

Lignocellulosic Biomass to Biofuel Production: Integration of Chemical and Extrusion (Screw Press) Pretreatment

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Abstract

Application of mechanical pretreatment in lignocellulosic biomass using screw press or extruder pretreatment recently gained more interest due to high shear, rapid mixing, short residence time, no inhibitor formation (e.g. furfural and HMF), and moderate operating condition. Eventhough, the physical structure of biomass can be modified through this process, the lignin is stay still. This remaining lignin cannot be removed and it subsequently inhibits the enzyme activity to hydrolyze cellulose and hemicellulose. Therefore, the chemical addition to remove lignin is considered as the option to combine with mechanical pretreatment to improve the overall pretreatment efficiency. This review provided the study cases focusing on the feasibility of this process and the selection of suitable chemicals in order to implement this process to practical applications in industries.

Keywords: Lignocellulosic biomass, Extrusion and chemical pretreatment, Biofuel production

1 Introduction

Lignocellulosic biomass, including dedicated crops and agricultural residues, has been projected to be one of the main resources for biofuel production, especially in bioethanol. The annual production of lignocellulosic biomass reaches 150–170 x 10⁹ tons in 2008 [1]. Approximately 90% of the dry weight of most plant materials is stored in the form of cellulose, hemicelluloses, and lignin, as shown in Table 1. The conversion of biomass to bioethanol begins with biomass pretreatment process due to properties of lignocellulosic biomass that mostly is not susceptible to enzymatic hydrolysis.

Cellulose fiber has a crystalline structure which can prevent the access of hydrolase enzyme to the

substrate. The presence of lignin in lignocelluloses functions as a protective barrier that prevents destruction of plant cell by fungi and bacteria in nature [2]. For the conversion of biomass to fuel, the cellulose and hemicelluloses must be broken down into their corresponding monomers or simple sugars (Figure 1). Then, the microorganisms can utilize them easily. Therefore, the pretreatment process is necessary to firstly execute to break down those barriers.

The pretreatment process plays an important role since it attenuates the accessibility of cellulase in enzymatic hydrolysis by disrupting lignin-hemicellulose-cellulose- (LHC) complex [3]. Pretreatment process is also considered as the second most expensive step in biorefinery process, after enzymatic hydrolysis, for the conversion of lignocelluloses to ethanol [4].

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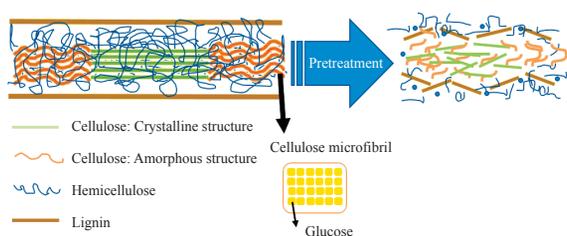


Figure 1: Lignocellulose structure and the role of pretreatment in lignocellulosic structure.

Brown reported that the pretreatment process contributes 33% of total cost and often produces byproducts or biological inhibitors that can reduce the yields of the hydrolysis and fermentation process [5]. In general, there are three major groups of inhibitors: aliphatic acids (acetic, formic, and levulinic acid), furan derivatives furfural and 5-hydroxymethylfurfural (HMF), and phenolic compounds (phenol, vanillin, p-hydroxybenzoic acid) [6]. Thus, establishment of the efficient pretreatment method with low cost makes the biomass refining process becomes economical feasible.

