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Subcritical CO2 shows no effect on liquid hot water pretreatment of poplar wood

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ABSTRACT

Pretreatment of lignocellulosic biomass is required for many biorefinery processes. Previous studies have described hydrolysis of hemicelluloses by using liquid hot water (LHW) pretreatment. We evaluated the effect of carbonic acid originating from pressurized carbon dioxide during LHW pretreatment of poplar. The conditions applied covered temperatures from 120 to 200 °C, pretreatment times from 5 to 240 min and pressures from 1.0 to 2.2 MPa CO_2 or N_2. The pressure and the type of gas (CO_2 or N_2) did not have an effect on production of acetic acid, which functioned as a marker of progress of biomass hydrolysis. Results suggested that the presence of carbonic acid in the process does not significantly contribute to acidification. Deacetylation of lignocellulosic biomass can be achieved by LHW pretreatment irrespective of pressure and of gas type used, at the conditions tested.

1. Introduction

Considerable efforts have been made in the past decades towards investigating options to solve the fossil fuels depletion in combination with the increasing energy consumption and CO_2 emissions by our society (Goldemberg, 2007). This situation has led to a path where biorefineries are promising options, picturing a scenario with industrial activities using bio-based sources and biological operations as main trend (Hassan et al., 2019).

Potential biomass sources are side streams from well-established processes, waste and excess production from agricultural activities, forestry, and crops grown specifically for biorefinery purposes (Kim and Dale, 2004). Lignocellulosic biomass has been investigated intensively, with special interest in the disruption of its structure in order to increase the digestibility of the compounds present in its matrix (Hendriks and Zeeman, 2009; Kim and Holtzapple, 2006; Kumar and Sharma, 2017).

Lignocellulosic biorefinery processes typically consist of four main parts: pretreatment, enzymatic hydrolysis, fermentation and purification. Due to the complex matrix and structure of lignocellulosic biomass, the pretreatment and enzymatic hydrolysis steps usually produce derived substances, apart from the desired and expected sugars, which could limit the activity of the microorganisms and reduces the efficiency during the fermentation (Liu et al., 2019).

In this paper, we focus on pretreatment, which hydrolyses hemicelluloses and improves accessibility to cellulose for subsequent enzymatic hydrolysis (Kumar et al., 2009). Several pretreatment methods have been extensively studied, involving different technologies (Alvira et al., 2010; Mosier et al., 2005b). By using high temperatures and pressures in liquid hot water (LHW) pretreatment, it is possible to hydrolyse and dissolve hemicelluloses, while partially solubilising the lignin with almost no influence on the cellulose fibres (Garrote et al., 1999; Liu and Wyman, 2005; Zhuang et al., 2016). Optionally, acids or other catalysts can be applied to shorten reaction time or decrease temperature and pressure conditions (Cybulska et al., 2013; Esteghlalian et al., 1997; Hu and Ragauskas, 2012). For a green process, one would like to take out and reuse such catalysts. However, acid catalysts usually have to be neutralised to allow subsequent enzymatic hydrolysis, leading to alkali costs and to waste salts that can hardly be recovered. Therefore, using carbon dioxide as volatile (and hence recyclable) acid catalyst has been proposed as a green alternative pretreatment method, due to decrease on pH promoted by the production of carbonic acid (Magalhães da Silva et al., 2014; Morais et al., 2015).

The use of supercritical CO_2 has been extensively studied for pretreatment purposes (Alinia et al., 2010; Kim and Hong, 2001; Luterbacher et al., 2010; Narayanaswamy et al., 2011). It has been reported that supercritical CO_2 easily penetrates cellulose such that explosion caused by depressurization increases accessible surface area in cellulose for enzymatic hydrolysis. This is an alternative to steam

explosion, but requires no increase in temperature (Zheng et al., 1995). Compared to inert gases (nitrogen, helium), carbon dioxide showed more effective glucose yield when pretreating cellulose (Zheng et al., 1998). However, the use of supercritical CO_2 entails certain limitations at industrial scale due to the level of pressure utilized (Agbor et al., 2011).

At pressures below critical (7.4 MPa), CO_2 use can be considered a modification of LHW pretreatment. In the literature, however, there is no agreement on the influence of subcritical CO_2. Rogalinski et al. (2008) found no change in the solubilisation of lignocellulosic material by using CO_2 during LHW treatment. In addition, McWilliams and van Walsum (2002) also reported no different outcome on xylose recovery when carbonic acid was present during LHW treatment of aspen wood. On the other hand, other authors noticed enhancement of corn stover hydrolysis from higher values of xylose and xylan oligomers obtained in presence of CO_2 (van Walsum and Shi, 2004), and even a kinetic model has been proposed for the hydrolysis of wheat straw in water at high pressure CO_2 (Relvas et al., 2015). One reason for these discrepancies is that experimental conditions varied, including the type of biomass used, and another is that the performance of pretreatment is judged from the concentration of unstable reaction products or from the performance of subsequent enzymatic hydrolysis.

