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Reaction engineering for process intensification of supercritical water biomass refining

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ABSTRACT

Status reports from public and private organizations make a roadmap for achieving a bioeconomy for society. Biobased industries, based on renewable materials and energy, are still in development to supporting a decentralized production that can be an alternative to the well-supported centralized petrochemical production plants. The use of pressurized water has been proposed as an environmentally compatible process to integrate the depolymerization–reaction–separation of the biomass supported processes. Supercritical water is emerging as a solvent and reaction medium capable of providing selective processes while significantly reducing the reaction time, leading to the possibility of developing compact equipment for the use in biomass decentralized production plants. The main ways of biomass upgrading in a hydrothermal medium are reviewed in this work: hydrolysis, fractionation, gasification and reaction. In the last years, a significant progress was achieved in obtaining of added value products from biomass by hydrothermal technologies. However, some challenges must still be overcome before a sustainable and efficient decentralized production is achieved.

1. Introduction

In the last years there is a general tendency toward a society supported by a bioeconomy. This term refers to the sustainable production and conversion of biomass into a range of food, health products, fibers, industrial products and energy as it is referred in “The European bioeconomy in 2030 Delivering Sustainable Growth by addressing the Grand Societal Challenges” presented by BECOTEPS [1] and in the “The Bioeconomy to 2030 Designing a policy agenda” report presented by OECD [2]. Achieving a European society supported in bioeconomy is one of the challenges of the European Strategy Horizon 2020.

The petrochemical industry has been an engine of rapid economic development in the 20th century. The large-scale centralized production has achieved rapid marketing of chemicals and energy. Biobased industries however, based on renewable materials and energy, are still in development to success in supporting a decentralized production that can be an alternative to the well-supported centralized petrochemical production plants [3].

To accomplish this challenge, the research must be focused on achieving the development of environmentally compatible processes, the efficient handling of energy and on reducing the equipment costs. Environmentally friendly processes are characterized by high yield and high selectivity. This is achieved by simplifying the number of process steps, by searching opportunities among new raw materials and by using clean solvents as water or carbon dioxide. Equipment cost reduction involves the development of compact apparatus with short operation times: changing the reaction time from minutes to milliseconds allows a reactor volume reduction from m^3 to cm^3.

The use of pressurized fluids has been proposed as an environmentally compatible process to integrate the depolymerization–reaction–separation processes. Particularly, high-temperature pressurized water has proven to be a good solvent for clean, safe and environmentally benign organic reactions [4–7]. Main advantages that make hydrothermal media a promising alternative for biomass processing are: (1) direct use of raw material regardless of its water content, which implies an important energy saving; (2) the same reaction medium can be used for the transformation of different biomass fractions; (3) mass transfer limitations can be reduced or avoided, thus reaction rates are faster [8–12]. Furthermore, tunable properties of the reaction

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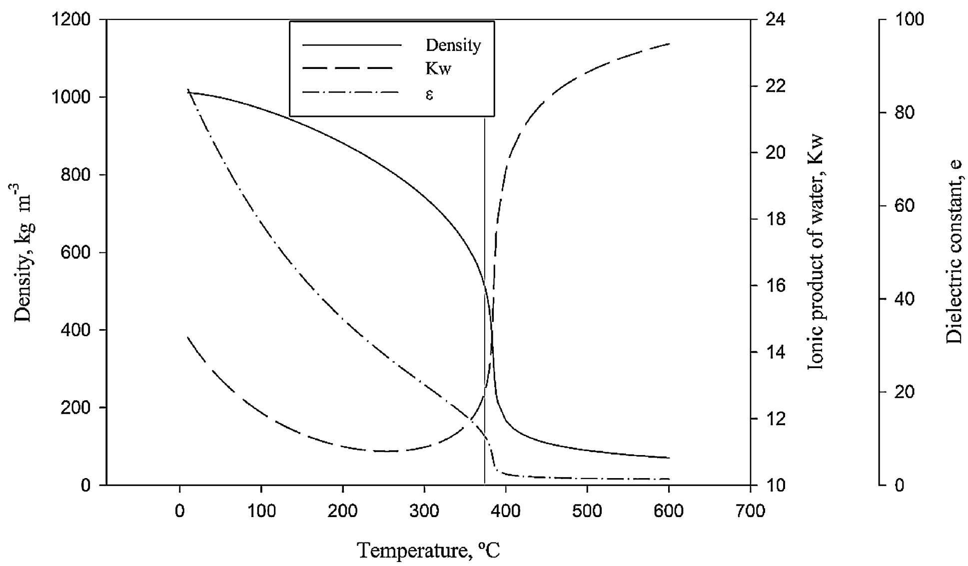

