

## Chapter 2

# Thermo-Mechanical Pretreatment of Feedstocks

**Chinnadurai Karunanithy and Kasiviswanathan Muthukumarappan**

**Abstract** Pretreatment is the first step to open up the complex structure of feedstock and to facilitate the access of hydrolytic enzymes to carbohydrates. Researchers are paying utmost care to pretreatment since it has pervasive impact in downstream processing. Numerous pretreatments have been investigated in the past with various degrees of success and still several new investigations are under progress. Extrusion/thermo-mechanical process is a continuous viable pretreatment and easy to adapt at industry scale with flexibility in process modifications. Agricultural residues and dedicated energy crops such as corn stover, prairie cord grass, wheat straw, rice straw, rape straw, barley straw, wheat bran, soybean hull, switchgrass, miscanthus, big bluestem, and forest products such as poplar, pine, Douglas fir, and eucalyptus were subjected to extrusion pretreatment with or without chemicals. This chapter provides an overview of extrusion pretreatments including the mechanism influencing extruder and feedstock parameters, evaluation of pretreatment efficiency including production of potential fermentation inhibitors, torque requirements, and direction for future work.

**Keywords** Extrusion • Screw speed • Barrel temperature • Particle size • Moisture content • Sugar recovery • Hydrolysis • Torque • Fermentation inhibitors

---

C. Karunanithy (✉)

Food and Nutrition, University of Wisconsin-Stout, Menomonie, WI 54751, USA  
e-mail: chinnaduraik@uwstout.edu

K. Muthukumarappan

Department of Agricultural and Biosystems Engineering, South Dakota State University, Brookings, SD 57007, USA  
e-mail: kas.muthukum@sdsstate.edu

## 2.1 Introduction

About 60 % of the world's ethanol is produced in the US and Brazil exploiting sugarcane and corn, respectively. Economics and limitation in grain supply lead to search for alternative resources. In order to meet the ever-growing fuel demand, worldwide researchers are exploring alternate renewable resources for more than three decades. Biomass is an attractive feedstock due to its renewable nature, positive environmental impact, and abundant supply. According to the US National Research Council (National Research Council 2000), biobased industry should provide at least 10 and 50 % of liquid fuel by the year 2020 and 2050, respectively. Further, the 2007 Energy Act mandates the production of 21 billion gallons of biofuels from noncorn starch materials by 2022.

Ethanol production from biomass is quite different from corn, because the accessibility of carbohydrates in biomass to hydrolytic enzymes is more difficult than the starch in grain (Gibbons et al. 1986). The complex structure and recalcitrant nature of biomass necessitates an additional step called pretreatment. The primary purposes of pretreatment are to open up the biomass structure, to increase accessible surface area, to reduce the cellulose crystallinity, and to increase the porosity, pore size, and pore volume. In other words, pretreatment should address the factors influencing enzymatic hydrolysis. Yang and Wyman (2008) reported that pretreatment is a key step in converting biomass into biofuel because of its pervasive impact on the downstream processing. Numerous pretreatment methods such as physical, chemical, biological, and their combinations can be found in the literature. Most of these pretreatments often involve high temperature and acidic conditions resulting in degradation and leading to the formation of potential fermentation inhibitors. Moreover, most of the conventional pretreatment methods are batch in nature with low throughput and low solids loading rate resulting in high energy consumption. Dilute acid pretreatment requires corrosion resistant construction materials, neutralization of the pretreated feedstocks; hydrothermal pretreatment requires elevated temperature; chemicals are expensive and difficult to recover and reuse; and in addition safety becomes an important concern. An effective pretreatment must expose the fiber, thereby the cellulose fraction could be hydrolyzed by cellulases without significant trouble, preserve the hemicellulose, and avoid the inhibitory by-products formation (Laser et al. 2002). Inexpensive chemicals, simple equipment and procedures enable the pretreatment to be economical. Thermo-mechanical/extrusion pretreatment meets the above listed criteria and address the listed issues associated with other pretreatment methods. This chapter presents in-depth a review and discussion on extrusion pretreatment of different feedstocks.

## 2.2 Extrusion Pretreatment

### 2.2.1 Extruder's Capability

Extrusion is a continuous cost-effective, fast, and simple process hence practical and useful for large-scale operation with high throughput and adaptability for many different process modifications (high pressure, explosion, chemical addition,

and reactive extrusion). Extruder screw and barrel can be made using acid-resistant stainless steel and its alloy, such as SS 316L (Chen et al. 2011) and AL6XN (Miller and Hester 2007) even if one has to add acid during extrusion pretreatments. Extrusion pretreatments of different feedstocks revealed that no effluent disposal cost is involved due to the absence of any effluent production, no solid loss, and no safety issues are involved. The unique advantages of extrusion pretreatment are high shear, rapid mixing, short residence time, excellent temperature and screw speed control, and flexibility in screw configuration to mention a few. Moderate temperature employed in extrusion pretreatment prevents the degradation and formation of potential fermentation inhibitors (de Vrije et al. 2002). Extruder can accommodate wide range of feedstock sizes especially larger sizes when compared to other leading pretreatment methods; thereby extruder leads to remarkable saving in terms of size reduction.

### ***2.2.2 Mechanism of Extrusion Pretreatment***

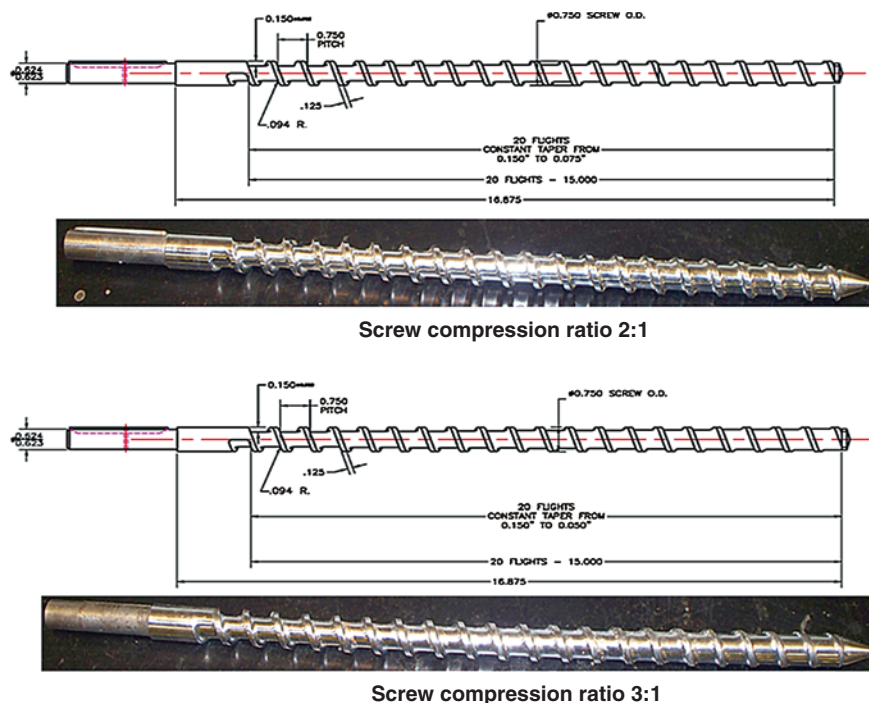
In general, as the feedstock pass through an extruder barrel, high shear is exerted by the screw, high pressure and temperatures are developed (Lamsal et al. 2010) causing defibration, fibrillation, and shortening the fibers (change in aspect ratio) (de Vrije et al. 2002). When the pretreated feedstock exits through die section, some of the moisture present in the feedstock is flashed off into steam due to sudden drop in the pressure resulting in expansion and porous structure (de Vrije et al. 2002). Several researchers have attributed possible reasons for the increase in sugar recovery in extrusion pretreatment includes increases in surface area (Karunanithy and Muthukumarappan 2011a, b, c, d), specific surface area (Chen et al. 2011; Lee et al. 2009, 2010), pore size (Jurisic et al. 2009; Zhang et al. 2012a), and pore quantity (Zhang et al. 2012b), a decrease in cellulose crystallinity (Lamsal et al. 2010; Zhang et al. 2012b), and induction of micro/nano fibrillation (Zhang et al. 2012b), all of these facilitate the access of enzymes to cellulose. The developed mechanical high shear breaks down the structure of feedstock and facilitates contact between feedstock and chemicals (acid/alkali/cellulose affinity additives) added during extrusion due to effective mixing. Further, the shear exerted by the screw helps in continuous removal of softened regions of the feedstock and expose fresh interior surface to chemical and thermal action that improves the overall rate of decrystallization (Lamsal et al. 2010).