To understand better the influence of CO_2 on LHW pretreatment, we aim to quantify pretreatment on basis of acetic acid formation. Acetic acid originates from cleavage of acetyl groups in hemicelluloses, and undergoes no subsequent reaction. Most of the previous studies on LHW pretreatment are focused on the monosaccharides release (mainly xylose) as preeminent indicator of the degradation of hemicelluloses (Laser et al., 2002; Mosier et al., 2005a; Negro et al., 2003; Pérez et al., 2008). In this work, acetic acid is considered as predominant indicator of hemicellulose hydrolysis. It is a stable compound, and the main compound contributing to acidity in conventional LHW pretreatment.

For the current study, poplar wood was selected as relevant lignocellulosic biomass type, because it has been widely studied already and has a high acetyl content. Release of acetyl groups from hemicelluloses and depolymerisation of hemicellulose typically occur at 170–190 °C, whereas cellulose hydrolysis occurs at temperatures above 200 °C (Thomsen et al., 2006; Weil et al., 1997). Focusing on hemicellulose hydrolysis, and therefore acetic acid release, the conditions applied in this work during this hydrothermal pretreatment cover temperatures between 120 and 200 °C, pretreatment times from 5 to 240 min and subcritical pressures of CO_2 or N_2 up to 2.2 MPa. Compressed nitrogen is designated as inert gas, in order to provide a comparable reference and assess the possible catalytic effect of carbon dioxide on acetic acid release during LHW pretreatment.

2. Materials and methods

2.1. Materials

Acetic acid ($\geq 99.7\%$) was from Sigma-Aldrich. The lignocellulosic material (poplar wood with stems and bark) was provided by Woodoo GmbH & Co. KG, through the Bioprocess Pilot Facility B.V. Samples were pre-milled in a bench mill and sieved to a mesh size of ~1 cm.

2.2. Pressurized reactor

A pressurized reactor was used, which consists of a stainless steel 100 mL vessel with an electrical heating and an agitation system. The reactor was connected to independent inlet lines for CO_2 and N_2, and to two outlet lines for gas, one of them with a safety relief valve set at 2.2 MPa. The reactor is depicted in Fig. 1.

The reactor vessel was filled with 5 g of biomass (on wet basis) and 45 g of water. Insulation fabric was placed around. Before starting the experiments, all pipes and valves were shortly flushed with CO_2 or N_2, assuming negligible evaporation of water. Then, agitation was switched
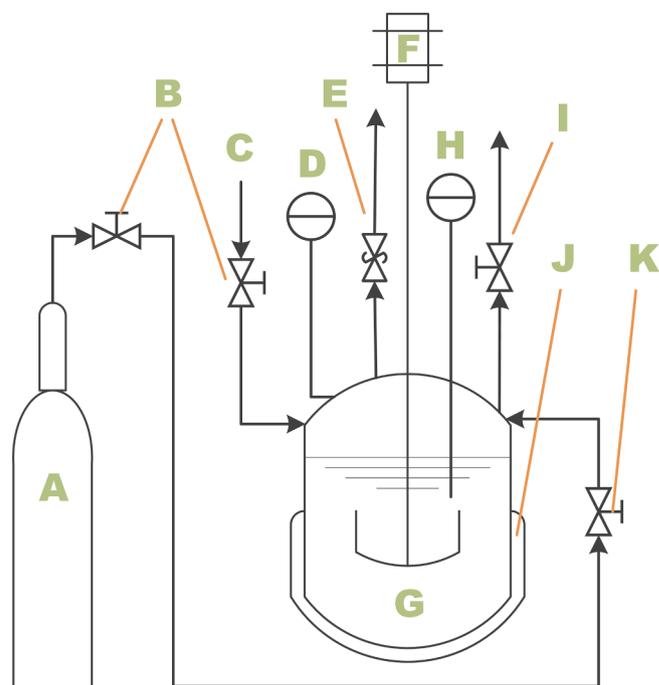

Fig. 1. Scheme of the pressurized reactor setup. A: Compressed CO_2; B: gas valves (for CO_2 and N_2); C: compressed N_2 line; D: pressure meter; E: pressure relief valve; F: motor for stirrer; G: pressurized reactor; H: temperature controller; I: outline gas valve; J: heating system; K: extra CO_2 valve.

