

Chapter 2

Dilute Acid Hydrolysis of Agro-Residues for the Depolymerization of Hemicellulose: State-of-the-Art

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Abstract Geo-political, long-term economic and sustainable concerns are promoting researchers and entrepreneurs to harness the potential of lignocellulosic feedstock (LCF) into industrially significant products. Agro-residues (sugarcane bagasse, wheat straw, rice straw, corn stover, etc.) constitute the principal fraction of LCF and are available in large amounts globally. The judicious exploration of agro-residues into important products such as D-xylitol, an artificial sweetener, may provide a strong platform for its sustainable supply to the medical and non-medical applications-based sectors. Pretreatment of agro-residues by dilute acid hydrolysis is an inevitable process for the depolymerisation of hemicellulosic fraction into xylose and other sugars. Dilute acid catalyses hemicellulose fractionation at high temperature within short reaction times. Significant developments have been made in the past towards the chemical hydrolysis of agro-residues, particularly for the hemicellulose breakdown. Critical parameters such as acid load, temperature, residence time and solid-to-liquid ratio play pivotal roles in the kinetics of dilute acid hydrolysis of agro-residues. Furthermore, reactor configurations such as counter-current, plug-flow, percolation and shrinking-bed have been designed in order to maximize the sugars recovery with minimum inhibitors generation. This chapter reviews the process parameters, kinetics, methods and reactor engineering for the dilute acid catalysed processes employed for agro-residues.

Keywords Agro-residues · Dilute acid hydrolysis · Hemicellulose depolymerization · Pretreatment · Reaction kinetics · Reactor design

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2.1 Introduction

The low cost and renewable nature of agro-residues such as sugarcane bagasse, wheat straw, rice straw, corn stover, etc. represent the ideal feedstock for their conversion into value-added products by biotechnological routes (Mantanis et al. 2000; Mussatto and Teixeira 2010). These agro-residues, like other lignocellulosic materials, are constituted primarily of lignin, hemicellulose(s) and cellulose. The carbohydrate fraction (hemicellulose and cellulose) can be depolymerised into sugars which act as a primary carbon source for the microbial biocatalysts for the production of xylitol, ethanol, organic acids, industrial enzymes, etc. (Carvalho et al. 2008; Mussatto and Teixeira 2010; Chandel et al. 2011a). Figure 2.1 demonstrates the process configuration for dilute acid hydrolysis of various agro-residues into monomeric constituents and subsequently their conversion into value-added products by microbial fermentation. Due to the large variations of the chemical compositions of agro-residues, especially polysaccharides and lignin, it is important to choose an appropriate method of biomass fractionation for their effective biotechnological utilization (Howard et al. 2003). In this context, the complex cellular structure of the agro-residues must be fractionated into C6 or C5 sugars with minimum side (or by)-products (Mosier et al. 2005). Thus the procedure applied will be a hydrolysis and/or a pretreatment, depending on the purpose of the released sugars.

During the acid hydrolysis of the hemicellulose fraction of plant cell wall, sugars are liberated in addition to some undesired compounds. The recovered solid residue, so-called cellulignin, is readily available for the subsequent cellulases-mediated enzymatic hydrolysis into glucose. Thus the pretreatment step involving dilute acid facilitates the enzymes accessibility to the cellulose for maximizing sugars recovery (Chandel et al. 2011b). Dilute acid hydrolysis is a simple and fast method to obtain hemicellulosic hydrolysates. These hydrolysates mainly contain xylose (80 % of the sugar content in hemicellulosic fraction), arabinose, glucose, galactose and mannose in conjunction with cell wall-derived inhibitors such as furans, phenolics, weak acids and others (Canilha et al. 2006, 2008; Chandel et al. 2007a).

During dilute acid hydrolysis of agro-residues, parameters such as temperature, time, acid concentration and solid-to-liquid ratio play critical roles in obtaining optimum sugar recovery and minimum generation of inhibitors (Taherzadeh and Karimi 2007). The establishment of these parameters is of fundamental importance to define optimal conditions of hydrolysis to ensure the success of the process, in view of concerns taken into account since the hydrolyzate will be used as fermentation medium (Gírio et al. 2010). Thus, the knowledge about the cell wall chemical composition of agro-residues is very important in order to identify the raw materials with higher content of hemicellulose and bioprocesses using pentose sugars as substrates for the production of several chemical commodities (Saha 2003). The choice of the optimal hydrolysis conditions is very important for maximum yield of sugars and minimal formation of toxic compounds for the

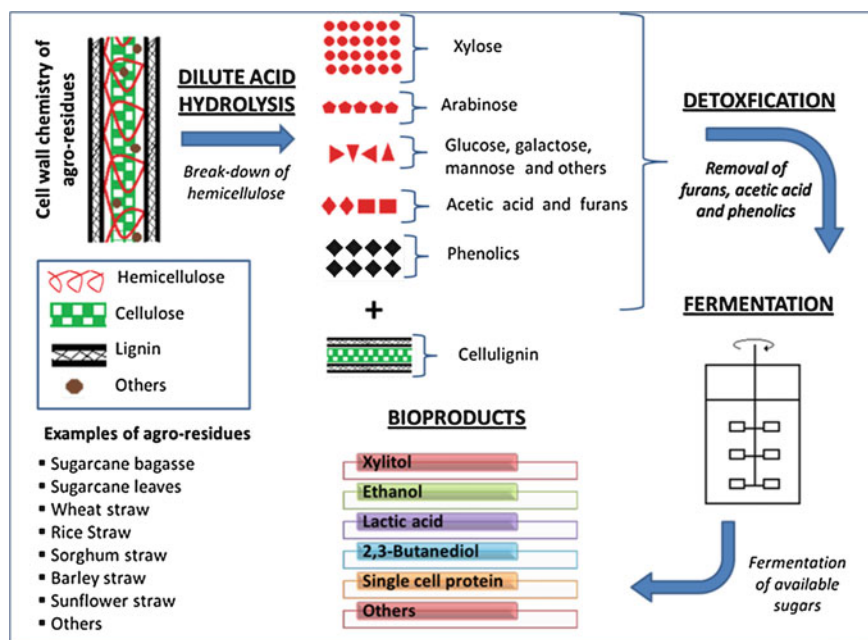


Fig. 2.1 Process configuration summarizing the dilute acid hydrolysis of various agro-residues into monomeric constituents and their conversion into value-added products

