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Kinetic Evaluation of Carbohydrate Biomass Conversions

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Recent developments done in the scope of the biorefinery concept have emerged as alternatives to remove economic obstacles, thus making production of chemicals from ligno-cellulosic feedstocks become a reality. Biomass conversions employing pretreatments of hemicellulose and lignin, and acid hydrolysis of cellulose were carried out to break the polymeric structures. The saccharide components obtained produced reaction media that could be processed into value added polyols by subsequent hydrogenations.

1. Introduction

Lignocellulosic biomasses (LCB) such as energy crops and agro-industrial residues have been investigated over the last decades as sources for the sustainable production of a myriad of chemicals. LCB consists of three major components: cellulose, hemicelluloses and lignin. These macromolecules comprise approximately 90% of the vegetable biomass. The saccharide molecules present a wide variety of functional groups, which allow the formation of compounds with different chemical structures. This feature, together with their great availability from agricultural sources, qualify them as products of increasing value as feedstocks.

Cellulose is a high molecular weight linear hexose unbranched homopolymer of D-glucose molecules. The building blocks are bound to each other by β-1,4-glucosidic linkages in chains of up to 15.000 glucose units (Fan et al.1980). Hemicellulose was identified as a polysaccharide (Selvendran and O'Neill,1985) composed of a variety of monosaccharide units including xylose, arabinose, and mannose (Wilkie, 1979).

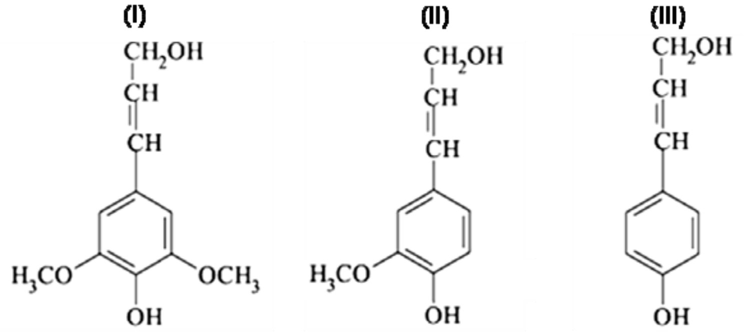

Figure 1: Lignin precursors: (I) p-coumaryl alcohol; (II) coniferyl alcohol; (III) sinapyl alcohol. (Fengel and Wegener, 1989)

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Lignin is a complex, three-dimensional, cross-linked macromolecule of phenyl propane units, held together by ether and carbon-carbon bounds. Lignin cements and anchors the cellulose and hemicellulose fibers together and at the same time stiffens and protects them from physical and chemical damage. The heteropolymer is composed by different units of p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohols (Bidlack et al.,1992). In the above Figure 1 the chemical structures of the three major components of lignin are shown (Fengel and Wegener, 1989).

Carbohydrates and lignin from vegetable biomasses may be depolymerized to oligosaccharides and lignin compounds soluble in aqueous medium. In the presence of homogeneous or heterogeneous catalysts (Garrote et al., 2004) the oligomeric mixtures selected may be processed in order to produce value added chemicals (Hamoudi et al., 1999). Ionic liquids have been evaluated as an environmentally friendly alternative to biomassa processing (Rocha etal., 2014). First and second generation ethanol from sugarcane have been studied, and recent developments promoted alcohol integrated production (Dias et al. , 2014).

In the present work, biomass conversions employing pretreatments of hemicellulose and lignin, and acid hydrolysis of cellulose were carried out to break the polymeric structures, and produce mainly carbohydrates and lignin-based compounds.

2.Carbohydrates from biomass

Biomass processing can be developed via degrading and functional reactions to obtain intermediate valuable products. The main components of the plant tissue, as cellulose, hemicellulose, lignin, and starch consist basically of carbon, hydrogen, and oxygen, besides some minor components as minerals and other species. The natural polymers, which are rich in oxygen, may be also be converted to oxygenated compounds through catalytic hydrogenation, which under more drastic conditions of temperature and pressure leads to cleavage of the carbon chain (Yoon at al., 2012).The processing of raw materials rich in saccharides (sugarcane, starch) and their derivates (molasse, sugarcane bagasse) to obtain products with industrial application as polyols (Baudel et al., 2005) and organic acids, has been the object of several studies (Lichtenthaler, 2004).

Carbohydrate hydrogenations (saccharides → monosaccharides → polyols) have been studied using nickel supported catalysts. Catalysts based on nickel, cromium and copper (Turek et al.,1983) where used to hydrogenate glucose, fructose and sucrose to sorbitol and mannitol) (Maranhão et al.,2004).