## **2.3 Extruder Parameters Influencing Sugar Recovery**

Pretreatment efficiency (sugar recovery) depends on several extruder parameters such as compression ratio, screw configuration, screw speed, and barrel temperature and they are presented below.

### 2.3.1 Screw Compression Ratio

Compression ratio is the channel depth at feed to channel depth at discharge that has a direct impact on shear development within the extruder barrel; it affects sugar release from the feedstock due to the process of plasticization which occurs in the compression zone. Harper (1981) listed several ways to achieve the desired compression ratio by varying the screw and barrel configuration: by increasing the root diameter, by decreasing the pitch or barrel diameter with constant root diameter, by decreasing the screw pitch in a decreasing barrel diameter, and by introducing restrictions. However, the most common ways to achieve compression are gradual decrease of flight depth in the direction of the discharge and a decrease in the pitch in the compression section (Harper 1981). Among the literature surveyed, only researchers from South Dakota State University studied the effect of screw compression ratio on different feedstocks (Karunanithy and Muthukumarappan 2010a, b). Though screw compression ratio used in food industries typically ranges from 1:1 to 5:1 that are widely available, the authors used only 2:1 and 3:1 in their study to understand the influence of screw compression ratio on sugar recovery. As Harper (1981) described,

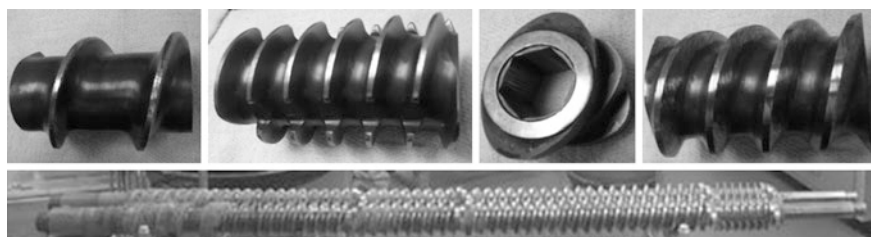


**Fig. 2.1** Screw diagram showing the difference between 3:1 and 2:1 compression ratio (with permission: C.W. Brabender Instruments Inc, NJ). Reprinted from BioEnergy research, a comparative study on torque requirement during extrusion pretreatment of different feedstocks, © 2011, Chinnadurai Karunanithy, 5, with kind permission from Springer Science+Business Media and any original (first) copyright notice displayed with material

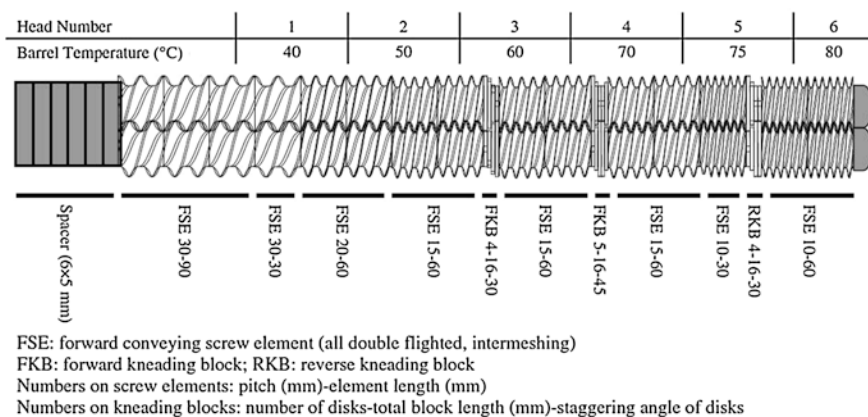
the screws were identical except for the depth of the discharge flight at the screw end and had a continuous taper (decrease of flight depth) from the feed to the discharge of 3.81–1.27 mm and 3.81–1.90 mm for the screws with compression ratios of 3:1 and 2:1, respectively (Fig. 2.1). They concluded that a screw compression ratio of 3:1 was better than 2:1 due to more work (shear force and long residence time) applied on the feedstocks. Recently, Chen et al. (2011) used twin screw extruder with a screw compression ratio of 5:1; however, no comparison was possible due to lack of data with other screw compression ratios.

### 2.3.2 Screw Configuration

It is an important factor that would affect pretreatment efficiency. In order to use different screw configurations in a single screw extruder, one has to change different screw since the screw shaft and flights are made of single solid rod/shaft or inseparable. In the case of twin screw extruder, one has the flexibility of arranging different screw elements such as forward conveying, forward kneading, eccentric kneading, neutral kneading, mono or bilobal kneading, and reverse kneading in any order for maximizing pretreatment efficiency or other objectives. Different screw elements and screws made thereof is shown in Fig. 2.2. In general, screw elements are arranged to have a constantly decreasing pitch to enhance the shear on the feedstock (Lamsal et al. 2010). N'Diaye et al. (1996) used twin screw extruder for hemicellulose extraction from poplar and they arranged the conveying screw elements to facilitate conveying and heating due to decrease in pitch for compacting, removing of air, and starting impregnation of alkali; followed by bilobal and eccentric kneading elements for homogenizing the slurry and increasing impregnation of alkali; then reverse screw element for separating liquid through the filter and finally conveying screw elements. de Vrije et al. (2002) used twin screw extruder with conveying and reverse screw elements for accumulating and compressing miscanthus between elements space that resulted in high shear development. Lee et al. (2009) arranged left and right corrugated conveying elements for continuous movement of Douglas fir followed by reverse screw elements for increasing the residence time as well pulverization effect and finally conveying elements for forward conveying. One such arrangement is shown in Fig. 2.3 used for soybean hull pretreatment.