Table 1: Cellulose, hemicellulose and lignin contents in common agricultural residues and wastes

Lignocellulosic Materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ref
Bermuda grass	47.8	13.3	19.4	[7]
	25	35.7	6.4	[8]
Reed	39.5	29.8	24	[7]
Nut shells	25–30	25–30	30–40	[9]
Corn cobs	45	35	15	[9]
	35–39	38–42	4.5–6.6	[10]
Corn stover	36.8	30.6	23.1	[11]
Grasses	25–40	35–50	10–30	[9]
Paper	85–99	0	0–15	[9]
Wheat straw	30	50	15	[9]
	36.6	24.8	14.5	[12]
	44	29.6	10.4	[13]
	33	23	17	[14]
	36.3	21.1	25.5	[15]
	38	29	15	[16]
	44.1	23.8	20.5	[17]
Rice straw	41	21.5	9.9	[12]
Douglas fir	50	17.8	28.3	[12]
	44	19.2	30	[11]
Switchgrass	33.5	26.1	17.4	[18]
Spruce	45	22.9	28.3	[11]
<i>Miscanthus</i>	52.1	25.8	12.6	[19]

Screw press or extruder is a promising mechanical pretreatment for biomass refining in large scale. However, this process cannot remove lignin, which is the main barrier in biomass refining. Therefore, the combination of chemicals addition in the mechanical pretreatment is considered as the alternative way to solve this problem. The chemicals are considered to function as catalysts when they are combined with screw press reactor. However, the chemicals can also be applied after the mechanical pretreatment to remove lignin. The reason of conducting the chemicals into the screw reactor or extruder is to develop more synergistic effect between screw press and chemicals. During operation of the screw press, raw materials are mixed together with twisting screws that cause frictions among each components leading to increasing of the temperature inside the reactor. This review mainly focuses on the integration between screw press and chemical pretreatment (so called mechano-chemical pretreatment) for lignocellulosic biomass. The development and process optimization of this process to establish a decomposition process of lignocellulosic biomass are discussed in many study cases to provide more insight on the applications in industrial purpose.

2 Pretreatment Process for Lignocellulosic Biomass

The major structural barriers for the biodegradation of cellulose are their strong association with the lignin and hemicelluloses, crystallinity, degree of polymerization and surface area. Lignin is phenolic compound with heterogeneous in bond type and most of the bonds are not susceptible to hydrolytic cleavage. It is insoluble and difficult to wet. Cellulose with low degree of polymerization will be more susceptible to cellulolytic enzymes, particularly exocellulases [20]. All of these barriers require pretreatment process to obtain the substrate that can be hydrolyzed easily by cellulolytic enzymes, or by enzymes producing microorganisms to release sugars for bioethanol fermentation later on. Hence, the bioethanol can be produced by fermentation process.

In general, the primary goal of pretreatment process is to disrupt the biomass composition, as shown in Figure 1. Furthermore, removing lignin and other inhibitors, reducing the crystallinity of cellulose fibrils, and increasing the porosity or surface area

of the lignocellulosic materials are also benefits of pretreatment process [2]. Based on these characteristics, pretreatments must meet the following requirements: 1) improve the formation of sugars or the ability to subsequently form sugars by hydrolysis, 2) avoid the degradation or loss of carbohydrate, 3) avoid the formation of byproducts that are inhibitory to the subsequent hydrolysis and fermentation process, and 4) be cost-effective. To achieve these specifications, many pretreatment processes have been tailor-made and developed based on properties of raw materials, and scale of production.

The pretreatment methods can be classified into physical/mechanical, chemical, biological and the combination of those pretreatments. In brief, biological pretreatments employ microorganisms, such as brown-, white-, and soft-rot fungi, to disrupt the biomass structure and degrade lignin [2]. The physical/mechanical pretreatments include comminution, grinding, milling, irradiation, and extrusion. Chemical pretreatments using acids, bases or other chemicals to promote the hydrolysis, remove lignin and separate the cellulose and hemicellulose.