on and the pressure of gas (CO_2 or N_2) was progressively increased until the desired "initial pressure" was reached in the reactor vessel. After 30 min (estimated time to reach liquid/gas equilibrium), the heating system was switched on, increasing the temperature inside the vessel up to the set point (see Supplementary data for heating times), which increased the pressure, up to the "pretreatment pressure" value. The reactor was kept at the set temperature by the temperature controller during a time that will be indicated as "pretreatment time". Subsequently, the heating system was switched off and the insulating fabric was removed from the reactor, allowing a fan to speed up cooling of the vessel (see Supplementary data for cooling times). Once the reactor was cooled to room temperature, the outline gas valve was opened to proceed with decompression. When ambient pressure was reached, the reaction suspension was centrifuged and filtered (Whatman 0.2 μm), and the pH of the liquid fraction was measured. Several liquid samples were taken and stored at −20 °C until further analysis by HPLC, while the solids were discarded.

2.3. Analysis of samples

Acetic acid was analysed on a Waters HPLC system with a Bio-Rad HPX-87H column (300 × 7.8 mm) at 59 °C. Phosphoric acid (1.5 mmol/L at 0.6 mL/min) was used as eluent. Quantification was by refraction index detection (Waters 2414) using external standards. Volumes of injection of standards and samples were 10 μL at 15 °C. All samples were analysed in duplicate for acetic acid content.

2.4. Severity factor

Overend and Chornet (1987) have proposed a severity factor (log R_0) to combine parameters applied to a pretreatment process:

$$R_0 = \exp\left(\frac{T - 100}{14.75}\right) \cdot t$$

T is the temperature in °C and t is the pretreatment time in minutes. This severity factor is used to represent the results of the present study.

Table 1

Pretreatment conditions used during experiments for LHW of poplar.

Experiment	Temperature, °C	Time, min	Pressure, MPa	Gas type	Severity (log R_0)
P10	180	50	1.75	CO_2	4.054
P11	180	40	1.80	CO_2	3.958
P12	180	100	1.64	CO_2	4.355
P13	180	130	1.26	CO_2	4.469
P14	180	140	2.08	CO_2	4.502
P15	180	110	1.07	CO_2	4.397
P16	180	120	2.05	CO_2	4.435
P17	180	70	1.88	CO_2	4.201
P18	180	30	1.99	CO_2	3.833
P19	180	107	0.95	CO_2	4.385
P20	180	90	0.97	CO_2	4.310
P21	200	90	1.51	CO_2	4.899
P22	200	240	1.50	CO_2	5.325
P23	200	170	1.50	CO_2	5.175
P24	120	10	0.38	CO_2	1.589
P25	140	5	0.48	CO_2	1.877
P26	160	5	0.67	CO_2	2.466
P27	144	54	0.48	CO_2	3.031
P28	100	5	0.28	CO_2	0.699
P29	159	5	0.66	CO_2	2.436
P30	160	140	0.75	CO_2	3.913
P31	160	25	0.74	CO_2	3.165
P32	140	20	0.52	CO_2	2.479
P12N	180	125	1.34	N_2	4.452
P13N	180	130	1.14	N_2	4.469
P14N	180	120	1.92	N_2	4.435
P15N	180	120	1.01	N_2	4.435
P16N	180	120	1.77	N_2	4.435
P17N	180	70	1.76	N_2	4.201
P18N	180	30	1.79	N_2	3.833
P19N	180	120	0.97	N_2	4.435
P20N	180	90	0.97	N_2	4.310
P21N	200	90	1.49	N_2	4.899
P22N	200	240	1.50	N_2	5.325
P23N	200	170	1.51	N_2	5.175
P24N	120	5	0.35	N_2	1.288
P25N	140	5	0.44	N_2	1.877
P26N	160	5	0.64	N_2	2.466
P27N	128	50	0.35	N_2	2.545
P28N	100	5	0.28	N_2	0.699
P30N	159	60	0.66	N_2	3.515
P31N	160	30	0.68	N_2	3.244
P32N	140	20	0.47	N_2	2.479

3. Results and discussion

3.1. Effect of severity

During LHW treatment, in presence of CO_2 or N_2, different combinations of temperature and pretreatment time were applied to the lignocellulosic biomass, associated in the severity factor of the reaction conditions (see Table 1). Conditions applied covered severity values from 0.7 to 5.6 (log R_0). Fig. 2A shows that with increasing severity the concentration of acetic acid increased up to approximately 5.3 g/L, regardless the gas used. This maximum acetic acid concentration was obtained at log R_0 of 5.17, corresponding to 200 °C and 170 min. For beech wood LHW pretreatment, Nitsos et al. (2013) reported a similar trend at a severity range (log R_0) between 2.0 and 5.0, obtaining up to 3.4 g/L acetic acid. Analogous results were also obtained by Morais et al. (2014) when processing wheat straw, although they included higher pressures of CO_2 (closer to the critical point) within a narrower range of severity.