**Fig. 2.2** Different screw elements and screws made thereof



**Fig. 2.3** Schematic showing lab-scale twin screw extruder screw profile and barrel temperature setting (Yoo et al. 2012). Reprinted from applied biochemistry and biotechnology, Soybean hulls pretreated using thermo-mechanical extrusion—hydrolysis efficiency, fermentation inhibitors, and ethanol yield, © 2011, Juhyun Yoo, 2, with kind permission from Springer Science+Business Media and any original (first) copyright notice displayed with material

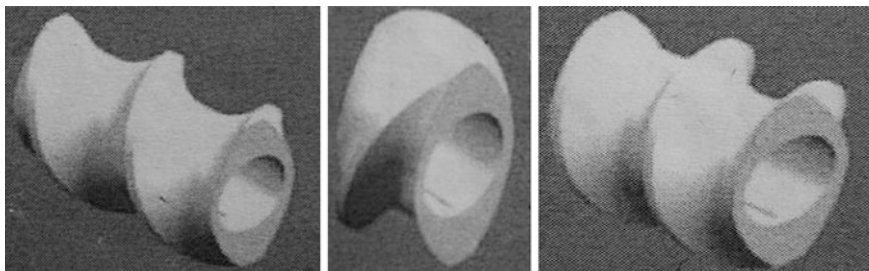
Chen et al. (2011) used twin screw extruder with different screw elements such as conveying, kneading, and combing mixer blocks for transport, mixing, and granulation of rice straw, respectively. Recently, Choi and Oh (2012) employed twin screw extruder with forward conveying and kneading screw elements for accomplishing effective conveying, mixing, and pretreatment of rape straw. Researchers from University of Nebraska, Lincoln has used different screw configuration (Fig. 2.4) with conveying element, reverse element for enhancing mixing and pulverizing, and again conveying element for creating more pressure (Zhang et al. 2012a, b).

### 2.3.3 Screw Speed

The authors reported that *screw speed* is responsible for the rate of shear development and the mean residence time (Karunanithy and Muthukumarappan 2010a, b), wherein these are two sides of a coin and competing factors (Yoo et al. 2012). In general, the screw speed is inversely proportional to the mean residence time of the feedstock in the extruder (Chen et al. 2011; Lamsal et al. 2010). Researchers have reported that the effect of screw speed was inconsistent with respect to sugar recovery from different feedstocks.

Soybean hull pretreated using twin screw extruder exhibited mixed behavior depending upon the barrel temperature i.e., sugar recovery decreased with an increase in screw speed (220–420 rpm) at 110 °C, whereas sugar recovery increased with an increase in screw speed at 150 °C (Lamsal et al. 2010). In another soybean hull twin screw extrusion study, an increase in screw speed from 220 to 350 rpm increased sugar recovery and further increase to 420 rpm





**Fig. 2.4** Screw configurations used for corn stover pretreatment (Zhang et al. 2012b). Reprinted from applied biochemistry and biotechnology, pretreatment of corn stover with twin-screw extrusion followed by enzymatic saccharification, © 2011, Shujing Zhang, 2, with kind permission from Springer Science and Business Media and any original (first) copyright notice displayed with material

decreased sugar recovery (Yoo et al. 2011). Similarly, rice straw pretreated in a twin screw extruder with dilute acid also revealed that an increase in screw speed from 30 to 80 rpm increased the sugar recovery and further increase to 150 rpm decreased the sugar recovery (Chen et al. 2011). Twin screw extrusion pretreatment of corn stover revealed that screw speed significantly influenced sugar recovery (Zhang et al. 2012b). In addition, they reported that shear rate developed at 80 rpm would be sufficient for lignin softening, further increase in screw speed lessened the residence time that possibly resulted in insufficient destruction of lignin sheath. The possible reasons are as lower screw speed allows more time for hydration, thermal degradation, and mechanical separation of lignin and cellulosic components at the same time reduces mechanical energy input and less intensive treatment. Since residence time and mechanical energy input are competing factors, their effects might mitigate each other to some extent (Yoo et al. 2011). Therefore, one has to identify whether residence time or rate of shear development plays a major role in the pretreatment of specific feedstocks. Accordingly, Karunanithy and Muthukumarappan (2010a, b); Karunanithy et al. (2012) found that the rate of shear development (high screw speed) was critical for corn stover, switchgrass, and pine chips and the mean residence time was critical for big bluestem and prairie cord grass.

Karunanithy and Muthukumarappan (2010a, b, c, 2011a, b, c, d, e, f, g, h); Karunanithy et al. (2012) observed that screw speed had a strong influence on sugar recovery from variety of feedstocks. Screw speed had a positive influence on sugar recovery from different feedstocks such as corn stover, switchgrass and big bluestem when pretreated in a single screw extruder, whereas it exerted a negative impact on sugar recovery when alkali soaked corn stover, switchgrass, big bluestem, and prairie cord grass pretreated in a single screw extruder. More energy is available for fiber breakage as the screw speed increases that the fiber length and aspect ratio. Moreover, the applied high shear forces during extrusion influences the fiber length reduction, which is similar to pelletizing (Baillif and Oksman 2009). The reduction in fiber length increases the accessible surface area

for enzymes during hydrolysis (as presented in Sects. 2.6.1 and 2.6.2). Though the linear term of screw speed did not have significant effect on sugar recovery from prairie cord grass (Karunanithy and Muthukumarappan 2011d) and miscanthus (Jurisic 2012), its quadratic term and interaction with other variables had a significant effect. Screw speed influenced sugar recovery from corn stover when pretreated in twin screw extruder without alkali, whereas it was not an influencing factor when alkali was added for moisture balancing and extruded in a twin screw extruder (Zhang et al. 2012a, b). Possible reasons might be that the differences in screw speeds (40–140 rpm vs. 40–100 rpm) and moisture content (22.5–27.5 vs. 50 % wb). These studies also emphasize that the screw speed is one of the factors influencing the pretreatment efficiency.

### **2.3.4 Barrel Temperature**

Extruder barrel temperature is another important extrusion parameter that facilitates the melting or softening/plasticizing of the feedstock; and thereby affects the flow pattern and residence time. Though there is several extrusion pretreatments literature found, only a few studies the effect of barrel temperature on sugar recovery. Lee et al. (2009) achieved fine and even fibrillated (most of them  $<1\text{ }\mu\text{m}$  and some of them  $<100\text{ }\mu\text{m}$ ) Douglas fir fibers when extruded in a twin screw extruder at a barrel temperature of  $40\text{ }^{\circ}\text{C}$  as compared to  $120\text{ }^{\circ}\text{C}$ . They attributed the fibrillation to high torque at low temperature. Researchers from South Dakota State University have investigated the temperature effect with a wide range of temperature  $45\text{--}225\text{ }^{\circ}\text{C}$  for corn stover, switchgrass, big bluestem, and prairie cord grass using a single screw extruder with or without alkali soaking. The authors observed that the barrel temperature had a positive influence on the sugar recovery from switchgrass and big bluestem when pretreated with or without alkali soaking (Karunanithy and Muthukumarappan 2011a, b, c, d). They also reported that barrel temperature had a positive effect on sugar recovery for corn stover without alkali soaking, whereas it had negative effect when alkali soaked and extruded in a single screw extruder. Although barrel temperature was not an influencing factor for prairie cord grass without alkali soaking, it turned to be an influencing factor when prairie cord grass alkali soaked and extruded. Optimization extrusion pretreatment conditions for different feedstocks revealed that not only linear term of barrel temperature affected sugar recoveries but also its quadratic term and interaction with other factors (Karunanithy and Muthukumarappan 2011a, b, c, d, e, f, g, h). Recently, Jurisic (2012) and Karunanithy et al. (2012) observed that the barrel temperature had a strong impact on sugar recovery from miscanthus and pine chips, respectively. On one hand, an increase in the barrel temperature would enhance the moisture evaporation that develops more friction thereby more disturbances to the feedstocks. On the other hand, an increase in the barrel temperature would decrease viscosity, which resulted in a more flowable material and decrease in residence time. Chen et al. (2011) reported an increase in