3 Mechanical Pretreatment

Mechanical pretreatment is a subgroup of physical pretreatment. In mechanical pretreatment, input energy is primarily required to generate mechanical forces for size reduction such as grinding, milling and comminution, rather than for building up temperature and pressure. In general, primary size reduction could be executed by using hammer mills to produce small particles that can pass through selective-sized screen openings [20], [21]. The shearing and compressive forces in ball milling can cause reduction in crystallinity, decrease of the degree of cellulose polymerization, decrease of the particle size, increase of the bulk density, and increase of the external surface area [22]. Yu, *et al.* also reported that comminution of lignocellulosic materials through a combination of chipping, grinding, and/or milling can be applied to reduce cellulose crystallinity [23]. Pandey reported that the effectiveness of ball milling varies with the cellulose content, e.g., milling of softwood has the least efficiency [20]. Mais *et al.* investigated application of simultaneous ball milling to enhance enzymatic hydrolysis of cellulosic materials [24]. They used a ball mill reactor for the pretreatment

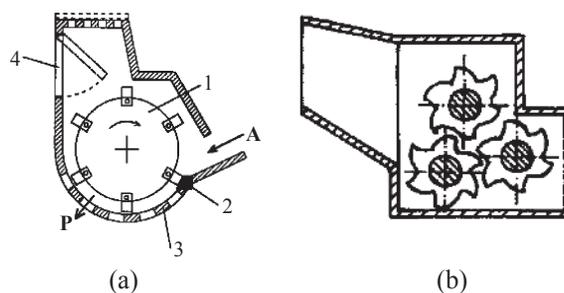


Figure 2: Types of rotary shredders; (a) swing-hammer shredder; (b) rotary shredder used for comminution of aluminum scrap [26].

and hydrolysis of α -cellulose and SO_2 -impregnated steam-exploded Douglas-fir wood chips.

However, this technology requires high energy consumption. Almost of all energy in grinding process is wasted as heat and only 0.06–1% of the input energy actually functions in disintegration of the biomass [23]. The energy requirements in mechanical reactor depends on the type of mill, initial and final particle size and biomass characteristics such as moisture content [20]. Taherzadeh and Karimi concluded that two-roll, attrition, hammer or knife mills are suitable for comminuting of dried biomass with moisture contents of 10–15% (wet basis), whereas colloid mills and extruders are suitable for comminuting of wet materials with moisture content of more than 15–20% (wet basis) [25].

In order to reduce high energy consumption in mechanical pretreatment and increase the pretreatment effectiveness, screw extruder and screw press appear as alternative technologies in lignocellulosic biomass pretreatment. Initially, screw extruder is widely used in polymer and food processing, while screw press is widely used in palm oil processing [27]. Nowadays, people tend to apply these machines in biomass pretreatment due to their high shear stress, rapid mixing and short residence time.

Extruder is not a typical size reduction machine, it has been often operated for biomass disintegration due to its ability [22]. Two different types of screw extruder, single screw and twin screw, have been developed for biomass pretreatment process. Actually, screw press is a single screw extruder which has larger difference between the flights [Figure 3(b)]. This difference allows the changing in compression and stretching/relaxation.

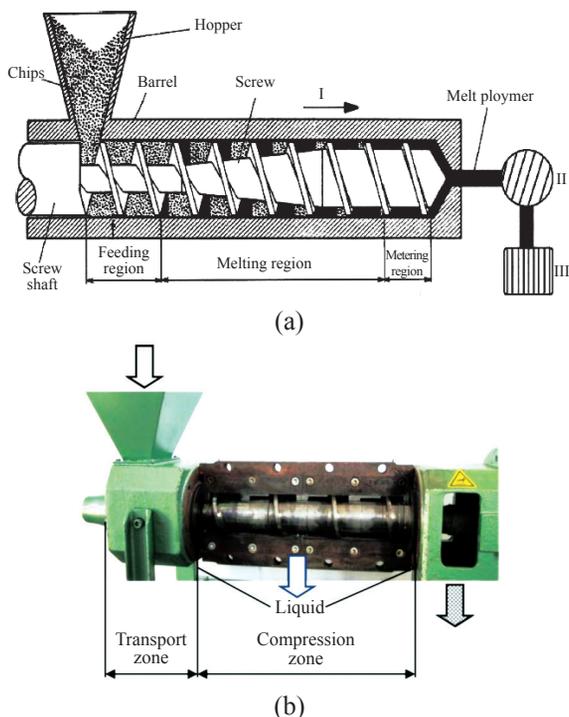


Figure 3: (a) Schematic picture of single screw extruder and (b) screw press in MVT-AVT RWTH Aachen [29]–[31].