Furthermore, our results are in line with the absence of significant acetyl group release for LHW pretreatment of poplar below log R_0 values of 3.5 (Bouchard et al., 1991) and the trend observed for carbonated subcritical water pretreatment of switchgrass at higher temperatures (Dhamdere et al., 2012). Comparing results from this work with literature values of acetyl content of poplar (Kim et al., 2009)
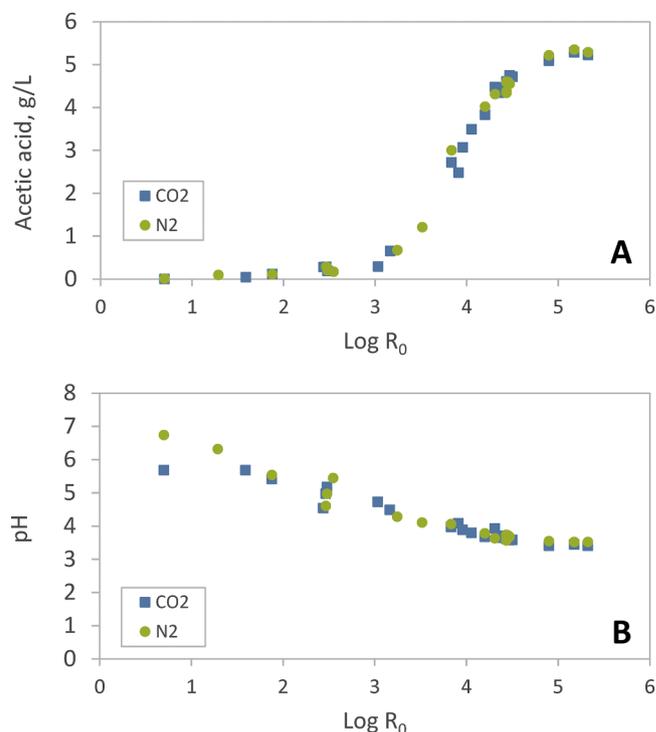

Fig. 2. Effect of severity on acetic acid release (A) and pH (B) for LHW pretreatment at pressures in the range from 1.01 to 2.08 MPa CO_2 or N_2.

suggests complete deacetylation of poplar at values of log $R_0 > 5$. However, that was not confirmed since the structure and composition of the solid fraction of the pretreated biomass was not analysed in this work. At less severe conditions, some acetyl groups remained in the solid phase linked to hemicelluloses, while part of it was bound to xylooligosaccharides (Garrote and Parajó, 2002; Kabel et al., 2007).

Like generally observed in studies on biomass pretreatment, higher severity promoted not only acetic acid release, but also release of other hydrolysis products such as xylose and glucose, and of their degradation products such as formic acid, furfural and 5-hydroxymethylfurfural (Kim et al., 2009). Data for these other compounds are available in the Supplementary material but will not be discussed, because the observed patterns are in line with those generally described in pretreatment literature and here. Still other components, such as lignin, were not measured, though.

3.2. Effect of pressure and gas type

Several initial subcritical pressure values of CO_2 and N_2 were applied (0.2, 0.4, 0.6, 0.8 and 1 MPa) at otherwise the same reaction conditions: 180 °C during approximately 2 h (log $R_0 \approx 4.4$). Pressures increased once the reactor was heated up, slightly more in case of CO_2 than in case of N_2, while the concentrations of acetic acid obtained in all these experiments were similar (see Fig. 3A). This outcome was opposite to those of some other studies in which hydrolysis of biomass increased in the presence of CO_2, although for different biomass types and at higher but still subcritical pressure values (Morais et al., 2015; Relvas et al., 2015; van Walsum and Shi, 2004; Zhang and Wu, 2013). Fig. 3A shows that the gas type (CO_2 or N_2) and its pressure during pretreatment have no significant effect on the hydrolysis of poplar.