barrel temperature (150–155 °C) increased sugar recovery and further increase (170 °C) led to decrease in sugar recovery from rape straw pretreated in a twin screw extruder. They (Chen et al. 2011) also reported a similar trend when rice straw pretreated in a twin screw extruder, as the barrel temperature increased from 80 to 120 °C sugar recovery increased and further increase to 160 °C decreased the sugar recover. A possible reason is that degradation of sugar into by-products occurs at high severity factor (high temperature and acid concentration).

## **2.4 Feedstock Parameters Influencing Sugar Recovery**

Feedstock parameters such as type of feedstocks, moisture content, and particle size affect not only the sugar recovery but also economics. The following section presents the details of them.

### ***2.4.1 Type of Feedstock***

Optimum pretreatment conditions depends upon the type of feedstocks especially the chemical composition including lignin content. The chemical composition is different for agricultural residues, perennial grasses, and wood species as shown in Table 2.1. Lignin is considered as key hurdle in the conversion process and it varied from 2 to 34.7 % depending upon the feedstocks. In general, the low cellulose and high lignin would affect the pretreatment efficiency (sugar recovery). Literature survey reveals that there was no study conducted to understand the effect of feedstock's extractives on extrusion pretreatment and the impact of ash content on wear and tear of the extruder screw and barrel and they are potential topics that should be addressed before adopting at industrial scale. So far several researchers have optimized extrusion parameters for individual feedstocks, whereas finding the optimum pretreatment conditions for mixed feedstocks is difficult. In reality, a biorefinery plant may get a mixed feedstocks from different farms, wherein separating them is a difficult task. This indicates the research opportunities for optimizing pretreatment conditions for mixed feedstocks.

### ***2.4.2 Feedstock Moisture Content***

Moisture content is an important factor in most of the mechanical and physicochemical pretreatments such as disc refining, wet ball milling, steam pretreatment, and steam explosion used for softening the matrix of feedstocks. In extrusion pretreatment, feedstock moisture content plays a role in the development of friction and residence time, in addition to thermal softening by utilizing the barrel

**Table 2.1** Chemical composition of different feedstocks used in extrusion pretreatments (% dry basis)

Feedstock	Cellulose	Hemicellulose	Lignin	Ash	Extractives	References
Corn stover	33.2	22.0	14.9	10.9	12.9	Zhang et al. (2012a, b)
Corn stover	35.2–38.4	19.0–21.6	19.2–21.2	6.6–7.2	8.8–12.5	Karunanithy and Muthukumarappan (2012a)
Switchgrass	25.5–31.3	22.3–25.6	24.7–26.8	3.0–5.6	18.5–23.8	Karunanithy and Muthukumarappan (2012a)
Big bluestem	34.0–36.5	17.3–19.3	19.1–21.1	9.2–11.2	12.5–19.2	Karunanithy and Muthukumarappan (2012a)
Prairie cord grass	33.1–33.5	13.1–17.7	20.5–21.5	5.0–5.6	20.3–22.	Karunanithy and Muthukumarappan (2012a)
Miscanthus	38.2	24.3	25.0	2.0	5.6	de Vrije et al. (2002)
Miscanthus	34.3	36.8	24.8	4.9	5.7	Jurisc (2012)
Rice straw	38.8	12.3	19.5	13.1	13.1	Chen et al. (2011)
Barely straw	39.1	25.7	16.4	6.8	10.2	Duque et al. (2011)
Rape straw	32.9	17.1	NR	NR	NR	Choi and Oh (2012)
Wheat bran	10	37	7	NR	NR	Lamsal et al. (2010)
Soybean hull	31	19	14	NR	NR	Lamsal et al. (2010)
Soybean hull	36.2	17.2	2	NR	NR	Yoo et al. (2011)
Poplar	44.9	36.8	17.7	0.19	5.0	N'Diaye et al. (1996)
Douglas fir	46.8	28.9	25.3	NR	NR	Lee et al. (2010)
Eucalyptus	42.1	34.6	28.8	NR	NR	Lee et al. (2010)
Pine	33.8	27.6	34.7	0.5	3.8	Karunanithy et al. (2012)
NR not reported						

temperature and rate of shear development. In a single screw extruder, the feedstock is mainly conveyed by friction (Yeh and Jaw 1998), therefore grooved barrel is required for conveying action (Akdogan 1996). Feedstock with low moisture content enhances friction development due to resistance offered by the feedstock. An increase in moisture content would decrease the friction between the feedstock, screw shaft, and extruder barrel (Chen et al. 2010) due to softening of the cellulose, hemicellulose, lignin complex of the feedstock; moreover, high moisture acts as lubricant (Hayashi et al. 1992) contributes to slippage. Because of the above facts, as expected when corn stover, switchgrass, big bluestem, prairie cord grass, and pine wood chips with a wide range of moisture contents (10–50 % wb) were pretreated in a single screw extruder, the sugar recovery decreased remarkably (Karunanithy and Muthukumarappan 2011a, b, c, d). Optimization of extrusion pretreatment conditions for many feedstocks revealed that the moisture content has a strong influence on sugar recovery i.e., the lower the moisture content, better the sugar recovery. Most of the ground feedstocks would have moisture content in the range of 5–8 % wb; however, feedstocks with these low moisture contents cannot be pretreated in an extruder since it would get stuck in the extruder barrel. Therefore, addition of moisture becomes inevitable. Instead of adding water to bring the feedstock moisture content to a target level, it is better to use the feedstocks from the field with the desired range of moisture thereby one can save drying cost.

Researchers from University of Nebraska, Lincoln reported that twin screw extrusion of corn stover with a moisture content of 22.5–27.5 % wb did not contribute to the sugar recovery due to narrow range of moisture content (Zhang et al. 2012b). However, in another study these authors adjusted corn stover moisture content to 50 % wb by adding required alkali solution (Zhang et al. 2012a). Twin screw extrusion of soybean hull with high in-barrel moisture contents (45–50 % wb) resulted in a better sugar recovery. In most of the twin screw extrusion pretreatment, chemical solutions are added to different feedstocks during extrusion that brings up the moisture content. When compared to single screw extruder, the feedstock moisture content was high in twin screw extruder. A possible reason might be the difference in conveying mechanisms of single screw and twin screw extruders. Akodagan (1996) reported that the feedstock is transferred in bulk from one screw to the other that facilitates the forward conveyance of the feedstock in a twin screw extruder. Again literature survey indicated that only a few studies have investigated the effect of moisture content on sugar recovery. Since moisture content is a critical factor in extrusion pretreatment, optimum range should be identified for each feedstock and for the type of extruder.