3.Material and Methods

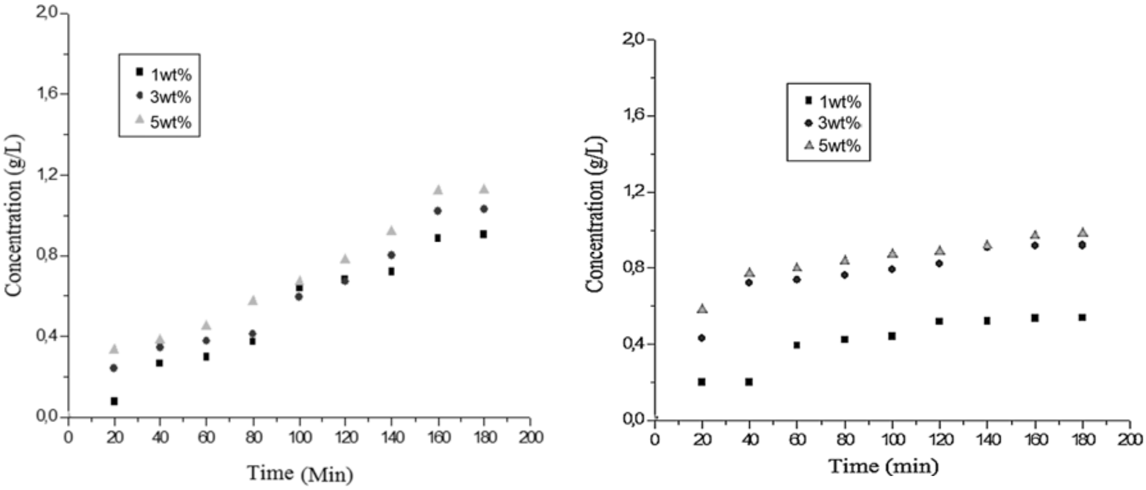
The delignification alkaline and acid hydrolysis were carried out in a stirring slurry reactor (3.0 L) using 50 g of biomass on a dry basis, maintaining a solid-liquid ratio of 1:25.The delignification was conducted with the bagasse from the process of pre-hydrolysis, with a solution of NaOH 1.0 wt.% at 70 °C during 3 h. The final material was vacuum filtered and analyzed in terms of total solids and soluble lignin. The solid phase was quantified (delignified residue) treating the liquid with hydrochloric acid (3.0 wt.%). The hemicelluloses extraction was carried out with a mixture of H_2SO_4 to 1.0 wt.% at temperatures of 90 °C during 2 h. After the operation the material was filtered under vacuum and quantified. The cellulosic fraction was hydrolyzed with HCl solution (20 wt.%) containing the catalyst-additive 8.0 wt.% $LiCl_2$ at 160 °C for 3 h. Analyses of the liquid phases were performed via liquid chromatography (HPLC) with an Aminex HPX-87 column BioRad, having H_2SO_4-0,001N as mobile phase. The solid phases (residual and hydrolyzed bagasse) was analyzed in terms of the saccharides and degradation products (furfural) contents.

4.Experimental Results and Discussion

The evolutions of the biomass macro structures into monosaccharides and oligosaccharides were observed and quantified considering the reaction media as intermediates to be processed in valuable products.

4.1 Pre-diluted acid hydrolysis of biomass

Pre-hydrolysis of biomass was performed to make it more susceptible to attack by alkalis in the subsequent process of delignification. In Figures 2a and 2b the concentration evolutions of xylose and arabinose are presented. The influence of acid concentration was evaluated at 80 °C with three different concentrations of hydrochloric acid. In mild conditions adopted, degradation of arabinose and xylose, by dehydration occurred at low levels.


(a)

(b)

Figure 2: Concentrations evolutions of xylose (a) and arabinose (b). Pre-hydrolysis of biomass. Influence of the acid concentration. Conditions: 80 °C, mb = 50 g and Vℓ = 1.5 L

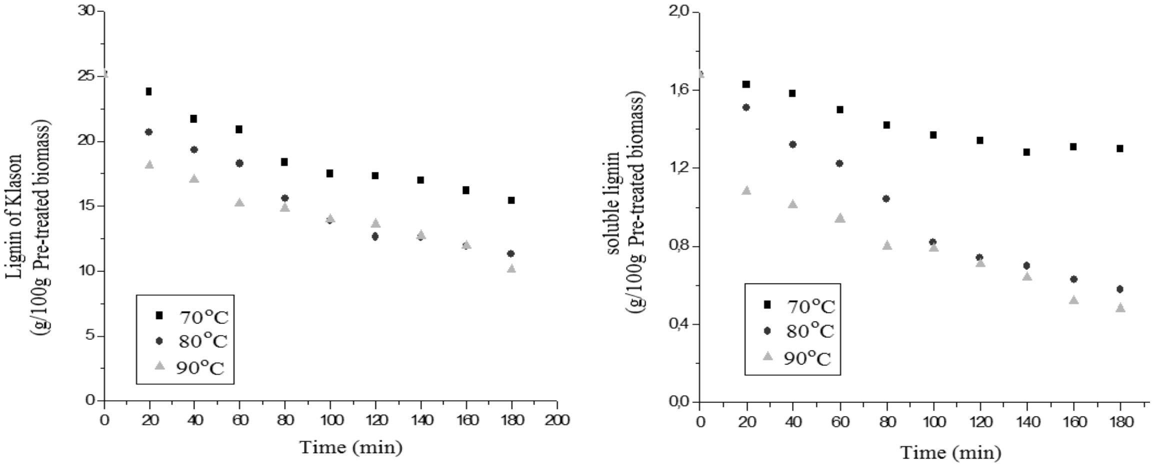
4.2 Delignification of pre-hydrolyzed biomass