Fig. 1. Properties of pressurized water below and above critical point. Continuous line Density (kg/m^3); dashed line represents ionic product of water (pK_w) and dashed-dotted line represents the dielectric constant.

medium act as a control factor for the reaction selectivity, avoiding the generation of by-products. The change in the dielectric constant is proportional to the density and inversely proportional to the temperature. Hydrogen bonds behavior is analogous to that of the dielectric constant [4]. Another important property of the aqueous reaction media is the ionic product of water (K_W). The maximum value of the ionic product of water is presented at a temperature around 300 °C ($K_W = 10^{-11}$). This creates a medium with high H^+ and OH^- concentrations, favoring in this way acid/basis catalyzed reactions. Above the critical temperature of water (374 °C), K_W decreases drastically ($K_W = 10^{-25}$) [13] as shown in Fig. 1. At higher pressures ($P > 60$ MPa) the K_W again presents values similar to those of ambient water.

The combination of these properties with high reaction rates associated with high temperature makes water an excellent solvent for the development of environmentally compatible processes and can lead to efficient handling of materials and reduction in equipment cost since reaction time is very low.

Sub/supercritical water hydrolysis, gasification, fractionation, and transformation in high added value compounds will be reviewed in this manuscript to demonstrate that sub/supercritical water can contribute to the decentralized development of industries based on the use of renewable raw materials and energy. The aim of this work was to evaluate the reaction engineering and process intensification aspects of biomass processing in pressurized water. However, the authors would like to mention that the research and industrial sector which is developing the biomass upgrading with supercritical water must also take into account another topics. For example, the modeling studies about biomass reactions (Arrhenius parameters), particle size effects, ash content effects, heating rates effects are important in the design of reactors. In addition, the post processing of the obtained products (purification and concentration) as well as the material resistance are also important stages that should be developed to achieve the industrial scale production. Finally, the hydrothermal carbonization is an alternative process that is not reviewed in this work.

2. Hydrolysis

Hydrolysis is defined as the process in which a molecule is split into other two molecules by adding a molecule of water. The general equation for a hydrolysis reaction is shown in reaction equation (R1).

$$\text{R—R} + \text{H—O—H} \rightarrow \text{R—H} + \text{R—OH} \tag{R1}$$

The hydrolysis of non-human food biomass has been studied extensively in the last decades due to the possibility of producing chemical compounds from natural polymers. As it is shown in Fig. 2, biomass is mainly composed of three polymers: cellulose, hemicellulose and lignin. Cellulose is the major component of vegetal biomass, representing in general 50% in mass [14]. In Fig. 2A it shown the repeating β-D-gluco-pyranose which is linked through acetyl functions of the OH group of C-4 and C-1 carbon atom to form the polymer, cellulose [15]. This bond is called β-1,4-glucan. The hydrolysis of cellulose produces glucose molecules. Hemicellulose is the second major component of biomass, being in general, the 25% in mass of vegetal biomass [14]. This compound is a hetero-polymer formed by pentoses: xylose and arabinose; and hexoses: glucose, galactose and mannose (Fig. 2B). Glucuronic, acetic and ferulic acid are present in the polymer structure [16]. The composition of hemicellulose varies from one resource to another and it is generally classified by its main sugar component as: xylans (β-1,4-D-xylopyranose as backbone with a variety of side chains), mannans (linear polymer of β-1,4-mannopyranosyl) and glucans (β-glucan: alternate β-1,4 and β-1,3 glucose links; and xyloglucan: straight β-1,4-glucopyranose polymer with linked α-1,6-xylose) [16,17]. Therefore, the hydrolysis of hemicellulose produces mainly, glucose, galactose, mannose, xylose, arabinose and organic acids. Lignin is another polymer comprising around 20% in mass of the biomass [14]. This fraction is a highly amorphous polymer formed basically by phenolic units. The structure of lignin is complex due to the random polymerization reaction when it is produced in nature. However, the frequency of the internal bonds is well known [18]. This compound is mainly formed by three monomers: p-coumaryl, coniferyl and sinapyl alcohols (Fig. 2C) [19,20]. From the hydrolysis of lignin several kinds of compounds can be obtained, such as phenols, catechols, alcohols, aldehydes and acids among others [21]. Depending on the biomass, proteins and oils can be present in biomass. Proteins can be partly hydrolyzed into amino acids and oils would be hydrolyzed into free fatty acids and glycerol [22–26].

Another important compound found in some vegetal biomass is starch. Starch is composed of glucose linked via