### ***2.4.3 Feedstock Particle Size***

Feedstock particle size depends on the type of pretreatment methods e.g. most of the chemical pretreatments require 1–2 mm particle size. According to an US patent 5677154 (Draanen and Mello 1997), for ethanol production process

requires feedstock particle size in the range of 1–6 mm. Smaller particle sizes contribute to higher surface to mass ratio that are more readily hydrolyzed by enzymes. Cadoche and Lopez (1989) reported that the power requirement for size reduction of feedstocks depends on the final particle size and characteristics of feedstocks. In general, size reduction costs and energy requirements has inverse relation with particle sizes. Particle size not only affect the cost of size reduction but also affects the diffusion kinetics and effectiveness of pretreatment (Kim and Lee 2002; Chundawat et al. 2007), sugar yield (Chang et al. 2001; Hu et al. 2008; Yang et al. 2008), lignin removal (Hu et al. 2008), hydrolysis rate, rheological properties (Chundawat et al. 2007; Desari and Bersin 2007), and acetic acid formation (Guo et al. 2008). The authors investigated the effect of feedstock particle size (2–10 mm) as part of the optimization study and found an 8 mm particle size can be used in single screw extruder without compromising sugar recovery (Karunanithy and Muthukumarappan 2011a, b, c, d). Jurisic (2012) also evaluated the effect of miscanthus particle size on sugar recovery but in a narrow range (0.67–2.33 mm) using a single screw extruder. The effect of feedstock particle size in a twin screw extruder was not found in the literature; therefore, it is another research area that should be addressed before moving into industrial scale.

## 2.5 Extrusion Pretreatment of Different Feedstocks

Researchers evaluated the pretreatment efficiency in terms of ruminant digestibility, sugar recovery, and enzymatic digestibility. Summary of extrusion pretreatment of different feedstocks is divided before and after the year 2000 and presented in the following section.

### 2.5.1 *Earlier Extrusion Studies*

In the early days, extrusion has been used as means to enhance delignification, ruminant digestibility, nutritive value, and fermentability. Mostly extrusion was used in combination with chemicals such as dilute sulfuric acid (Noon and Hochstetler 1982), sodium hydroxide, sodium sulfide, anthraquinone, anthrahydroquinone, hexamethylenediamine, hexamethylenetetramine, hydrogen peroxide, and ferrous ammonium sulfate (Carr and Doane 1984), and alkaline hydrogen peroxide (Gould et al. 1989; Helming et al. 1989) for improving nutritive value or digestibility of straw/biomass. Noon and Hoschtetler (1982) utilized pilot-scale single screw extruder with dilute sulfuric acid injection at three different locations along the barrel for exploring alcohol fuel from saw dust, corn stover and wheat straw. The authors fed the moisture balanced feedstocks (40 % wb) to the extruder, acid (1.78 % of gross mass flow) was injected about hallway or more down the barrel and they reported 40, 33, and 33 % cellulose conversion for saw dust,

corn stover, and wheat straw, respectively. Extrusion treatments (stainless steel interrupted-flight screw and stationary pins) of wheat straw (20 % solids loading rate, 98 °C,  $5.6 \pm 1$  min; 35 rpm) with sodium hydroxide (15.7 % DM), sodium hydroxide (15.7 %) and anthrahydroquinone (0.3 %), and sodium hydroxide (12.7 %) and sodium sulfide (5.0 %) resulted in a lignin removal of 64–72 % and pentosans of 36–43 %, whereas they were 46–56 and 23–27 %, respectively, for without extrusion. The cellulase treatment of the residues converted 90–92 % of the cellulose to glucose compared to 61–69 % for without extrusion (Carr and Doane 1984). The same authors carried out another experiment to disrupt wheat straw lignin, hemicellulose, cellulose complex in a twin screw compounder (200–450 rpm, 103 °C) with sodium hydroxide (0–24 %), sodium hydroxide and anthraquinone (0–0.5 %) and water (1:1–1:9) only. Twin screw compounder treatment of wheat straw with 16 % sodium hydroxide and 30 s residence time resulted in a lignin removal of 62–64 % and cellulose to glucose conversion of 87–92 % (Carr and Doane 1984).

Earlier studies using alkaline hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) on the digestibility of wheat straw and similar materials employed as high as 250 g  $\text{H}_2\text{O}_2$ /kg of straw to be considered nonpractical for a commercial process (Gould 1984, 1985; Kerley et al. 1985, 1986; Lewis et al. 1987). Significant amount of liquid stream was also produced with good amount of solubilized hemicellulose. In order to reduce the amount of chemical used and liquid stream, Gould et al. (1989) used an extruder (with flighted screw sections separated by flight interrupting steam-locks) for treating biomass and they reported the addition of  $\text{H}_2\text{O}_2$  and sodium hydroxide (NaOH) to wheat straw (1.6 cm) in the extruder. The highest in-situ digestibility of more than 75 % was reported with 25 g  $\text{H}_2\text{O}_2$ /kg of wheat straw coupled with extruder and it was tenfold reduction in the amount of  $\text{H}_2\text{O}_2$  though the digestibility was only slightly lower than the highest values obtained in earlier studies (Kerley et al. 1985, 1986). Helming et al. (1989) reported synergistic effects between alkaline hydrogen peroxide and twin screw extrusion treatments of wheat straw. Chopped wheat straw (1.5–2.5 cm, 50 % moisture content) impregnated in different amounts of NaOH,  $\text{H}_2\text{O}_2$ , and sodium silicate before extruding in a twin screw extruder. By treating wheat straw with 1–2 %  $\text{H}_2\text{O}_2$  and 4–5 % NaOH in a twin screw extruder, the amount of cell-wall available for microbiological digestion increased from 30 to 40 % for untreated substrate to over 80 % for the treated.

Xylan-Delignification-Process (XDP) utilizes extrusion technology in conjunction with alkali soak and  $\text{H}_2\text{O}_2$  injection. Chen and Wayman (1989) also employed this sort of treatment for aspen wood chips adding  $\text{SO}_2$  prior to extrusion followed by soaking in a 4 % hot NaOH solution as post-extrusion delignification process. When the pretreated wood chip stream was added to water and hydrolysed using cellulase resulted in 10.7 g/l ethanol during a simultaneous saccharification and fermentation with 31.9 % yield of ethanol from dry matter (Tyson 1993). The xylan method continuously treats the biomass by first reacting with a medium containing an alkali agent (pH 11.5), which softens lignin and allows water to enter the biomass. The high temperature and pressure allow the minimization of

chemicals as compared to other technologies for cellulose pretreatment- low acid and high temperature or high acid and low temperature. The extrusion mixes, grinds, sterilize, and disrupts the biomass cell-wall. Dale et al. (1995) employed XDP on switchgrass and corn stalk at the extrusion temperature of 200 °C and pressure of 300–400 psi. The authors first added 50 % NaOH solution to biomass and it was 3 % of the biomass weight. After mixing for 15 min, it was fed to extruder and 1 % w/w H<sub>2</sub>O<sub>2</sub> (9 % solution) was injected near the entrance of the extruder. The residence time was about 15 s. Authors added H<sub>2</sub>O<sub>2</sub> to the extruder barrel to catalyze the breakdown of the biomass structure. They defined the yield as grams of cellobiose and glucose released per gram of cellulose and it was about 85 % within 7 h of enzymatic hydrolysis. The concentration of 4.8 g/l glucose, 3.2 g/l cellobiose, and 2.6 g/l xylose were noted in 24 h for the treated corn stalks. They used ground corn stover (40 mesh) as control and reported a yield of 50 and 72 % in 7 and 24 h, respectively. The treated switchgrass yielded 65 % in 7 h and it increased to 78 % in 24 h, whereas  $\alpha$ - cellulose (control) showed 97 % yield.