utmost production of compounds after fermentation reaction. This should be a low-cost process to ensure the sustainability of this technology and successful agro-residual feedstock management (Mantanis et al. 2000; Mussatto and Teixeira 2010; Chandel et al. 2010a). In this context, designing of reactors or changes in their configuration is an important consideration for the maximum de-polymerization of hemicellulose during dilute acid hydrolysis (Mosier et al. 2005; Thaezadeh and Karimi 2007; Lenihan et al. 2011). The emergence of plug-flow reactors (PFR), counter-current reactors, percolation reactors and shrinking bed counter current reactors have shown promising results for dilute acid mediated hydrolysis of agro-residues (Lee et al. 1999; Taherzadeh and Karimi 2007; Lenihan et al. 2011). Among all these process configurations, counter-current reactors have shown better results for the maximum hemicellulosics breakdown with fast reaction rates consequently producing low concentration of cell-wall derived inhibitors (Lee et al. 1999). However, a considerable amount of work is still required to establish a robust and reproducible technology for the maximum hemicellulose de-polymerization at industrial scale.

This chapter discusses the chemical nature and influential parameters of dilute acid hydrolysis of agro-residues, hydrolysis kinetics with sugar recovery, and the improvements in reactor configuration for maximum hemicelluloses de-polymerization into their monomeric constituents.

2.2 Cell Wall Chemistry of Various Agro-Residues

The cell wall consists of three main components: cellulose microfibrils (with characteristic distributions and organization), hemicellulose and lignin. Also, smaller amounts of pectin, protein, extractives and ash are found. The structure of these materials is very complex, and native biomass is generally resistant to chemical/enzymatic hydrolysis (Saha 2003).

The lignocellulosic biomass chemical composition differs with the source of plant species (Table 2.1). Cellulose is the main constitute(s) of bagasses and straws. The highest content of this fraction was found for sugarcane bagasse, an average of 42.8–45.0 %. Hemicellulose is the second major compound of these biomass sources, usually between 22 and 35 % of dry mass. Celluloses and most of the hemicelluloses are structural carbohydrates as they form the bulk of the plant cell's supporting structure (Ek et al. 2009). Coffee husk showed the highest hemicellulosic content (36.7 %) of the materials available, while sunflower stalks showed the lowest (20.2 %). In general, straws showed higher lignin content than others materials. For instance, sugarcane leaves straw showed high lignin content (26–32 %). According to Ek et al. (2009), the lignin contents in non-woody plants are, however, much lower (1–20 %) than in woody plant tissues. There is also a variation in cell wall composition between individual biomass sources of the same plant species, depending on the age of plant, genetic factors and growth conditions, e.g. climatologic and geographic factors (Ek et al. 2009). Cellulose is the most common polysaccharides in nature and consists of repeating units of cellobiose. It is a glucan polymer of D-glucopyranose units, which are linked together by β -(1 \rightarrow 4)-glucosidic bonds (Rowell et al. 2005). The number of glucose units in one wood cellulose molecule (i.e. the degree of polymerization) is at least 9,000–10,000 and possibly as high as 15,000 (Rowell et al. 2005). In this case, cellulose molecules aggregate with each other due to hydrogen bonding and form microfibrils, which are the building blocks of fibrils, and in turn build the cellulose fiber (Sjöström 1993).

In general, the hemicellulose fraction is a polymer that is composed of several different sugars like D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, L-rhamnose and is sometimes referred to by the sugars they contain, for example, galactoglucomannan, arabinoglucuronoxylan, arabinogalactan, glucuronoxylan, glucomannan, etc. The hemicellulose also contains acetyl and methyl substitute groups (Rowell et al. 2005). The degree of polymerization of hemicellulose is lower than cellulose, achieving an average of about 100–200 and the molecules can be highly branched (Rowell et al. 2005). Due to the combination of several sugars and for presenting majority part of amorphous structure, the hemicellulose is more soluble in water and easily degraded than cellulose. In the lignocellulosic materials the cellulose and lignin are intimately linked, because hemicellulose acts as glue between those fractions (Fengel and Wegener 1984).

Next to cellulose, lignin is the most abundant and important polymeric organic substance in the plant world. Lignin increases the mechanical strength properties

Table 2.1 Cell wall composition of various agro-residues (% of dry material)

Lignocellulosic source		Components					References
		Cellulose	Hemi-cellulose	Lignin	Extractives	Ash	
Bagasse	Sorghum	40.4	35.5	3.9	na	0.2	Dogaris et al. (2009)
	Sugarcane	42.8	25.9	22.1	6.1	1.4	Silva et al. (2010a, b, c)
		43.1	25.2	22.9	4.3	2.8	Rocha et al. (2012)
		43.8	27.0	22.6	3.9	2.0	Martín et al. (2011)
		45.0	26.0	20.0	na	2.1	Boussarsar et al. (2009)
Grains	Barley spent	27.6	32.5	13.4	12.9	3.4	Dehnavi, (2009)
	Brewery's spent	16.8	28.4	27.8	5.8	4.6	Mussatto et al. (2007)
		21.2	30.4	22.2	na	1.1	Duarte et al. (2008)
	Coffee spent	8.6	36.7	na	na	1.6	Mussatto et al. (2011)
Husk	Oat	29.3	28.4	22.2	na	4.5	Tamanini et al. (2004)
	Rice	21.5	23.1	14.6	na	na	Megawati et al. (2011)
Straw	Corn	34.4	29.0	17.2	na	na	Bura et al. (2009)
	Rice	43.4	22.9	17.2	na	11.4	Roberto et al. (2003)
		35.1	24.0	25.4	na	na	Téllez-Luiz et al. (2002)
	Sugarcane	40.8	30.8	25.8	na	2.6	Mouta et al. (2011)
		33.6	28.9	31.8	na	5.7	Silva et al. (2010a, b, c)
	Wheat	33.0	33.0	20.0	na	na	Canilha et al. (2006)
		42.7	34.3	18.4	3.0	na	Cheng et al. (2009)
Others	Sunflower stalks	33.8	20.2	17.3	6.9	9.6	Ruiz et al. (2008)