The basic operation of a single screw extruder is rather straight forward. Materials enter from the feed hopper and flows down into the feeding region due to gravitational force into the extruder barrel. As the materials fall down, it is situated in the annular space between the extruder screw and the barrel. The barrel is stationary and the screw is rotating. As a result, frictional force will act on the material, in both the screw surface. This is happened in the melting region [Figure 3(a)]. These frictional forces are responsible for the forward transport of materials to the metering region and finally out of the extruder [28].

For the screw press, the principle is similar with the single screw extruder. The biomass feed is delivered to the hopper and due to gravitational force. It flows down into the transport zone. Since the screw is rotating, the biomass is transported into the compression zone. The difference in diameter of screw in the first part and in the end part of the reactor causes compression force to the biomass. The comparison between those diameters usually called the compression ratio. While the biomass

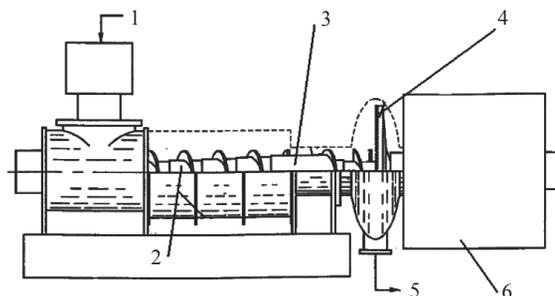


Figure 4: Single screw press combined with wet disc mill: 1) Biomass Input; 2) Screw Press; 3) Decompression Region; 4) Wet disc mill; 5) Biomass Output; 6) Power Drive [35].

is compressed, the water is removed out and the friction force between biomass and screw increase the screw temperature up to 90°C [29], [32]. The structure of biomass is broken down simultaneously due to high shear stress. In the end, the pretreated biomass is released out of the screw press (Figure 3).

The development of applications of single screw extrusion occurred in late 19th century. The first patent on screw extrusion is in 1879 that applied extrusion to extract white milky latex of a tree so called ‘gutta percha’, which used in wire coating application [33]. The single screw extrusion process has an Archimedean screw rotating in a stationary barrel and is only applicable in cases where the mixing tank is restricted (spatial rearrangement of the ingredients without changes in physical properties). On the other hand, high efficacies of both distributive and dispersive mixing are possible with some types of twin screw extrusion processes. This involves the changes in physical properties, for example, the reduction of particle size achieved by application of high shearing stresses [34].

In 2007, Sabourin invented a patent about single screw extruder combined with a wet disc mill. The principle of this technology is that biomass is fed to the screw extruder and then passed through watering, compressing, decompressing, and defiberizing zones consecutively. After that, the biomass is reduced in size by a wet disc mill. The recommended compression ratio, screw speeds, and disc speeds are 2:1 to 4:1, 70–100 rpm, and 800–1800 rpm respectively (Figure 4). After decompression region, there is a wet disc mill to reduce the size of biomass before getting out of the machine [35].

The second type of screw extruder is twin screw. Basically, the twin screw extruder consists of two independent screws which are turning into each other. Based on its geometry, twin screw extruder can be either intermeshing or non-intermeshing type. Besides, the direction can be co-rotating or counter rotating. These characteristics allow many different configurations in order to achieve particular mixing. Several research works have been demonstrated the application of screw extruder both single and twin screw in lignocellulosic biomass pretreatment. Litzen *et al.* provided a patent using twin screw extruder for biomass pretreatment for ethanol production. They claimed a method for pretreating biomass through a twin screw extruder prior hydrolysis resulting in significant increase in sugar recovery [36]. Karunanithy and Muthukumarappan investigated the single screw extruder for various types of lignocellulosic biomass. They observed the influence and impact of many operational parameters such as screw speed, barrel temperature, moisture content of biomass, torque requirements and level of enzymes loading. From the results, they found that those parameters significantly influenced the sugars recovery. The optimum pretreatment conditions are significantly depended on biomass types. For example, a maximum of 28.2%, 66.2% and 49.2% of sugar recovery was achieved for switch grass, big bluestem, and prairie cord grass, respectively [37], [38].