Williams et al. (1997) conducted an experiment to find out the effects of extrusion on different feedstocks (corn silage and wheat straw) cell-wall quality and to determine whether the fermentability of their cell-wall can be altered. Wheat straw and corn silage were extruded in conical, corotating twin screw extruder at two temperature conditions (60–115–140–150 and 60–135–165–185 °C) and three screw speeds (10, 25, and 40 rpm) without die. The authors tested the extrudates for their fermentability in cumulative gas production method and compared with each other and controlled too. It was reported that an analysis of the cumulative gas production showed significant differences between substrates. Extrusion treatment also led to significant differences, though the effect of screw speed and temperature were not always consistent.

Dale et al. (1999) explored corotating, self-wiping twin screw extruder for ammonia fiber expansion (AFEX). The sugar yield of extrusion AFEX treated corn stover after enzymatic hydrolysis increased up to 3.5 times than that of control. The ruminant digestibility of corn stover increased up to 32 % (from 54 to 71 %) over completely untreated material, and 23 % (from 63 to 77 %) over material extruded without ammonia.

### **2.5.2 Recent Extrusion Studies**

It is very difficult to compare the results of the extrusion studies due to differences in the type of extruder, type of feedstocks, chemicals used, enzyme dose, ratios between cellulase and  $\beta$ -glucosidase, and enzymatic hydrolysis conditions. However, Tables 2.2 and 2.3 is presented here for comprehensive understanding and comparisons of different extrusion studies without and with chemicals. Though, this book primarily deals with ‘green pretreatments’, in order to provide up to date development on extrusion pretreatments the authors included extrusion pretreatments with chemicals. As observed from Tables 2.2 and 2.3, extrusion

**Table 2.2** Comparison of recent extrusion pretreatment of different feedstocks without chemicals

Extruder-type	Conditions	Feedstock condition	Hydrolysis condition	Sugar recoveries	References
Corotating twin screw extruder (no die)	Zone 1 and 2 set at 50 and 140 °C, 40–140 rpm, 0.22 kg/h	Corn stover, <2 mm, 22.5–27.5 % wb	Cellic ctec 2: 0.028 g enzy/g dm, 50 °C, 72 h	Glucose 48.8 %, xylose 25 %, and combined 40 %	Zhang et al. (2012b)
Twin screw extruder, l/d 30:1, 18 mm screw diameter, 2.4 mm circular die	Different heads set at 40–80 °C, 280–420 rpm, 0.54–0.6 kg/h	Soy hull, <1.04 mm, 40–50 % wb	Cellulast 1.5L: Novo 188, 0.2:1; 25 FPU/g cellulose, 50 °C, 72 h, 150 rpm	74 % glucose	Yoo et al. (2012)
Twin screw extruder, l/d 30:1, 18 mm screw diameter, 2.6 mm circular die	Different heads set at 40–150 °C, 220–420 rpm, 1.5 kg/h	Wheat bran, soy hull, 25 % wb	47 mg cellulose/g substrate, 50 °C, 120 rpm, 30 min	41–60 % glucose	Lamsal et al. (2010)
Corotating twin-screw extruder	50 °C, 100 rpm, 1 straw:2 water	Wheat straw	16 h	31 % glucose	Ng et al. (2011)
Single screw extruder l/d 20:1, 3:1 screw compression ratio (no die)	45–225 °C, 20–200 rpm	Big bluestem, 2–10 mm, 10–50 % wb	15 FPU Cellulast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	41–72 % glucose, 41–90 % xylose, 37–67 % combined	Karunanithy and Muthukumarappan (2011c)
Single screw extruder l/d 20:1, 3:1 screw compression ratio (no die)	45–225 °C, 20–200 rpm	Switchgrass, 2–10 mm, 10–50 % wb	15 FPU Cellulast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	27–40 % glucose, 24–60 % xylose, 29–48 % combined	Karunanithy and Muthukumarappan (2011b)
Single screw extruder l/d 20:1, 3:1 screw compression ratio (no die)	45–225 °C, 20–200 rpm	Corn stover, 2–10 mm, 10–50 % wb	15 FPU Cellulast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	68–89 % glucose, 79–90 % xylose, 74–90 % combined	Karunanithy and Muthukumarappan (2011a)

dm dry matter

(continued)



**Table 2.2** (continued)

Extruder-type	Conditions	Feedstock condition	Hydrolysis condition	Sugar recoveries	References
Single screw extruder l/d 20:1, 3:1 screw compression ratio (no die)	45–225 °C, 20–200 rpm	Prairie cord grass, 2–10 mm, 10–50 % wb	15 FPU Celluclast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	41–55 % glucose, 77–85 % xylose, 50–63 % combined	Karunanithy and Muthukumarappan (2011d)
Single screw extruder l/d 20:1, 3:1 screw compression ratio (no die)	100–180 °C, 100–200 rpm	Pine chips, 8 mm, 25–45 % wb	15 FPU Celluclast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	35–66 % glucose, 25–68 % xylose, 32–66 % combined	Karunanithy et al. (2012)
Single screw extruder l/d 20:1, 3:1 screw compression ratio (no die)	83–167 °C, 83–167 rpm	Miscanthus, 0.67–2.33 mm, 13.3–21.6 % wb	5 FPU Celluclast 1.5L and 18 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	17–78 % glucose	Jurisc (2012)