3.3. Effect on pH

Fig. 2B shows a decrease in pH with severity, as expected on basis of increased carboxylic acid amounts at higher severity (Jacobsen and Wyman, 2002). These values of pH were measured at room
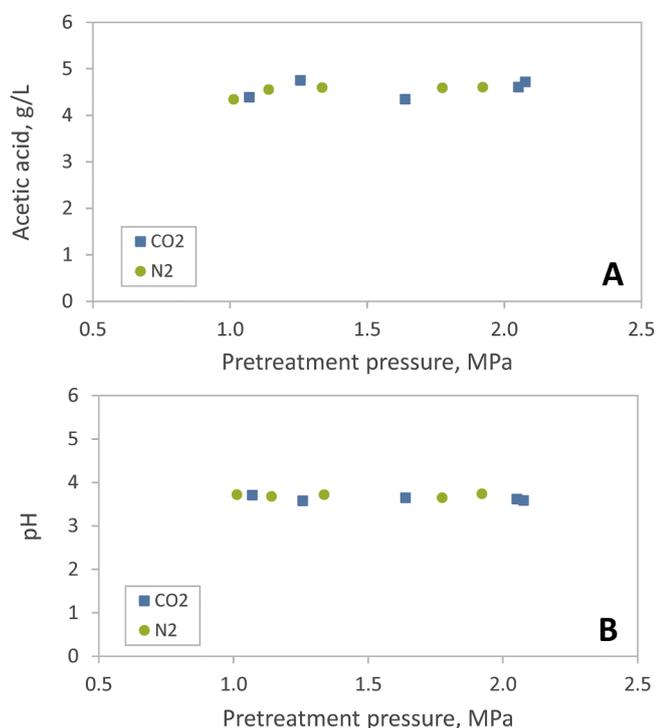
Fig. 3. Effect of pressure and gas type on acetic acid release (A) and pH (B) for LHW pretreatment performed at 180 °C and approximately 120 min (log $R_0 \approx 4.4$).

temperature, after cooling and filtering the liquid samples. Again, no difference is observed between using carbon dioxide and nitrogen during pretreatment, and pressure has no effect (Fig. 3B).

During LHW pretreatment of lignocellulosic biomass, the auto-ionization of water produces hydronium ions, which, in combination with the high temperatures, provokes hydrolysis of hemicelluloses, and therefore cleavage of acetyl groups, producing acetic acid. This acetic acid, and other carboxylic acids released such as uronic acids, contributes to the hydrolysis reaction, widely known as autohydrolysis (Garrote et al., 2002; Gírio et al., 2010). In addition, those carboxylic acids contribute to subsequent carbohydrate degradation towards other side-products (Mosier et al., 2005b). Although acetic acid is not yet present in the beginning of pretreatment, in previous studies of hydrothermal treatment, the hydronium ions generated from acetic acid were considered more important than those of water origin (Garrote et al., 1999; Gírio et al., 2010). The use of carbon dioxide during this process has been mentioned to enhance the hydrolysis by further lowering the pH due to the formation of carbonic acid (Luterbacher et al., 2012; Magalhães da Silva et al., 2014; Morais et al., 2015). Some authors suggested that the autocatalysis due to release of acetyl groups has similar influence as the presence of carbonic acid (McWilliams and van Walsum, 2002), while other researchers suggested that effect of dissociation of carbonic acid in water combined with the release of acetic acid from deacetylation of hemicelluloses is crucial for the hydrolysis of lignocellulosic biomass (Gurgel et al., 2014). At our conditions, CO_2 clearly plays no role in acidification.

At ambient conditions, an aqueous solution of 5 g/L acetic acid is at pH 3.0, according to $pK_a = 4.82$. The minimum pH in Fig. 2B is 3.4, corresponding to 0.5 g/L acetic acid and thus indicating the presence of buffering compounds. Their source might be minerals or proteins originating from the biomass. Other authors (Morais et al., 2014; van Walsum and Shi, 2004) found somewhat higher final values of pH, probably because their biomass contained less acetyl groups or more buffering compounds. At final (ambient) conditions, carbon dioxide does not contribute to low pH because of its low solubility. At 225 °C

and 5.4 MPa initial CO_2 pressure, it has been calculated that the pH of an aqueous CO_2 solution is 3.77 (van Walsum and Shi, 2004), suggesting that acetic acid is a stronger contributor to low pH than CO_2.

As a consequence, improvement of lignocellulosic biomass pretreatment should occur due to addition of acetic acid prior to LHW pretreatment. However, the literature does not report a clear picture on this (Laser et al., 2002; Lyu et al., 2019). Therefore, further research regarding the effect on acetyl group cleavage on hemicelluloses by initial addition of acetic acid to LHW pretreatment of lignocellulosic biomass could provide deeper understanding of this methodology. Besides, systematic studies of different reaction conditions and different biomass types might reveal why different studies find different effects of CO_2.

4. Conclusions

Liquid hot water pretreatment at log $R_0 > 5$ is an efficient methodology for deacetylation of hemicelluloses from poplar. Acetic acid released was proportional with the severity of the process but it has no direct relation with the pretreatment pressure up to 2 MPa, nor with the gas used for achieving this pressure. At the conditions applied, subcritical CO_2 does not affect acetic acid formation. Its role in acidification, even associated to the initial phase of pretreatment, is negligible. At different reaction conditions and with different types of biomass than tested in this work, CO_2 might still improve pretreatment.

