



Generation of biofuel from hydrothermal carbonization of cellulose. Kinetics modelling



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ABSTRACT

Kinetics of cellulose hydrothermal carbonization was investigated over different reactions times and temperatures, developing a first order-reaction model, where chemical and heat transfer processes were connected and resolved simultaneously. According to the model, mass species evolutions are described by sigmoid curves and the presence of an induction period confirms the importance of taking into account the heat-up time and not only the T-constant period during the experiments. Moreover, the model indicates that temperature plays a main role on cellulose HTC (hydrothermal carbonization) reaction, affecting both pre-exponential and exponential factors of the kinetic constant. Finally, it is interesting to remark, from a practical viewpoint, that the model was able to describe the changes in H/C, O/C and high heating value taking place during cellulose hydrocarbonization, allowing the chemical composition and energy densification to be forecasted.

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1. Introduction

There is an increasing awareness of the unsuitability of current energy consumption scheme based mainly on the use of fossil fuels. Emissions coming from using fossil fuels, lead to problems such as global warming, climate change and environmental pollution. Also fossil fuel reserves are rapidly depleting, while energy consumption is dramatically increasing [1]. Therefore there is a growing interest in the development of alternative sources for clean renewable energy production such as biomass. Besides, in general terms, biomass does not contribute to global warming since it recycles carbon dioxide from the atmosphere [2], and it is not geographically centralized.

A major part of the biomass is ligno-cellulosic. Ligno-cellulosic material is the no starch, fibrous part of plant material. Cellulose, hemicellulose, and lignin are its three major components, standing out cellulose due to abundance. In fact, cellulose is the most common organic compound on Earth, being the primary structural component of cell walls in plants. Cellulose and hemicelluloses fibers impart strength to the plant structure, while the lignin holds the fiber together. Unlike carbohydrate or starch, ligno-cellulose is not easily digestible by human, thus, it is not part of the human

food chain, and therefore its use for biofuel does not threaten the world's food supply [3]. Represented by the generic formula $(C_6H_{10}O_5)_n$, cellulose is a long chain polymer of β -(1 \rightarrow 4)-D-glucopyranose units with a high degree of polymerization (~10,000) and a large molecular weight (~500,000). This structure gives it high strength, permitting it to provide the skeletal structure of most terrestrial biomass materials [4].

Regarding its exploitation as energy source, biomass presents different problems such as low energy density and biological instability; thus several pre-treatments are generally used in order to improve its characteristics as a fuel. In this context, hydrothermal carbonization (HTC) of biomass has gained relevance during the last few years due to its simplicity and low cost [5], as pretreatment suitable to produce biofuels (namely hydrochars) adequate for other thermochemical process like gasification or combustion [6]. Moreover, it is suitable even for wet materials, without the need of previous energy consuming drying processes, thus opening up the range of potential starting materials.

HTC, also known as hydrous or wet pyrolysis, can be defined as the carbonization of biomass heated in water under autogenous pressure and temperatures in the lower region of liquefaction process (subcritical conditions) [7].

As a result of HTC, a liquid, gas and a solid carbonaceous phase (hydrochar, HC) are obtained; their distribution as characteristics depend upon the raw material and the processing conditions. The HC product has a greater carbon content than the raw material and

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also presents interesting additional features regarding its use as a fuel such as enhanced heating value and better self-binding properties [5,8]. Moreover, HCs present an incipient porosity and other interesting features such as hydrophobicity, which makes them suitable to be used as adsorbents or activated carbon precursors [9], as well as in other fields such as agricultural (soil remediation), catalytic or electronics applications.

Previous works in this line have examined the use of biomass materials such as grass cuttings [10], algae [11], maize [12], olive stones [13], invasive aquatic plants [14], tomato peel [15] and sewage sludge [16]. HTC has given evidence of being a suitable and promising procedure to convert cellulose into HCs with enhanced carbon content and a high energy content; subcritical water can disrupt the hydrogen bonds of cellulose, as well as its crystalline structure, forming glucose monomers [17].

Most studies focused on the HTC of cellulose [18–20], are specially devoted to the analysis of processing variables on the final characteristics of the HCs, regarding their surface properties, heating value and behavior in several applications. Less attention has been paid, however, to the study of the process kinetics, whose knowledge is essential for process design. Reza et al. (2013) [21] studied the kinetics of loblolly pine HTC, and developed a model considering, in parallel, the decomposition of hemicellulose and cellulose via pseudo-first order reaction mechanisms. Their model, however, did not consider heating up process.