na not available

to such an extent that huge plants such as trees with heights to even more than 100 m can remain upright (Fengel and Wegener 1984). Lignins are complex polymers consisting of phenyl propane units linked together by ether or carbon-carbon bonds (Brunow et al. 1999). Lignins can be classified in several ways, but they are usually divided according to their structural elements (Sjöström 1993). All wood lignins consist mainly of three basic building blocks of guaiacyl, syringyl, and p-hydroxyphenyl moieties, although other aromatic units also exist in many different types of woods. There is a wide variation of structures within different wood species. The lignin content of hardwoods is usually in the range of 18–25 %, whereas the lignin content of softwoods varies between 25 and 35 % (Rowell et al. 2005).

2.3 Bioconversion of Xylose and Other Hemicellulosic Sugars into Bioactive Products

Agro-industrial wastes/byproducts represent a large portion of biomass which does not compete with food production (Doherty et al. 2011). Considering the large amount of agro-industrial byproducts discarded, the development of a technological platform for the production of any value-added product has yet to be established on a large scale (Felipe et al. 1997).

The conversion of the hemicellulosic fraction to fermentable sugars is essential for its use in various biochemical processes (Chandel et al. 2010b; Gfrio et al. 2010). Due to the recalcitrant characteristic of agro-residues, a pretreatment step can depolymerise the hemicellulosic fraction into fermentable sugars such as xylose, glucose and arabinose (Mosier et al. 2005). These hemicellulosic-derived sugar solutions are used for the production of commercially significant products. A wide variety of pretreatment methods aiming at hemicellulose de-polymerization such as dilute acid hydrolysis, steam explosion, and liquid hot water pretreatment have been developed (Mosier et al. 2005). Among these methods, dilute acid mediated hydrolysis has been found more effective towards complete hemicellulose hydrolysis in short reaction times (Taherzadeh and Karimi 2007). Acid hydrolysis with dilute sulfuric acid under mild conditions has proven to be a method that is reliable, easy to operate and low cost (Shatalov and Pereira 2012).

Table 2.2 summarizes the examples of various bioproducts of commercial interest produced by microbial fermentation using the sugars derived from agro-residues.

The application of xylose in xylitol production has being widely studied. Xylitol is a polyalcohol with great importance in food, pharmaceutical and dental care industries because of its interesting properties, as its sweetness is metabolically independent of insulin and anticariogenic properties (Milessi et al. 2011). Branco et al. (2008) obtained a conversion of xylose to xylitol (0.87 g/g) using the yeast *Candida guilliermondii* in a bench reactor. Rodrigues et al. (2011) recently evaluated xylitol production (0.61 g/g) from *Pichia stipitis* YS-30 using corn stover acid hydrolysate. Hemicellulose hydrolysate from various agro-residues has shown great potential in other added value products such as ethanol (Chandel et al. 2007a; Mouta et al. 2011), citric acid (Kirimura et al. 1999), lactic acid (Ou et al. 2011), single cell protein (SCP) (Anupama and Ravindra 2000), and 2,3-butanediol (Zhao et al. 2011). Recently, Rabelo et al. (2011) evaluated the potential of hemicellulose-derived sugar solution for biogas production.

Looking at the potential of pentose sugars as fermentable feedstock for the production of commercially valuable products, the importance of pentose sugars recovery and subsequently their utilization in fermentation processes is highly remarkable.

Table 2.2 Dilute acid hydrolysis of various agro-residues for the production of hemicellulosic-derived products

Agro-residue	Conditions for acid hydrolysis	Sugars (g/L)	Inhibitors (g/L)	Reference
Rice straw	1.5 % H ₂ SO ₄ , 130 °C, 30 min, S: L = 1:10	Xylose, 17.2; Glucose, 4.3; Arabinose, 3.3	Acetate, 1.43; HMF, 0.15; Furfural, 0.25	Baek and Kwon (2007)
Wheat straw	1.85 % (w/v) H ₂ SO ₄ , 90 °C, 18 h, S: L = 1:20	Xylose, 12.80 ± 0.25; D-glucose, 1.70 ± 0.30; L -arabinose, 2.60 ± 0.21	Furfural, 0.15 ± 0.02; acetic acid, 2.70 ± 0.33	Nigam (2001)
Corn stover	2.13 % H ₂ SO ₄ , 180 min, 121 °C, S: L = 1:10	Xylose, 9.09; Glucose, 2.13; Arabinose, 1.01	Acetic acid, 1.48; Furans, 0.56; Phenolics, 0.08	Cao et al. (2009)
Sugarcane bagasse	2.5 % (v/v) HCl, 140 °C, 30 min, S: L = 1:10	Total reducing sugars (TRS), 30.29	Furans, 1.89; Phenolics, 2.75; Acetic acid, 5.45	Chandel et al. (2007a)
Brewary's spent grain	Combined severity, 1.94 (3 % (w/w) H ₂ SO ₄ , 130 °C, 15 min, S:L = 8 % w/w)	Xylose, 26.7; Arabinose, 12.8; Glucose, 4.0	Acetic acid, 1.5; Formic acid, 0.23; Furfural, 0.29; HMF, 0.02; Total phenolics 0.91	Carvalho et al. (2004)
Sugarcane leaves straw	130 °C, 2.9 % H ₂ SO ₄ w/v, S:L = 1:4, 30 min	Total reducing sugars (TRS), 56.5	Acetic acid, 3.19; Furfural, 0.56; HMF, 0.15	Mouta et al. (2011)
Sorghum straw	2 % H ₂ SO ₄ , 122 °C, 71 min	Xylose, 54.2; Glucose, 13.5; Arabinose, 12	Furfural, 0.2; acetic acid, 0.00	Sepúlveda-Huerta et al. (2006)
De-oiled rice bran	3.5 % v/v H ₂ SO ₄ , 120 °C, S:L = 1:10, 60 min	TRS, 38.50 ± 0.45	n.d.	Chandel et al. (2009)
Barley bran	3 % w/v H ₂ SO ₄ , 120 °C, S:L = 1:10, 60 min		n.d.	Cruz et al. (2000)