**Table 2.3** Comparison of recent extrusion pretreatment of different feedstocks with chemicals

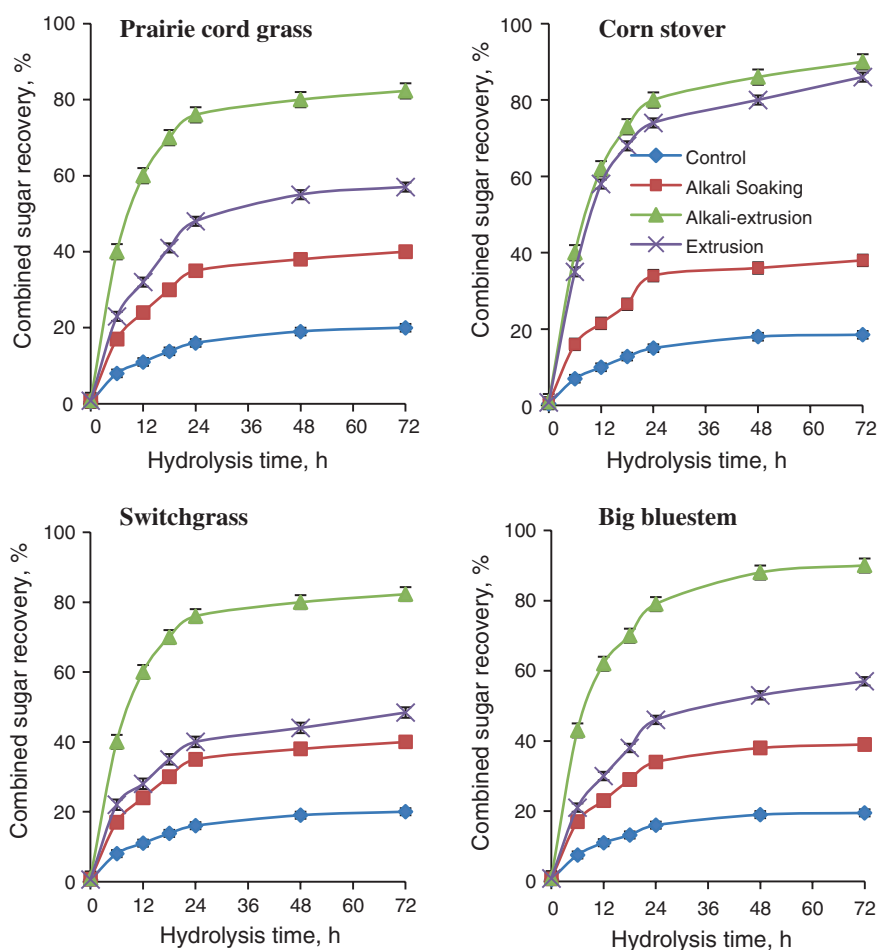
Extruder-type	Conditions	Chemical(s)	Feedstock condition	Hydrolysis condition	Sugar recoveries	References
Counter rotating twin screw extruder, l/d 17, barrel diameter 15.4 mm	40–180 °C, 50 rpm, 0.09 kg/h	Ethylene glycol, glycerol, dimethyl sulfoxide	Douglas fir, <0.2 mm	40 mg enzyme/g substrate, 45 °C, 250 rpm, 48 h	62.4 % glucose	Lee et al. (2009)
Twin-screw extruder	50–100 °C, 150 rpm	2.75–7.5 % NaOH/DM	Barley straw		89.9 % glucose and 83.5 % xylose	Duque et al. (2011)
Corotating twin-screw extruder, 1.25 m length and 55 mm screw diameter	100 °C, 100 rpm, 15.30 kg/h	12 % NaOH, 70 °C, 4 h	Miscanthus	1.6 FPU Celluclast 1.5L, 2.3 Novo/ g dm, 45 °C, 72 h	69 % glucose, 38 % xylose	de Vrije et al. (2002)
Twin-screw extruder l/d 27.8, 1000 mm length and 36 mm screw diameter, barrel and screw were made of SS316L	150–170 °C, 19.7 rpm, 7 min reaction time, 0.080 kg/h	1.5–3.5 % H <sub>2</sub> SO <sub>4</sub>	Rape straw, 1.4–2.36 mm, solid to liquid ratio 1:13–1:9	30 FPU and 70 pNPG/ g cellulose, 50 °C, 120 rpm, 48 h	70.9 % glucose	Choi and Oh (2012)
Corotating twin screw extruder l/d 56, diameter 50 mm, compression ratio 5:1	80–160 °C, 30–150 rpm, 50 % slr, 5–7 kg/h	1–3 % w/w H <sub>2</sub> SO <sub>4</sub>	Rice straw, <1 cm	20 FPU/g cellulose, 50 °C, 100 rpm, 72 h	32.9 % glucose	Chen et al. (2011)
Corotating twin screw extruder, l/d 24	Zone 1 and 2 set at 50 and 140 °C, 40–100 rpm, 0.22 kg/h	1–14 % NaOH w/w added to adjust moisture content to 50 % db	Corn stover, <2 mm, 50 % db	Celic Ctec 2: 0.028 g enzy/g dm, 50 °C, 72 h	86.8 % glucose, 50.5 % xylose	Zhang et al. (2012a)

*dm* dry matter (continued)

Table 2.3 (continued)

Extruder-type	Conditions	Chemical(s)	Feedstock condition	Hydrolysis condition	Sugar recoveries	References
Twin-screw extruder	68 °C	6 % NaOH/g d, H <sub>3</sub> PO <sub>4</sub> introduced at the end of the extruder	Barley straw, 5 mm	CTec 2 10–40 mg/g substrate, HTec 2 0:9–3:9, 50 °C, 72 h	60–68 % glucose, 52–59 % xylose	Barta et al. (2011)
Single screw extruder 1/d 20:1, 3:1 screw compression ratio	45–225 °C, 20–200 rpm	Soaked in 0.5–2.5 % w/w NaOH solution at room temperature for 30 min	Switchgrass, 2–10 mm	15 FPU Celluclast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	31–92 % glucose, 41–85 % xylose, 36–86 % combined	Karunanithy and Muthukumarappan (2011f)
Single screw extruder 1/d 20:1, 3:1 screw compression ratio	45–225 °C, 20–200 rpm	Soaked in 0.5–2.5 % w/w NaOH solution at room temperature for 30 min	Big bluestem, 2–10 mm	15 FPU Celluclast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	33–86 % glucose, 50–94 % xylose, 42–91 % combined	Karunanithy and Muthukumarappan (2011g)
Single screw extruder 1/d 20:1, 3:1 screw compression ratio	45–225 °C, 20–200 rpm	Soaked in 0.5–2.5 % w/w NaOH solution at room temperature for 30 min	Prairie cord grass, 2–10 mm	15 FPU Celluclast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	37–98 % glucose, 46–95 % xylose, 48–95 % combined	Karunanithy and Muthukumarappan (2011h)
Single screw extruder 1/d 20:1, 3:1 screw compression ratio	45–225 °C, 20–200 rpm	Soaked in 0.5–2.5 % w/w NaOH solution at room temperature for 30 min	Corn stover, 2–10 mm	15 FPU Celluclast 1.5L and 60 CBU Novo 188/g dm, 50 °C, 72 h, 150 rpm	25–95 % glucose, 30–90 % xylose, 29–92 % combined	Karunanithy and Muthukumarappan (2011e)

pretreatments without chemicals resulted in a less sugar recovery than that of extrusion pretreatment with chemicals. We performed extrusion pretreatment of different feedstocks with and without alkali soaking and the results are depicted in Fig. 2.5 for easy understanding. The reduction or absence of processing aid led to burning of the feedstock and blocking of the die during extrusion (Lamsal et al. 2010), in order to avoid these problems, Yoo et al. (2011) added starch (5–20 %) and adjusted moisture high range of 20–40 % (wb). If Yoo et al. (2011) would have carried out the extrusion pretreatment without (circular die) as most of the studies listed in Table 2.2, these issues would not have risen due to smooth flow of the feedstock.



**Fig. 2.5** Comparison of sugar recovery profile from control, alkali soaked, and alkali soaked-extruded feedstocks

## 2.6 Evaluation of Pretreatment Efficiency

Researchers employed different techniques or methods such as measurement of mean particle size, surface area, pore size and quantity (SEM images), crystallinity index, fermentation inhibitors, and mass balance analysis to support their findings and they are presented in this section.