CRediT authorship contribution statement

Jose M. Jimenez-Gutierrez: Methodology, Investigation, Writing - original draft. **Luuk A.M. van der Wielen:** Conceptualization, Supervision, Writing - review & editing. **Adrie J.J. Straathof:** Supervision, Methodology, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biteb.2020.100442.

References

Agbor, V.B., Cicek, N., Sparling, R., Berlin, A., Levin, D.B., 2011. Biomass pretreatment: fundamentals toward application. Biotechnol. Adv. 29, 675–685. https://doi.org/10.1016/j.biotechadv.2011.05.005.

Alinia, R., Zabihi, S., Esmaeilzadeh, F., Kalajahi, J.F., 2010. Pretreatment of wheat straw by supercritical CO2 and its enzymatic hydrolysis for sugar production. Biosyst. Eng. 107, 61–66. https://doi.org/10.1016/j.biosystemseng.2010.07.002.

Alvira, P., Tomás-Pejó, E., Ballesteros, M., Negro, M.J., 2010. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. Bioresour. Technol. 101, 4851–4861. https://doi.org/10.1016/j.biortech.2009.11.093.

Bouchard, J., Nguyen, T.S., Chornet, E., Overend, R.P., 1991. Analytical methodology for biomass pretreatment. Part 2: characterization of the filtrates and cumulative product distribution as a function of treatment severity. Bioresour. Technol. 36, 121–131. https://doi.org/10.1016/0960-8524(91)90169-K.

Cybulska, I., Brudecki, G., Lei, H., 2013. Hydrothermal pretreatment of lignocellulosic biomass. In: Gu, T. (Ed.), Green Biomass Pretreatment for Biofuels Production. Springer Briefs in Molecular Science Springer, Dordrecht, pp. 87–106. https://doi.org/10.1007/978-94-007-6052-3_4.

Dhamdere, R.T., Srinivas, K., King, J.W., 2012. Carbochemicals production from

switchgrass using carbonated subcritical water at high temperatures. In: 10th International Symposium on Supercritical Fluids, San Francisco, pp. 274–282.

Esteghlalian, A., Hashimoto, A.G., Fenske, J.J., Penner, M.H., 1997. Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. Bioresour. Technol. 59, 129–136. https://doi.org/10.1016/S0960-8524(97)81606-9.

Garrote, G., Parajó, J.C., 2002. Non-isothermal autohydrolysis of Eucalyptus wood. Wood Sci. Technol. 36, 111–123. https://doi.org/10.1007/s00226-001-0132-2.

Garrote, G., Dominguez, H., Parajo, J.C., 1999. Hydrothermal processing of lignocellulosic materials. Holz Roh Werkst. 57, 191–202.

Garrote, G., Domínguez, H., Parajó, J.C., 2002. Autohydrolysis of corncob: study of non-isothermal operation for xylooligosaccharide production. J. Food Eng. 52, 211–218. https://doi.org/10.1016/S0260-8774(01)00108-X.

Gírio, F.M., Fonseca, C., Carvalheiro, F., Duarte, L.C., Marques, S., Bogel-Łukasik, R., 2010. Hemicelluloses for fuel ethanol: a review. Bioresour. Technol. 101, 4775–4800. https://doi.org/10.1016/j.biortech.2010.01.088.

Goldemberg, J., 2007. Ethanol for a sustainable energy future. Science 315, 808–810. https://doi.org/10.1126/science.1137013.

Gurgel, L.V.A., Pimenta, M.T.B., Curvelo, A.A.d.S., 2014. Enhancing liquid hot water (LHW) pretreatment of sugarcane bagasse by high pressure carbon dioxide (HP-CO2). Ind. Crop. Prod. 57, 141–149. https://doi.org/10.1016/j.indcrop.2014.03.034.

Hassan, S.S., Williams, G.A., Jaiswal, A.K., 2019. Lignocellulosic Biorefineries in Europe: current state and prospects. Trends Biotechnol. 37, 231–234. https://doi.org/10.1016/j.tibtech.2018.07.002.

Hendriks, A.T.W.M., Zeeman, G., 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresour. Technol. 100, 10–18. https://doi.org/10.1016/j.biortech.2008.05.027.

Hu, F., Ragauskas, A., 2012. Pretreatment and lignocellulosic chemistry. Bioenerg. Res. 5, 1043–1066. https://doi.org/10.1007/s12155-012-9208-0.

Jacobsen, S.E., Wyman, C.E., 2002. Xylose monomer and oligomer yields for uncatalyzed hydrolysis of sugarcane bagasse hemicellulose at varying solids concentration. Ind. Eng. Chem. Res. 41, 1454–1461. https://doi.org/10.1021/ie001025.