Alkaline extraction of lignin occurs with low structural change in the polysaccharides fixed in the biomass. So, both bases NaOH and NH_4OH were used to obtain different lignin and carbohydrate yield. a influência de catalisador na extração da lignina, foram realizados ensaios com solução de teor 1.0 wt.% do álcali. In Table 1 are presented the parameters and operating conditions used in the extraction.

Table 1: Parameters of sugarcane delignification

Parameter	Conditions		
Alkaline activity	NH_4OH	Neutre	NaOH
Concentration	1.0 wt.%	1.0 wt.%	1.0 wt.%
Temperature	70ºC	80ºC	90ºC

In Figure 3 the evolutions of lignin contents from sugarcane bagasse from pre-hydrolysis treatment are presented. Soluble lignin and lignin Klason (insoluble) were measured in function of time at 70ºC, 80ºC and 90 ºC.


(a)

(b)

Figure 3: Conclusion evolution of liginin. Klason lignin (a) and soluble lignin (b). Influence of temperature. Conditions: pre-hydrolyzed biomass, NaOH (1 % by weight) mb = 50 g and Vℓ = 1.5 L

The evolution of the mass fractions of lignin occurred with a weight loss of the bagasse. The maximum amount of solubilized material, after 180 min was approximately 30 wt. % of the initial value in the alkaline Extraction yields between 20 %wt. and 70 %wt. (Khursheed and Vilas, 2014) were obtained via an hydrotropic process (sodium xylenesulfonate, XSS) that involved conversion into several chemicals, without degradation by-products.

4.3 Diluted acid hydrolysis of hemicellulose

The fractionation of biomass with hemicellulose extraction and consequent depolymerization was considered to operate with low saccharide degradation. Thus, the delignified pulp was subjected to an acid diluted hydrolysis, promoting high decomposition and removal of hemicelluloses. The effects of temperature and acid concentration were evaluated (Figures 4, 5).

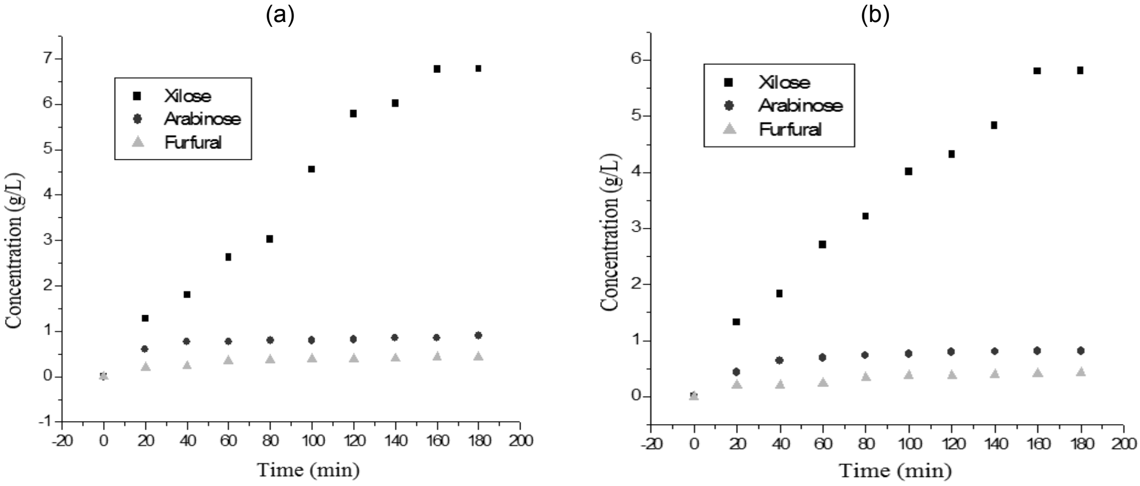

(a) (b)

Figure 4: Concentrations evolution of monosaccharides and furfural. Influence of temperature. Conditions: delignified biomass, mb = 50 g, (a) 90 °C, (b) 100 °C H_2SO_4 (1.0 wt.%).