S:L solid:liquid ratio, n.d. not detected

2.4 Factors Influencing the Dilute Acid Hydrolysis of Agro-Residues

The achievement of high levels of sugar after pretreatment is a crucial factor for the commercial competitiveness of the use of lignocellulosic materials. Pretreatment in the form of dilute acid hydrolysis is one of the most important cost contributing factors in overall bioconversion processing of agro-residues (Yang and Wyman 2008; Chandel et al. 2010a). Furthermore, dilute acid hydrolysis facilitates the enzymatic hydrolysis of the remaining cellulosic fraction into glucose (Chandel et al. 2011b). Pretreatment of agro-residues with diluted acid has been extensively studied and found to be an efficient method for recovery of fermentable sugars (Laopainboon et al. 2010; Akpinar et al. 2009). Dilute acid hydrolysis has the advantage over concentrated acid hydrolysis due to equipment corrosion (Gírio et al. 2010). However, this process has the disadvantage of formation of cell wall-derived inhibitors such as furfural and 5-hydroxymethylfurfural (HMF), weak acids, phenolics and others evidencing the importance of the optimization of the conditions used in the dilute acid-based process (Yang and Wyman 2008; Chandel et al. 2011c).

The concentration of released sugars during pretreatment is directly dependent upon the type of lignocellulosic material, composition of substrates, temperature, time, acid concentration, solid-to-liquid ratio and the reactors employed in the process (Lee et al. 1999; Lenihan et al. 2011; Mosier et al. 2005; Taherzadeh and Karimi 2007; Xiang et al. 2003; Akpinar et al. 2009).

Table 2.3 shows the effect of influencing factors on sugars recovery after hemicellulosics hydrolysis from a variety of agro-residues. The cell wall composition of the agro-residues and the operational conditions directly influence the recovery of sugars (Shatalov and Pereira 2012). Akpinar et al. (2009) found that two different lignocellulosic materials when subjected to similar hydrolytic conditions, showed different levels of xylose recovery. Biomass with high lignin content released a smaller amount of fermentable sugars due to its structural compactness. Studies carried out at our laboratory for dilute sulfuric and oxalic acid hydrolysis of sugarcane bagasse showed efficient hydrolysis of hemicellulose (more than 80 % sugar recovery). Figure 2.2 shows the scanning electron microscopic (SEM) analysis of sulfuric acid and oxalic acid pretreated sugarcane bagasse.

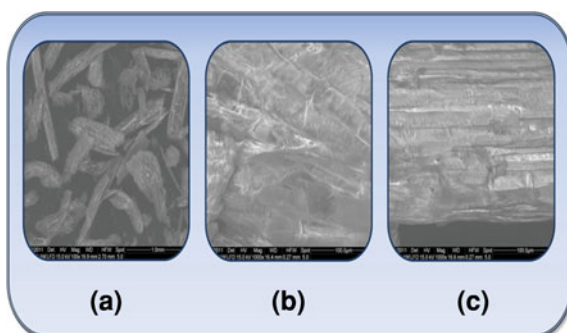
A clear-cut distinction is visible in the cell wall compactness of sugarcane bagasse after pretreatment compared with native sugarcane bagasse. Dilute acids act mechanistically on hemicellulose making the overall structure quite disorganized due to the disruption of hemicellulose. Sulfuric acid is the most commonly used acid for the pretreatment of agro-residues. Laopaiboon et al. (2010) tested different acids for sugarcane bagasse hydrolysis and found the maximum sugar recovery with HCl. Li et al. (2008) used double acid hydrolysis (HCl and H₂SO₄) for the sugars recovery from lignocellulosic waste. Rocha et al. (2011) used a mixture of many acids for the hydrolysis of sugarcane bagasse and reported more than 90 % hydrolysis of the hemicellulosic fraction.

Table 2.3 Dilute acid hydrolysates of various for the production of various industrially significant products by microbial fermentation

Agro-residue hydrolysate	Sugars released (g/L)	Fermenting microorganisms	Production profile of compounds (g/g or g/L)	References
Corn stover	Glucose, 2.39; Xylose, 21.50; Arabinose, 5.12	<i>Pichia stipitis</i> YS-30	Xylitol (0.61 g/g)	Rodrigues et al. (2011)
Wheat straw	Xylose, 37	<i>Candida guilliermondii</i> FTI 20037	Xylitol (0.59 g/g)	Canilha et al. (2008)
Sugarcane bagasse	Xylose, 30	<i>C. guilliermondii</i>	Xylitol (63 % conversion)	Silva et al. (2007)
Sugarcane bagasse	Xylose, 30	<i>C. guilliermondii</i> FTI 20037	Xylitol (0.58 g/g)	Carvalho et al. (2007)
Sugarcane bagasse	Xylose, 20	<i>Candida shehatae</i> NCIM 3501	Ethanol (0.48 g/g)	Chandel et al. (2007a)
Groundnut shell	Total sugars, 57.5	<i>P. stipitis</i> NCIM 3498	Ethanol (23.5 g/L)	Gajula et al. (2010)
Wheat straw	D-xylose, 45.00 \pm 0.33; D-glucose, 6.40 \pm 0.21; L-arabinose 9.00 \pm 0.12	<i>P. stipitis</i> NRRL Y-7124	Ethanol (0.41 g/g)	Nigam (2001)
Corn cob	D-glucose, 39.0 \pm 1.5 g/k of corn cob; D-Xylose 233 \pm 6.7 g/kg of corn cob	<i>Rhizopus oryzae</i> GY18	Lactic acid (355 g/kg of corn cob)	Guo et al. (2010)
Dried distillers grain (DDG)	na	<i>Aspergillus niger</i> ATCC 9142	Citric acid (5.25 g/kg of DDG)	Xie and West, (2009)
Sugarcane bagasse	D-Xylose, 47.2 \pm 0.82; D-Glucose, 4.5 \pm 0.17; L-Arabinose, 6.2 \pm 0.29	<i>Candida longirostris</i> RLJ Y-019	Single cell protein (0.4 g/g)	Nigam (2000)