4 Chemical Pretreatment

The chemical pretreatment is widely used for the biomass pretreatment to disrupt the recalcitrant structure of lignocellulosic biomass. The common groups in chemical pretreatment are acid pretreatment, alkaline pretreatment, organosolv and ionic liquids.

The advantage of acid pretreatment is its ability to remove hemicellulose [39]. This hemicellulose removal increases porosity and improves enzymatic digestibility. The most common acids are sulphuric acid, hydrochloric acid or succinic acid [39], [40]. Usually this pretreatment is operated in diluted acid at high temperature condition. Diluted acid is preferred to be used since concentrated acid is high corrosive and need to be neutralized before proceed to hydrolysis step [28]. Diluted acid pretreatment generally has high reaction rates and significantly improves cellulose

hydrolysis [41]. Additionally, it can also convert xylan to xylose efficiently. However, there are several drawbacks of this pretreatment that can affect the downstream process. Acid can cause inhibitor formation, such as furfural and HMF produced from degradation of hemicellulose [42]. These compounds are strong inhibitors to microbial fermentation process so it is recommended to be minimized. Besides that, acid can be corrosive to the equipment and environment and it needs pH neutralization which results in the formation of solid waste. Furthermore, acid pretreatment cannot remove lignin, the biggest barriers in enzymatic hydrolysis. Hence, this pretreatment method is suitable for biomass with low lignin content.

Alkaline pretreatment has different features comparing to acid. The benefit of alkaline pretreatment is removing out lignin from lignocellulosic biomass [39]. Alkaline can remove acetyl and uronic acid of hemicellulose [42]. The mechanism of alkaline pretreatment based on saponification of intermolecular ester bonds. The most common alkalines used in pretreatment are sodium hydroxide, calcium hydroxide and aqueous ammonia [40]. All of these alkalines can cause skin and eyes burn, and corrosive to the materials. Sodium hydroxide is strong alkaline and its dissolution is highly exothermic. By using sodium hydroxide or calcium hydroxide, the salts might be formed and need to be removed or recycled. Oppositely to acid pretreatment, operational condition of alkaline pretreatment is relative milder but it takes quite relatively longer time. The degradation of sugars into furfural and HMF is minimized due to this mild process condition [42].

The organosolv process uses an organic compounds or mixtures of organic solvents with water to dissolve the lignin fraction, while the cellulose remains in the solid fraction [43]. The principle of this process is based on different affinities of the lignocellulosic components towards different solvents [44]. The common solvents of this process are ethanol, methanol, acetone and ethylene glycol. Usually this pretreatment is operated in high temperature up to 200°C [45]. The main drawback is the organic compounds itself can be inhibitor for hydrolysis and fermentation. Therefore, it requires removal and recovery process of the solvents [42].

Additional, organic acid pretreatment is also considered to be one of the organosolv process. The

types of organic acids that have been applied for pretreatments are acetic acid [46], oxalic [47], [48], maleic [49], and fumaric acid [15]. Organic acid pretreatments were investigated as alternative options, despite their concentrations used for pretreatment are relatively high compared to inorganic acids. Dilute organic acid pretreatment has some desirable characteristics, including effective hydrolysis, less degradation products and more xylan sugars [50], [51]. The ionic liquid (IL) is considered as a new technology in chemical pretreatment. Compared to common organic solvents, such as dimethylacetamide, ILs display interesting properties and potential advantages, as reasonable chemical inertness, good thermal stability, low volatility, or unique solvation abilities. Like the concentrated acids, ionic liquids containing chloride, acetate, and other moderately basic anions disrupt the hydrogen bond networks of celluloses, and enable their dissolution [52]. However, Harmsen *et al.* reported that there are several drawbacks such as ability to recover the used ionic liquids, the toxicity of the compounds and the combination of water with ionic liquids. Besides, the ionic liquids is currently not feasible for large scale operation due to their relatively high cost and large loading requirements [53].