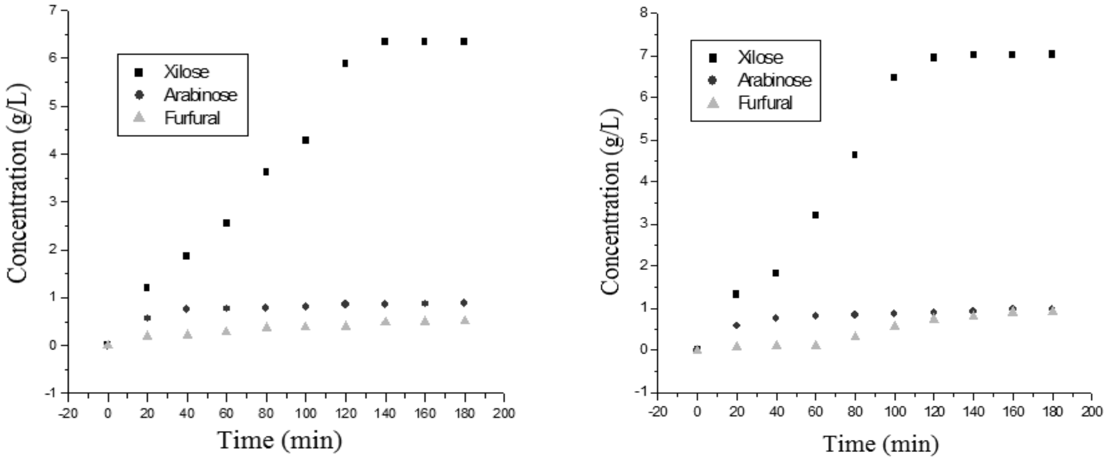

(a) (b)

Figure 5: Concentrations evolution of monosaccharides and furfural. Influence of temperature. Conditions: delignified biomass, mb = 50 g, (a) 90 °C, (b) 100 °C H_2SO_4 (5.0 wt.%).

The concentrations evolutions indicate that xylose extraction was more pronounced (15.0 wt.% /biomass) at 100 °C operating with 5.0 wt.% sulfuric acid solution after 100 min. Arabinose content was approximately 1.2 wt.% /biomass). The degradation products (furfural), produced via dehydration, was obtained in low concentrations (1.0 wt.% /biomass).

4.4 Acid hydrolysis of cellulose

The cellulosic biomass was treated by hydrolisis with acetic acid (HOAc) and sulfuric acid H_2SO_4) operating under conditions indicated by Lima et al. (1992) and Baudel (1995). The corresponding results are presented in Table 2.

Table 2: *Experimental parameters of the alkaline hydrolysis. Yield of extracted saccharide*

Experiment	Acid	Acid concentration (wt.%)	Temperature (°C)	Extracted (wt.%)
1	HOAc	25.0	160	35.4
2	HOAc	25.0	120	24.3
3	HOAc	25.0	160	33.9
4	HOAc	25.0	120	34.1
5	H_2SO_4	1.0	90	27.8
6	H_2SO_4	5.0	90	25.4
7	H_2SO_4	1.0	100	38.9
8	H_2SO_4	5.0	100	41.2

Extracted saccharides contents were obatined in the range of 35.0 wt.% to 25.0 wt.%, indicating that this higher yield should be associated with the low levels of sacharide degradation. The acid hydrolysis promoted the selective revomal of the hemicelluloses placed in vegetable cells. In this case, the following factors acid nature and concentration, temperature and biomasse type influenced the hydrolysis by cracking of lignin-carbohydrtae bond. Diluted solutions of strong acids or concentrated solutions of weak acids can be promoted the cited interactions.

In this work, acid concentration and operating temperature were evaluated to find high product selectivity with reduced levels of degradation by-products. Thus, the operations were carried out with H_2SO_4 wt.1.0 % at 100 ºC (Baudel, 1999), where lignin was insoluble, or the operations were conducted with the acid HOAc wt. 35 % at 120 ºC (Lima,1992), indicated as a reaction medium adequate to other operations with the final product.

5. Conclusions

Sugarcane bagasse conversion, employing treatments of hemicellulose, lignin and cellulose, was carried out with carbohydrate productions.

Sugarcane bagasse from pre-hydrolysis operating at 70 ºC, 80 ºC and 90 ºC produced soluble lignin and lignin Klason (insoluble). The fractionation of biomass with hemicellulose extraction produced xylose (15.0 wt.% /biomass) at 100 °C operating with 5.0 wt.% sulfuric acid solution, while arabinose content was approximately 1.2 wt.%/biomass. The cellusoc biomass treated by hydrolisis indicated saccharide contents in liquid phase ranging from 35.0 wt.% to 25.0 wt.%.

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