na not available

Fig. 2.2 Scanning electron microscopic (SEM) analysis of sugarcane bagasse: native (a), dilute sulfuric acid pretreated (b) and dilute oxalic acid pretreated (c)



Among the factors that influence the efficiency of acid hydrolysis, temperature, reaction time and acid concentration are the most widely investigated factors. However, some authors investigated the influence of particle size of biomass and solid/liquid ratio (Kapdan et al. 2011). The acid concentration is considered one of the most important factors regarding the release of sugars. High concentrations of acid may decompose the hemicellulosic structure, producing inhibitors and also causing damage to the equipment used. Therefore, an appropriate acid concentration is essential for acid hydrolysis of lignocellulose at industrial scale (Taherzadeh and Karimi 2007).

Temperature is also a crucial factor that affects directly the degradation of sugars into inhibitors, which eventually affect microbial metabolism (Akpinar et al. 2009; Chandel et al. 2007a). Temperature is directly connected to the energy waste of the process (Kim et al. 2011). In general, it is observed that mild temperature led to a significant recovery of sugars while higher temperatures caused more sugar degradation, aiding the formation of inhibitors (Yang and Wyman 2008).

According to Gírio et al. (2010), sulphuric acid/hydrochloric acid concentrations for hemicellulose hydrolysis are in the range of 0.5–1.5 % and temperatures between 121 and 160 °C. However, there is no direct recipe or formula which can be considered the same for all agro-residues. The pretreatment conditions will depend on the type and species of the used vegetal biomass. Canilha et al. (2011) found that temperature is the most important factor followed by acid concentration and time. Neureiter et al. (2002) found that the acid concentration is the most significant factor for hemicellulose hydrolysis. During acid pretreatment, more severe processes cause fast sugar degradation and thus yield poor hydrolytic efficiency (Bösch et al. 2010).

2.5 Dilute Acid Hydrolysis of Various Agro-Residues

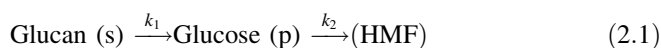
The use of diluted acids to break down the biomass structure and recovery of the hemicelluloses derived sugars have been studied extensively with varieties of agricultural residues (Table 2.3). Rodrigues et al. (2010) obtained approximately

74 % xylose yields from sugarcane bagasse at 130 °C for 10 min using 100 mg of sulfuric acid per gram of bagasse. Sugarcane leaves straw was submitted to dilute acid hydrolysis under the optimized conditions (130 °C, 2.9 % w/v sulfuric acid, solid:liquid ratio 1:4, and 30 min of residence time) and produced 56.5 g/L total reducing sugars (Mouta et al. 2011). Akpinar et al. (2009) found the optimized set of conditions of 120 °C, 30 min and 4 % acid concentration and 133 °C, 27 min and 4.9 % of acid for the hydrolysis of sunflower stalk and tobacco stalk, respectively. Kim et al. (2011) reported the best conditions (150 °C, 16.9 min and 1.16 % of acid concentration) for the maximum hemicellulose hydrolysis of barley straw. Roberto et al. (2003) studied the parameters for diluted acid hydrolysis of rice straw and reported the best conditions (1 % H₂SO₄, 27 min at 121 °C) for maximum hydrolysis.

Rahman et al. (2006) evaluated the production of xylose from oil palm empty fruit bunch fiber using sulfuric acid. Optimum conditions (6 % H₂SO₄ concentration, 120 °C, 15 min) produced 29.4 g/L xylose concentration. However, Zhang et al. (2012) investigated conditions of combined dilute acid-catalyzed hydrolysis of oil palm empty fruit bunch for the optimum production of xylose. Maximum xylose yield (91.3 %) was obtained after hydrolysis catalyzed by 0.5 % (w/v) of H₂SO₄ and 0.2 % (w/v) of H₃PO₄ at 160 °C at a liquid to solid ratio of 20 mL/g for 10 min. In this study, the authors concluded that combined use of H₂SO₄ and H₃PO₄ showed a synergistic effect on improved hemicelluloses hydrolysis as compared to H₂SO₄ alone. Herrera et al. (2003) evaluated the production of xylose (16.2 g/L) from sorghum straw using HCl under the optimized set of conditions 6 % HCl, 122 °C for 70 min. Mussatto and Roberto (2005) carried out statistical optimization studies for dilute acid hydrolysis of brewer's spent grain and found the best conditions (liquid/solid ratio of 8 g/g, 100 mg H₂SO₄/g of dry matter, 17 min) which yielded 92.7 % extraction of hemicellulosic sugars.