Therefore, there is need for a more complete understanding of processes taking place during hydrothermal processing of cellulose, to allow the development of predictive models, which are able to account for the chemical changes and energy densification of the resulting HC.

Given this context, the general objective of the present work was to provide a deeper insight of the HTC of cellulose. In particular, the specific objectives included: (1) to study the kinetics of cellulose HTC following a simple first-order reaction model, which does not only consider the reaction temperature, but also the heating up process, in which a significant part of the cellulose is readily converted into HC, and therefore should not be neglected; (2) to use this model to describe changes in the chemical composition and energy densification of the resulting HC.

The real novelty of this study stands on the second goal, which, to the best of the authors' knowledge, has not been addressed before. Taking into account the abundance of cellulose in the planet, and its potential as biofuel, developing a model able to forecast the final chemical composition of the biochar obtained after hydrothermal processing is a very interesting challenge.

1.1. Decomposition kinetics models

Investigating detailed reaction mechanisms taking place during hydrothermal carbonization of cellulose is beyond the scope of this study. Instead, a first-order reaction rate model and Arrhenius equations were used.



According to this scheme, at a given time the solid fraction will be:

$$m_s = m_{\text{cell}} + m_{\text{HC}} \quad (2)$$

where m_{cell} is the mass of cellulose (on a dry weight basis) at reaction time (t) and m_{HC} is the hydrochar mass.

The reaction rate depends on the amount (mass) of cellulose present,

$$r = -\frac{dm_{\text{cell}}}{dt} = k_1 \cdot m_{\text{cell}} \quad (3)$$

where k_1 is the reaction rate constant. The reaction rates for cellulose and hydrochar are

$$r_{\text{cell}} = \frac{dm_{\text{cell}}}{dt} = -r \quad (4)$$

$$r_{\text{HC}} = \frac{dm_{\text{HC}}}{dt} = r \cdot F_{\text{HC}} \quad (5)$$

where F_{HC} is the fraction of cellulose that is converted to hydrochar. According to Eq. (1), the fraction $(1 - F_{\text{HC}})$ is the fraction of cellulose that is converted to liquid and gas.

The reaction rate constant, k_1 , can be defined by the amplified Arrhenius equations:

$$k_1 = A \cdot T^n \cdot e^{\left(\frac{-E_a}{R \cdot T}\right)} \quad (6)$$

where A is the frequency factor, T is the temperature, E_a is the activation energy and R is the constant gas ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). In this equation, both the pre-exponential and exponential factor depend on temperature.

In most cases, authors consider T constant during experiments; however this is far from reality in hydrothermal carbonization in autoclave reactors, where there is a heat-up time and a T -constant period [19]. For this reason, and as a remarkable difference with respect to previous works, we have considered temperature as function of time, $T(t)$. As a consequence, m_{cell} and m_{HC} can not be calculated resolving differential Eqs. (4) and (5) by trivial methods. In this work, we have resolved the kinetics equations using COMSOL software, developing a model where chemical and heat transfer processes were connected and resolved simultaneously.

The solid yield of the hydrothermal process can be determined by the ratio

$$\text{SY} = \frac{m_s}{m_{\text{cell}_0}} \quad (7)$$

where m_{cell_0} is the initial mass of cellulose.

For a given temperature and time processing conditions, and provided that A , n , E_a and F_{HC} are known, the SY (solid yield) of the hydrothermal process can be determined by this model, as it is described in next section.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (Sigma–Aldrich) was dried at $105 \text{ }^\circ\text{C}$ until constant weight and then stored in closed flasks placed in desiccators for further analysis.

2.2. HTC processes and HC characterization

HTC processes were performed in a stainless steel autoclave (Berghof, Germany), provided with a 0.2 L teflon vessel. 10 g of cellulose and 100 mL of deionised water at room temperature were added to the vessel and then, it was sealed and placed into the autoclave, and the system remained overnight at room temperature. Afterwards, the system was heated up in an electric furnace at selected temperatures ($170\text{--}245 \text{ }^\circ\text{C}$), during a chosen processing time ($2\text{--}11.8 \text{ h}$). The runs were performed under the following

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