Kabel, M.A., Bos, G., Zeevalking, J., Voragen, A.G.J., Schols, H.A., 2007. Effect of pretreatment severity on xylan solubility and enzymatic breakdown of the remaining cellulose from wheat straw. Bioresour. Technol. 98, 2034–2042. https://doi.org/10.1016/j.biortech.2006.08.006.

Kim, S., Dale, B.E., 2004. Global potential bioethanol production from wasted crops and crop residues. Biomass Bioenergy 26, 361–375. https://doi.org/10.1016/j.biombioe.2003.08.002.

Kim, S., Holtzapple, M.T., 2006. Effect of structural features on enzyme digestibility of corn stover. Bioresour. Technol. 97, 583–591. https://doi.org/10.1016/j.biortech.2005.03.040.

Kim, K.H., Hong, J., 2001. Supercritical CO2 pretreatment of lignocellulose enhances enzymatic cellulose hydrolysis. Bioresour. Technol. 77, 139–144. https://doi.org/10.1016/S0960-8524(00)00147-4.

Kim, Y., Mosier, N.S., Ladisch, M.R., 2009. Enzymatic digestion of liquid hot water pretreated hybrid poplar. Biotechnol. Prog. 25, 340–348. https://doi.org/10.1002/btpr.137.

Kumar, A.K., Sharma, S., 2017. Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. Bioresour. Bioprocess 4, 7. https://doi.org/10.1186/s40643-017-0137-9.

Kumar, P., Barrett, D.M., Delwiche, M.J., Stroeve, P., 2009. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Ind. Eng. Chem. Res. 48, 3713–3729. https://doi.org/10.1021/ie801542g.

Laser, M., Schulman, D., Allen, S.G., Lichwa, J., Antal, M.J., Lynd, L.R., 2002. A comparison of liquid hot water and steam pretreatments of sugar cane bagasse for bioconversion to ethanol. Bioresour. Technol. 81, 33–44. https://doi.org/10.1016/S0960-8524(01)00103-1.

Liu, C., Wyman, C.E., 2005. Partial flow of compressed-hot water through corn stover to enhance hemicellulose sugar recovery and enzymatic digestibility of cellulose. Bioresour. Technol. 96, 1978–1985. https://doi.org/10.1016/j.biortech.2005.01.012.

Liu, C.-G., Xiao, Y., Xia, X.-X., Zhao, X.-Q., Peng, L., Srinophakun, P., Bai, F.-W., 2019. Cellulosic ethanol production: progress, challenges and strategies for solutions. Biotechnol. Adv. 37, 491–504. https://doi.org/10.1016/j.biotechadv.2019.03.002.

Luterbacher, J.S., Tester, J.W., Walker, L.P., 2010. High-solids biphasic CO2-H2O pretreatment of lignocellulosic biomass. Biotechnol. Bioeng. 107, 451–460. https://doi.org/10.1002/bit.22823.

Luterbacher, J.S., Tester, J.W., Walker, L.P., 2012. Two-temperature stage biphasic CO2–H2O pretreatment of lignocellulosic biomass at high solid loadings. Biotechnol. Bioeng. 109, 1499–1507. https://doi.org/10.1002/bit.24417.

Lyu, H., Zhang, J., Zhou, J., Shi, X., Lv, C., Geng, Z., 2019. A subcritical pretreatment improved by self-produced organic acids to increase xylose yield. Fuel Process.

Technol. 195, 106148. https://doi.org/10.1016/j.fuproc.2019.106148.

Magalhães da Silva, S.P., Morais, A.R.C., Bogel-Łukasik, R., 2014. The CO2-assisted autohydrolysis of wheat straw. Green Chem. 16, 238–246. https://doi.org/10.1039/C3GC41870G.

McWilliams, R.C., van Walsum, G.P., 2002. Comparison of aspen wood hydrolysates produced by pretreatment with liquid hot water and carbonic acid. In: Finkelstein, M., McMillan, J.D., Davison, B.H. (Eds.), Biotechnology for Fuels and Chemicals. Humana Press, Totowa, NJ, pp. 109–121. https://doi.org/10.1007/978-1-4612-0119-9_9.

Morais, A.R.C., Mata, A.C., Bogel-Lukasik, R., 2014. Integrated conversion of agroindustrial residue with high pressure CO2 within the biorefinery concept. Green Chem. 16, 4312–4322. https://doi.org/10.1039/C4GC01093K.

Morais, A.R.C., da Costa Lopes, A.M., Bogel-Łukasik, R., 2015. Carbon dioxide in biomass processing: contributions to the green biorefinery concept. Chem. Rev. 115, 3–27. https://doi.org/10.1021/cr500330z.