2.6 Some Aspects of Kinetics of Dilute Acid Hydrolysis

The kinetics of dilute acid hydrolysis of agro-residues mainly depends upon the temperature of reaction, acid concentration, time, substrate concentration and substrate composition (Mosier et al. 2005; Taherzadeh and Karimi 2007). There are two different phases involved in dilute acid hydrolysis—solid phase (agro-residues) and liquid phase (dilute acid-catalyst). Saeman (1945) initially proposed the kinetic model for the hydrolysis of Douglas-fir wood. This model was found as an irreversible pseudo-homogeneous first order reaction. In fact, this model was based on the cellulose conversion into glucose followed by its conversion into decomposition products:

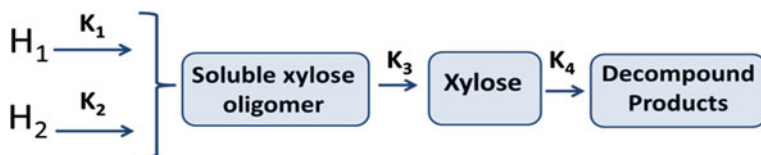


K_1 Rate of glucan conversion into glucose

K_2 Rate of glucose decomposition into hydroxyl methyl furfural (HMF)

Both reactions can be considered as first order and irreversible. This model can also be considered for hemicelluloses hydrolysis. McMillan (1992) reported that hemicellulose hydrolysis at high temperature (more than 160 °C) is not homogeneous and has two types of kinetic patterns, i.e. fast hydrolysis and slow hydrolysis.

The kinetics of hemicellulose hydrolysis can be presented as follows (Lee et al. 1999):



where

H_1 Kinetics of hemicelluloses hydrolysis (easy to hydrolyse)

H_2 Kinetics of hemicelluloses hydrolysis (difficult to hydrolyse)

Grohman et al. (1986) proposed that the dilute acid hydrolysis of hemicellulose is a pseudo-homogenous first order reaction consisting of a fast hydrolyzing reaction and a slow hydrolyzing reaction. Lenihan et al. (2011) described the hemicellulose hydrolysis as follows:



Monomers (xylose or other sugars) concentration (M) is a function of time (t) which can be represented as:

$$M = [k_1 \cdot P_0 / k_2 - k_1](e^{-k_1 t} - e^{-k_2 t}) + M_0 e^{-k_2 t} \quad (2.2)$$

where

M Monomer concentration (g/L)

P Polymer concentration (g/L)

M_0 Initial monomer concentration (g/L)

Consider that initial monomer concentration (M_0) is equal to zero, then Eq. (2.2) can be represented as (Lenihan et al. 2011):

$$M = [k_1 \cdot P_0 / k_2 - k_1](e^{-k_1 t} - e^{-k_2 t}) \quad (2.3)$$

As described before, there are two fractions in hemicellulose polymer, i.e. fast hydrolyzing and slow hydrolyzing. The ratio between both the fractions is α . This equation can be further simplified as (Lenihan et al. 2011):

$$M = \alpha[k_1.P_0/k_2 - k_1](e^{-k_1 t} - e^{-k_2 t}) \quad (2.4)$$

If hemicelluloses hydrolysis is 100 % fast hydrolyzing then $\alpha = 1 \text{ g/g}$.

2.7 Process Configurations Considering the Reactors used for Dilute Acid Hydrolysis

Dilute acid hydrolysis is probably one of the most common and largely explored methods to hydrolyse the hemicellulosic fraction of agro-residues or other lignocellulosic materials. Batch hydrolysis is the simplified process where substrate and dilute acid are mixed first followed by the reaction at high temperature for a certain period of time and recovery of the liquid fraction consisting of hemicellulosic-derived sugars in addition to cell wall-derived inhibitors. The acid-pretreated agro-residues are enzymatically digested to depolymerise cellulose into glucose.

Among all the available technologies, dilute acid hydrolysis followed by enzymatic hydrolysis by less expensive and more efficient cellulases has been found more promising towards the potential economics and environmental impact (Taherzadeh and Karimi 2007; Chandel et al. 2007b). Dilute acid hydrolysis was first demonstrated by Faith (1945) treating wood chips with dilute sulfuric acid (0.5 %) for 45 min at 11–12 bar pressure. Since then, a lot of developments have been seen aiming towards the development of a dilute acid hydrolysis process with less acid load, less reaction time and high temperature.

Batch processes of dilute acid hydrolysis generally show more than 80 % recovery of hemicellulose (xylose-rich hydrolysate containing arabinose, mannose, glucose and galactose) in addition to cell wall-derived inhibitors (furfurals, 5-hydroxy methyl furfural, weak organic acids, lignin derived phenolics and others). Batch hydrolysis can be carried out in a variety of vessels (Erlenmeyer flasks to stainless cylindrical steel vessels, Parr reactor, stirred tank reactor, rotating drum reactor, etc.). Lignocellulosic material and dilute acid are added in Erlenmeyer flasks or cylindrical vessels made of stainless steel which are kept in autoclave, Parr reactor or oil bath reactor for reaction at higher temperatures. The required temperature in a Parr reactor, stirred tank reactor and drum reactors is approached by providing heat or cooling water from an outside source through the jacket. Figure 2.3 shows the examples of vessels/reactors used for dilute acid hydrolysis at the Engineering School of Lorena, University of Sao Paulo (USP), Lorena, São Paulo, Brazil. Dilute acid hydrolysis is carried out in two stages.

2.7.1 First-Stage Dilute Acid Hydrolysis

The lignocellulosic material is first placed in contact with dilute sulfuric acid (0.75 %) and heated to approximately 50 °C, then transferred to the first-stage acid



Fig. 2.3 Systems explored for dilute acid hydrolysis of various agro-residues at Engineering School of Lorena (EEL), University of Sao Paulo, Lorena. **a** Large reactor of capacity 1,000 L. **b** Medium size rotator reactor. **c** Autoclave equipped for acid hydrolysis of biomass. **d** Parr reactor. **e** Oil bath reactor with stainless steel made hydrolytic vessels. **f** Medium size static reactor

impregnator where the temperature is raised to 190 °C. Approximately, 80 % of the hemicellulose and 29 % of cellulose are hydrolyzed in the first reactor. The hydrolysate is further incubated at a lower temperature for a residence time of 2 h to hydrolyse most of the oligosaccharides into monosaccharides followed by the separation of solid and liquid fractions (Chandel et al. 2007b). The solid material is then again washed with plenty of water to maximize sugar recovery. The separated solid material is sent to the second-stage acid hydrolysis reactor. Figure 2.4 shows the configuration outline of batch processes for acid hydrolysis of lignocellulosic materials.