5 Combination of Mechano-Chemical Pretreatment Process

The combination of mechanical (screw press) and chemical method is revealed to have a synergistic effect in biomass pretreatment [40]. In this case, the role of chemicals is acting more like a catalyst to modify biomass to be more vulnerable to enzymatic hydrolysis. Examples of integration of mechano-chemical pretreatment have been listed in Table 2. In 1989, Huber and Gordon invented the extrusion processing machine for wood chips, sawdust, food fibers, agricultural residue and other fibrous materials to produce refined product by impregnating the fiber with a desired chemical [54]. The extruder machine, as shown in Figure 5, has one injection port through the barrel. This port allows addition of chemicals into the reactor during processing with the internal screw having sequential compression and absorption zone for enhancing the chemical impregnation of fibrous materials.

In 1984, Carr and Doane reported that sodium

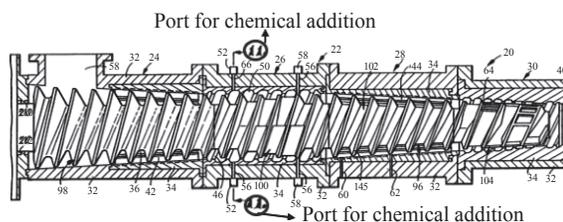


Figure 5: Screw apparatus for the extrusion processing [54].

hydroxide pretreatment in extrusion could remove lignin up to 65% [55]. Dale *et al.* integrated ammonia fiber explosion (AFEX) process into the twin screw extruder. The results showed that after enzymatic hydrolysis, the sugar yield has been increased up to 3.5 times over that of completely untreated material [56]. Vrije de *et al.* investigated the disintegration process using twin screw extruder combined with 12% w/w of sodium hydroxide solution and it was observed that 77% of lignin in *Miscanthus* was removed [57]. Razumovskii *et al.* also reported that the combination of mechano-chemical pretreatment had a synergetic effect reflecting in higher degradation of plant materials, lowering reaction temperature and reduction in inhibitor formation [40]. Optimization of integrated alkaline (NaOH)-extrusion pretreatment of barley straw was investigated by Duque *et al.* and the glucan yield could reach 86.9% [58]. A significant contribution of bioethanol production could be achieved as well from barley straw that treated by sodium hydroxide in a twin screw extruder [59].

N'Diaye *et al.* reported that thermo mechano-chemical fractionation system allows the integration of extrusion, cooking, liquid-solid extraction, and liquid/solid separation (filtration) in a single step and operates in a continuous mode [60]. With such a reactor, alkaline extraction can be operated at a lower L/S ratio (six times less than a batch reactor) and lower residence time and 90% of the initial hemicelluloses (pentosans) can be recovered. In the other hand, Chen *et al.* reported that a combination of a twin-screw extrusion and an acid-catalyzed hot water extraction process results 80% yield of the total saccharification [61]. Application of continuous twin screw-driven dilute acid pretreatment was conducted by Choi and Oh using sulfuric acid concentration 3.5 wt.% and reaction temperature 165°C. The result showed that the enzymatic digestibility reached 70.9% and the continuous

Table 2: Studies of pretreatment using mechanical (extrusion) and chemical pretreatment methods