Mosier, N., Hendrickson, R., Ho, N., Sedlak, M., Ladisch, M.R., 2005a. Optimization of pH controlled liquid hot water pretreatment of corn stover. Bioresour. Technol. 96, 1986–1993. https://doi.org/10.1016/j.biortech.2005.01.013.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M., 2005b. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour. Technol. 96, 673–686. https://doi.org/10.1016/j.biortech.2004.06.025.

Narayanaswamy, N., Faik, A., Goetz, D.J., Gu, T., 2011. Supercritical carbon dioxide pretreatment of corn stover and switchgrass for lignocellulosic ethanol production. Bioresour. Technol. 102, 6995–7000. https://doi.org/10.1016/j.biortech.2011.04.052.

Negro, M.J., Manzanares, P., Ballesteros, I., Oliva, J.M., Cabañas, A., Ballesteros, M., 2003. Hydrothermal pretreatment conditions to enhance ethanol production from poplar biomass. In: Davison, B.H., Lee, J.W., Finkelstein, M., McMillan, J.D. (Eds.), Biotechnology for Fuels and Chemicals. Humana Press, Totowa, NJ, pp. 87–100. https://doi.org/10.1007/978-1-4612-0057-4_7.

Nitsos, C.K., Matis, K.A., Triantafyllidis, K.S., 2013. Optimization of hydrothermal pretreatment of lignocellulosic biomass in the bioethanol production process. ChemSusChem 6, 110–122. https://doi.org/10.1002/cssc.201200546.

Overend, R.P., Chornet, E., 1987. Fractionation of lignocellulosics by steam-aqueous pretreatments. Philos. Trans. Royal Soc. A 321, 523–536. https://doi.org/10.1098/rsta.1987.0029.

Pérez, J.A., Ballesteros, I., Ballesteros, M., Sáez, F., Negro, M.J., Manzanares, P., 2008. Optimizing liquid hot water pretreatment conditions to enhance sugar recovery from wheat straw for fuel-ethanol production. Fuel 87, 3640–3647. https://doi.org/10.1016/j.fuel.2008.06.009.

Relvas, F.M., Morais, A.R.C., Bogel-Lukasik, R., 2015. Kinetic modeling of hemicellulose-derived biomass hydrolysis under high pressure CO2–H2O mixture technology. J. Supercrit. Fluids 99, 95–102. https://doi.org/10.1016/j.supflu.2015.01.022.

Rogalinski, T., Ingram, T., Brunner, G., 2008. Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures. J. Supercrit. Fluids 47, 54–63. https://doi.org/10.1016/j.supflu.2008.05.003.

Thomsen, M.H., Thygesen, A., Jørgensen, H., Larsen, J., Christensen, B.H., Thomsen, A.B., 2006. Preliminary results on optimization of pilot scale pretreatment of wheat straw used in coproduction of bioethanol and electricity. In: McMillan, J.D., Adney, W.S., Mielenz, J.R., Klasson, K.T. (Eds.), Twenty-seventh Symposium on Biotechnology for Fuels and Chemicals. Humana Press, Totowa, NJ, pp. 448–460. https://doi.org/10.1007/978-1-59745-268-7_37.

van Walsum, P.G., Shi, H., 2004. Carbonic acid enhancement of hydrolysis in aqueous pretreatment of corn stover. Bioresour. Technol. 93, 217–226. https://doi.org/10.1016/j.biortech.2003.11.009.

Weil, J., Sarikaya, A., Rau, S.-L., Goetz, J., Ladisch, C.M., Brewer, M., Hendrickson, R., Ladisch, M.R., 1997. Pretreatment of yellow poplar sawdust by pressure cooking in water. Appl. Biochem. Biotechnol. 68, 21–40. https://doi.org/10.1007/BF02785978.

Zhang, H., Wu, S., 2013. Subcritical CO2 pretreatment of sugarcane bagasse and its enzymatic hydrolysis for sugar production. Bioresour. Technol. 149, 546–550. https://doi.org/10.1016/j.biortech.2013.08.159.

Zheng, Y., Lin, H.-M., Wen, J., Cao, N., Yu, X., Tsao, G.T., 1995. Supercritical carbon dioxide explosion as a pretreatment for cellulose hydrolysis. Biotechnol. Lett. 17, 845–850. https://doi.org/10.1007/BF00129015.

Zheng, Y., Lin, H.M., Tsao, G.T., 1998. Pretreatment for cellulose hydrolysis by carbon dioxide explosion. Biotechnol. Prog. 14, 890–896. https://doi.org/10.1021/bp980087g.

Zhuang, X., Wang, W., Yu, Q., Qi, W., Wang, Q., Tan, X., Zhou, G., Yuan, Z., 2016. Liquid hot water pretreatment of lignocellulosic biomass for bioethanol production accompanying with high valuable products. Bioresour. Technol. 199, 68–75. https://doi.org/10.1016/j.biortech.2015.08.051.