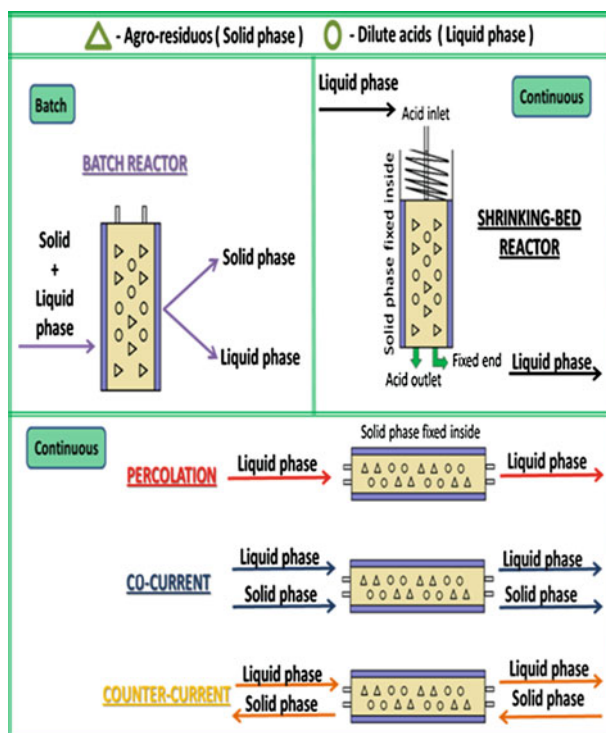


Fig. 2.4 Modified reactors configured for batch and continuous hydrolysis of agro-residues (Batch reactor, continuous reactors: counter-current, percolation reactor, plug-flow and shrinking-bed reactor)

2.7.2 Two-Stage Dilute Acid Hydrolysis

In the two-stage dilute acid hydrolysis process, first, biomass is treated with dilute acid at relatively mild conditions during which the hemicellulose fraction is hydrolyzed, and the second stage is normally carried out at a higher temperature for depolymerisation of cellulose into glucose (Nguyen et al. 2000). The liquid phase, containing the monomeric sugars is removed between the treatments, thereby avoiding degradation of monosaccharides formed. Sanchez et al. (2004) carried out the two-stage dilute acid hydrolysis using Bolivian straw material, *Paja brava*. In the first stage, *P. brava* was pretreated with steam followed by dilute sulfuric acid (0.5 or 1.0 % by wt.) hydrolysis at temperatures between 170 and 230 °C for a residence time between 3 and 10 min. The highest yield of hemicellulose-derived sugars was found at a temperature of 190 °C, and a reaction time of 5–10 min, whereas in second stage hydrolysis considerably higher temperature (230 °C) was found for hydrolysis of the remaining fraction of cellulose.

The two-stage dilute acid hydrolysis process is generally preferred over the first-stage dilute acid hydrolysis process due to less energy requirements,

minimization of sugars degradation and less derivation of inhibitors (Nguyen et al. 2000). Batch hydrolysis processes are most commonly employed for the hydrolysis of lignocellulosic materials. However, continuous processes for dilute acid hydrolysis have also been employed.

2.7.3 Continuous (Percolation Reactor, Plug-Flow Reactor, Counter-Current Reactor, Shrinking-Bed Reactor)

Figure 2.4 describes the configuration outline of the continuous dilute acid hydrolysis process employed for the acid hydrolysis of agro-residues.

2.7.3.1 Plug-Flow Reactor

Figure 2.4 shows the conceptual diagram of Plug flow reactor (PFR). In a PFR, it is quite difficult to control short residence time of biomass pretreatment (range of few seconds). Low concentration of acids is required in PFR in conjunction with high temperature (200–240 °C). Heat transfer limitations are also apparent due to uneven reaction within biomass that eventually reduces the overall sugar yield. In general, 50–70 % yield of sugars are obtained in PFRs (Lee et al. 1999; Taherzadeh and Karimi 2007).

2.7.3.2 Percolation Reactor (Packed-Bed Flow Through Reactor)

Percolation reactors are easy to use for dilute acid hydrolysis of lignocellulosic biomass due to immovable biomass and liquid fraction. In the percolation reactor, sugars can be obtained as they are formed and thus minimize the chances of sugar degradation consequently releasing a high amount of sugars (Lee et al. 1999). Figure 2.4 shows the conceptual diagram of a percolation reactor. There are many benefits to using a percolation reactor. High lignocellulosic biomass-to-liquid ratio can be used in a percolation reactor. Hydrolysate is easily removed from the solid fraction. An optimized feeding of solid and liquid is an important parameter to get the high sugars yield in the reactor. Slow feeding of lignocellulosic material will cause high sugar degradation while very fast feeding will leave the substrate untreated. In both circumstances, low sugar yield is obtained. On the basis of kinetics of hydrolysis reaction, a percolation reactor can be divided into two types: (1) a step change of temperature and optimum temperature difference, and (2) a two-stage reverse-flow percolation reactor. The former percolation strategy constituted two different basic characteristics (fast-hydrolysing and slow hydrolyzing reactions). Temperature change during the process, particularly a step change from uniform low to uniform high, showed the improved results (Lee et al.