Reference	Biomass	Extruder	Chemicals	Operating Cond.	Cellulose Conversion (%)	Xylan/Pentosan Conversion (%)	Lignin Removal (%)	Sugar Yield (glucan/glucose) (%)	EH Conversion (%)
Carr and Doane, 1983	Wheat straw	Continuous mixer (single screw)	NaOH (8.5–15.75), H ₂ O ₂ , Na ₂ S, AQ, AHQ	97°C for 5.5 min, 35 rpm	90–92 (cellulose to glucose)	36–43	64–72	n.a.	n.a.
Dale <i>et al.</i> 1999	Corn fodder	Twin screw	AFEX (Ammonia)	40–90°C,	n.a.	n.a.	n.a.	3.5 times over untreated material	n.a.
de Vrije <i>et al.</i> 2002	Mischantus	Twin screw	NaOH 12%	100 rpm, 50, 70, 950°C,	>95	44	77	n.a.	69
Razumovskii <i>et al.</i> 2010	Birch wood	Twin screw	Vary (NaOH, succinic acid)	2 min	n.a.	n.a.	n.a.	n.a.	n.a.
Karunanithy and Muthukumarappan 2013	Prairie cordgrass	Single screw	NaOH (0.5–2.5% w/v)	20–200 rpm, 45–225°C barrel temp, 30 min	86.8	n.a.	n.a.	n.a.	n.a.
Karunanithy and Muthukumarappan 2013	Big Bluestem	Single screw	NaOH (0.5–2.5% w/v)	20–210 rpm, 45–135°C	n.a.	n.a.	25	89.9	90
Chen <i>et al.</i> 2011	Rice Straw	Twin screw	Dilute H ₂ SO ₄ (1–3% w/w)	(30–150 rpm), (80–160°C), 5 to 15 min	n.a.	83.7	n.a.	80	n.a.
Brudecki <i>et al.</i> 2012	Prairie cordgrass	Single screw	MIBK (28%) and EtOH (organosolv)	129°C, 65 rpm, 39 minutes	n.a.	95	87	92	n.a.
Choi and Oh, 2013	Rape straw	Twin screw	Dilute H ₂ SO ₄ (1.5–3.5% w/v)	150–170°C, 19.7 rpm, 0.5 g/min feeding rate	92.5	n.a.	n.a.	n.a.	n.a.
Choi <i>et al.</i> 2013	Rape straw	Twin screw	Dilute H ₂ SO ₄ (1–5% w/v)	30–60 rpm, 160–175°C	n.a.	n.a.	n.a.	78.7	n.a.
Duque <i>et al.</i> 2013	Barley straw	Twin screw	NaOH 10% (w/v)	T: 50–100°C; R: 2.5–7.5% (w/w)	n.a.	71	n.a.	89.9	n.a.
Han <i>et al.</i> 2013	Barley straw	Twin screw	NaOH (0–0.8M)	Temp. 50–100°C, 72–120 mL/min, 100 rpm	n.a.	n.a.	n.a.	n.a.	77.36
Kang <i>et al.</i> 2013	Mischantus	Twin screw	NaOH (0.3–0.9 M)	Temp 95–200°C, 80–150 rpm.	n.a.	n.a.	n.a.	n.a.	88.1

process routinely gave around 28.8% higher yield for glucan digestibility than did the batch processing method [62]. Altogether, biomass pretreatment using mechano-chemical method can be applied in order to improve degradation of lignocellulosic biomass and produce higher sugar yield for fermentation.

6 Conclusion

The combination of mechano-chemical pretreatment process in lignocellulosic biomass have been developed and optimized to be applicable to different types of lignocellulosic biomass. This pretreatment method includes the advantage of mechanical and chemical

pretreatment to establish the high efficient pretreatment process. The synergistic effect is the contribution of generated heat of mechanical pretreatment that enhance the function of chemical pretreatment. On the other hand, the impregnated chemicals enhance the biomass disruption efficiency of mechanical pretreatment and help to reduce inhibitor formation. Further development mechano-chemical pretreatment could be the investigation of designing of reactor configuration to save energy and optimization of operational parameters such as chemicals, concentration of chemical, rotation speed of screw press and flow rate to get the highest yield of sugars that later used as materials for biofuel production.

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