is an imperative purpose for industrial applications. Thus, research on pyrolytic cracking chemistry of pectin is an interesting study case that would enable researchers to understand, model and control the degradation processes of lignocellulosic biomass as well as to predict its degradation mechanism according to the used experimental conditions. Therefore, the main objective of this study is to provide a detailed analysis of the thermal degradation kinetics together with the analyses of the gaseous products yielded during the pyrolysis of citrus pectin.

2. Materials and methods

2.1. Sample

The citrus pectin used in this study was purchased commercially from (Sigma-Aldrich), and was used as received without further purification. According to the supplier, the α -D-galacturonic acid content was around 74% and its esterification content close to 6.7%. A key feature identified in the solid pectin was the presence of alkali metals such as Na (22.9 g kg^{-1}) and K (1.8 g kg^{-1}), furthermore of Si (0.9 g kg^{-1}) as determined by atomic absorption with a Varian Spectra AA-220 spectrophotometer.

2.2. Fourier transform infrared spectrometry (FTIR)

FTIR spectra were used to determine the chemical characteristics of citrus pectin. The sample was mixed with KBr powder and dried in an oven at 100°C for 24 h. The FTIR spectrum was recorded in a Nicolet Nexus Spectrometer, and the result is shown in Fig. 1.

2.3. Thermal analysis

2.3.1. Simultaneous TGA-DSC/FTIR analysis

Decomposition of pectin, under pyrolysis conditions, was accomplished using a simultaneous TGA-DSC (NEZTSCHE STA 409 PC). To minimize and control the heat and mass transfer differences, the sample mass was kept at $\sim 20 \text{ mg}$. The samples were heated from room temperature up to 800°C at a constant heating rate of 5°C min^{-1} , using an ultra-dry nitrogen atmosphere and a flow rate of 100 mL min^{-1} . The analysis of the gaseous products during the pyrolysis of pectin was carried out in a NICOLET

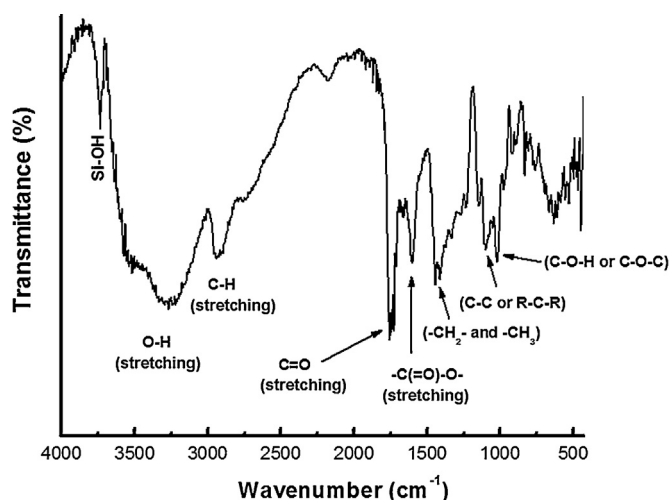


Fig. 1. FTIR spectra of citrus pectin.

Protégé 460 FTIR spectrometer coupled to TGA-DSC (NEZTSCHE STA 409 PC) thermogravimetric analyzer. The transfer line and gas cell of the spectrometer were heated to 220°C to avoid condensation or adsorption of semi-volatile products. Each IR spectrum was recorded every 5 s from 4000 to 500 cm^{-1} .

2.3.2. Hi-Res modulated TGA Analysis

A Thermogravimetric Analyzer Q5000 IR by TA Instruments, Inc. (USA) was used to obtain mass loss profiles on the heated sample. Samples ($\sim 20 \text{ mg}$) were placed in a Platinum-HT open pan and heated from room temperature to 800°C with heating rates of 2, 5 and $10^\circ\text{C min}^{-1}$. These analyses were carried out under dynamic ultra-dry nitrogen atmosphere with a flow of 25 mL min^{-1} , temperature perturbation amplitude of $\pm 3^\circ\text{C}$ and a period of 200 s. The TGA curves, were analyzed using the TA Instruments Universal Analysis 2000 software. Additionally, TGA measurements at different heating rates of 2, 5 and $10^\circ\text{C min}^{-1}$ were used to estimate the activation energy in each stage and its dependence on the transformation degree.

2.4. Computational details

The calculations were carried out with the Gaussian 09 program package [14]. Geometry optimizations and frequency calculations were performed using the LC- ω PBE functional [15,16]. This long-range-corrected hybrid has shown to be very accurate for a broad range of molecular properties, including thermochemistry, barrier heights of chemical reactions, and bond lengths [15]. In the present work, it was used in conjunction with the 60-311++G(d,p) basis set. Unrestricted calculations were used for open shell systems and local minima were identified by the absence of imaginary frequencies. Thermodynamic corrections at 298.15 K were included in the calculation of relative energies.

3. Kinetic study

3.1. Theoretical considerations

Often, kinetic analysis of heterogeneous processes [17] can be described by equation:

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

Here, the transformation degree, identified as α , with values $0 \leq \alpha \leq 1$, represents a global parameter obtained from the weight

Download English Version:

<https://daneshyari.com/en/article/1197222>

Download Persian Version:

<https://daneshyari.com/article/1197222>

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