1999). In a two-stage reverse flow percolation reactor, the biomass is first pre-treated at low temperature followed by high temperature reaction. The striking difference between a step-change and two-stage reverse flow percolation reactor is stream from high temperature is again exposed to fresh biomass at low temperature. The treated solid residue in this reactor is then treated with fresh acid at high temperature. This process is regularly repeated (Lee et al. 1999; Taherzadeh and Karimi 2007).

2.7.3.3 Counter-Current Reactor

These reactors are specialized moving bed reactors in which the direction of solid and liquid are reversed. Figure 2.4 shows the conceptual diagram of a counter-current reactor. A high concentration of sugars is obtained in counter-current reactors. The major part of sugars is formed near the liquid outlet point. The stream moves relatively short distances before it is washed out of the reactor thus reducing the time period for the sugar degradation, eventually increasing the high sugars yield (Lee et al. 1999; Taherzadeh and Karimi 2007). These reactors offer great advantages over plug flow or percolation reactors.

2.7.3.4 Shrinking Bed Counter-Current Reactor

Continuous counter current reactors have the property of bed shrinking causing improvements in sugars recovery with minimized sugar degradation. The shrinking bed causes the change of solid velocity within the reactor which improves the hydrolysis efficiency (Lee et al. 1999). Figure 2.4 shows the conceptual diagram of a shrinking bed counter-current reactor.

2.8 Economics and Environmental Aspects

The major parameters which influence the cost of dilute acid hydrolysis of agro-residues are the cost of raw material, amount of catalytic agent (acid) and utility expenses (steam, cooling water, electricity and maintenance of reactors) (Yang and Wyman 2008). The cost impact of these parameters directly influences the sugar recovery, processing time and generation of inhibitors. An ideal dilute acid hydrolysed process is one which has minimum operational and functional cost while largely influencing sugars recovery with the least amount of inhibitors generation (Yang and Wyman 2008). Removal of inhibitors from acid hydrolysates prior to fermentation adds the extra cost in biomass conversion. A generalized procedural break-up of expenses in ethanol production from lignocellulosic feedstock(s) shows that the cost of raw material (almost 34 %) is the main important factor to be considered, followed by total pretreatment cost (17.5 %), boiler energy (8.5 %) and utilities and storage (5 %) (Viikari 2004). Among the

LCF, agro-residues such as sunflower stalk, *Brassica compestris* stalks, cotton stalks, sugarcane leaves, groundnut shell, etc., which have minimum food/feed value and commercial applications would be of paramount importance.

Dilute acid hydrolysis of agro-residues in batch processes usually done using low concentration of acids, high temperature, and different time variations eventually release moderate amounts of sugars recovery (80–85 %) with considerable amount of cell wall derived inhibitors (Canilha et al. 2011). Dilute acid hydrolysis using modified continuous reactors (plug flow, percolation, counter-current and shrinking-bed) generally occur at high temperature (200–240 °C) for a short time (less than 1 min) using low acid concentration (Lee et al. 1999). Counter-current operations could be more economic in terms of yielding high amounts of sugars in short times with less operational cost (Lee et al. 1999). National Renewable Energy Laboratory (NREL)-based process engineering studies have developed a fully-integrated and mature material balance and financial modules (ASPEN PLUS) process simulation which can provide the net economic analysis of dilute acid hydrolysis of various agro-residues (Mosier et al. 2005).

With regards to net impact of dilute acid hydrolysis-based protocols on the environment, it can be stated that these processes are not very environmentally friendly (Taherzadeh and Karimi 2008). However, a much diluted concentration of acids is used in dilute acid hydrolysis of agro-residues. In addition to acid load, a high temperature range also poses a negative effect and an overall impact on the environment. Hemicellulase enzyme-based catalysed processes certainly have advantages over acid catalysed processes (Gírio et al. 2010). However, looking at the high sugars recovery in short time periods, dilute acid hydrolysis is still considered as a favorite compared to enzyme-based processes for hemicellulose break-down. Considering less acid load at high temperature is a preferred method since it causes less environmental pollution compared with strong acid hydrolysis. Another significant advantage using dilute acid hydrolysis is that generation of a low amount of inhibitors eventually requires milder detoxification methods to eliminate the inhibitors.

2.9 Conclusion and Future Recommendations

Agro-residues constitute the important part of total biomass available on earth for their readily available application in bioconversion systems. However, pretreatment of agro-residues with dilute acid hydrolysis is an important step for their fullest utilization. Dilute acids catalyze the hemicellulose degradation into simpler constituents and thus increase the amenability of cellulolytic enzymes towards the hydrolysis of the cellulosic fraction into fermentable feedstock. During hemicellulose hydrolysis by dilute acid catalyzed processes, a number of inhibitors are also generated which hamper the fermentation reaction for the production of important metabolites by microorganisms. In the last 30 years, significant work has been carried out in order to establish the successful and reproducible

technological protocol for hemicellulose depolymerisation with fewer number of inhibitors. Parameters involved in dilute acid hydrolysis of agro-residues viz. acid load, substrate to liquid ratio, residence time and temperature play the decisive role in obtaining the maximum hydrolysis efficiency. Consideration of these parameters also depends upon the selection of raw material. Batch reactors have been used more often for agro-residues hydrolysis. However, various modifications in reactors have also been adopted in order to maximize hemicellulose hydrolysis within short time periods. Reactor modifications such as percolation, plug-flow, counter-current and shrinking bed have been used for acid hydrolysis of agro-residues. Counter-current reactors have shown improved results in some studies carried out at the National Renewable Energy Laboratory (NREL), Colorado, USA. Better understanding of kinetic models for their implication in these reactor modifications may further improve the hemicellulose hydrolysis. Economics and environmental impact are two important considerations for the selection of dilute acid hydrolysis-based pretreatment technology. In future, technologies based on robust optimization tools for dilute acid hydrolysis, finding the ideal acid or mixed dilute acids considering the basic parameters and suitable reactors would be the ultimate choice. Application of nano-particles-based membrane systems and their implication in hemicellulose hydrolysis may also provide better results in short times with fewer by-products.

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