### 2.6.1 Mean Particle Diameter

Lee et al. (2009, 2010) observed most of the fibers had a diameter of 20 nm and some in the 100 nm when douglas fir was extruded with cellulose affinity additives, whereas hot compressed water-extrusion resulted in a submicron fiber diameter (5 nm). Different feedstocks pretreated using a single screw extruder is shown in Fig. 2.6 for easy visualization of the changes in particle sizes and they were subjected to particle size analyses (Karunanithy and Muthukumarappan 2011a, b, c, d) The authors reported about 90 % of the control passed through 8 mm and about 95 % of optimum pretreated corn stover, switchgrass, big bluestem, and prairie cord grass passed through 1.78, 1.85, 1.79, and 1.80 mm, respectively. Recently, Chen et al. (2011) found the mean particle diameter of extrusion pretreated rice straw in the range of 400–500  $\mu\text{m}$  depending upon the screw speed, whereas extrusion followed by hot water extraction resulted in lower range of 90–300  $\mu\text{m}$ . The above results provide evidence for increase in sugar recovery from different feedstocks is due to decrease in fiber diameter.

### 2.6.2 Surface Area

In general, greater the surface area, greater the sugar recovery or hydrolysis yield. Lee et al. (2009) found the specific surface area using two different methods namely, BET method and Congo red dye absorption. They reported the specific surface area as 21.3 and 19.4  $\text{m}^2/\text{g}$  and amount dye absorbed was 14.3 and 13  $\text{mg}/\text{g}$ , respectively, for Douglas fir with an ethylene glycol as cellulose affinity additive pretreated at a barrel temperature of 40 and 120  $^{\circ}\text{C}$  in a twin screw extruder. Zhang et al. (2012b) also reported a similar observation i.e., specific surface area of 367–439  $\text{m}^2/\text{g}$  and amount of dye absorbed was 246–293  $\text{mg}/\text{g}$  when corn stover pretreated in a twin screw extruder. Karunanithy and Muthukumarappan 2011a, b, c, d) reported that optimum extrusion pretreated corn stover, switchgrass, big bluestem, and prairie cord grass had a surface area of 0.772, 0.688, 0.790, and 1.15  $\text{m}^2/\text{g}$  when compared to an 8 mm control of 0.400, 0.445, 0.469 and 0.347  $\text{m}^2/\text{g}$ , respectively, when measured using Beckman Coulter SA3100

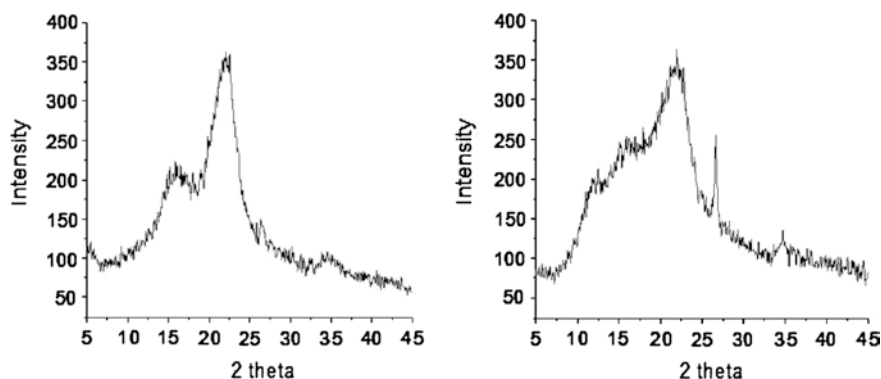


Fig. 2.6 Feedstocks pretreated in a single screw extruder

surface area analyzer. Recently, Chen et al. (2011) observed when rice straw pretreated with acid in a twin screw extruder had a BET surface area of 2.8–4.0 m<sup>2</sup>/g

### 2.6.3 Crystallinity Index

Cellulose crystallinity is considered as one of the factors impeding the enzymatic hydrolysis. Crystalline cellulose offers resistance to enzymatic hydrolysis because of strong interchain hydrogen-bonding network, whereas amorphous cellulose is readily digestible, thereby lowering the cellulose crystallinity is desirable. A few researchers have evaluated the crystallinity index of control and extrusion pretreated feedstocks. Though there was an absolute differences among the crystallinity index of raw Douglas fir, extrusion pretreated at 40 and 120 °C were 68.4, 54.7, and 47.1 %,



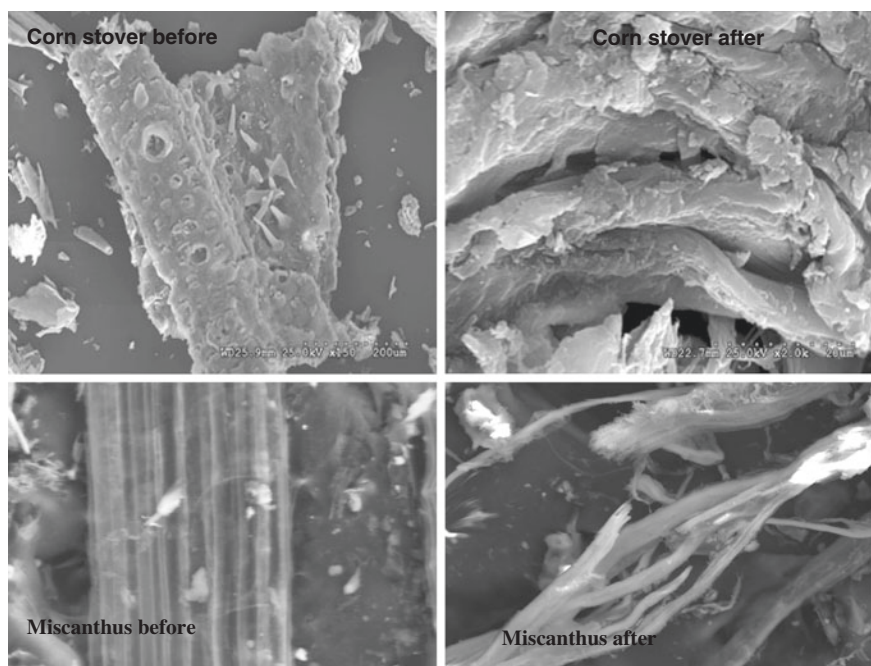
**Fig. 2.7** X-ray diffractograms of control and twin-screw extruded at 80 rpm with 27.5 % wb moisture content corn stover (Zhang et al. 2012b). Reprinted from applied biochemistry and biotechnology, pretreatment of corn stover with twin-screw extrusion followed by enzymatic saccharification, © 2011, Shujing Zhang, 2, with kind permission from Springer Science and Business Media and any original (first) copyright notice displayed with material

respectively, they were not significantly different (Lee et al. 2009). Lamsal et al. (2010) noticed that extrusion pretreatment of soybean hull and wheat bran did not lower their crystallinity index. Recently, Zhang et al. (2012b) found that corn stover had a tendency of crystal lattice transition from cellulose I to cellulose II as a result of extrusion pretreatment (Fig. 2.7). The characteristic peaks observed around  $12.1^\circ 2\theta$  and a shoulder between  $19$  and  $20^\circ 2\theta$  indicate the presence of cellulose II. However, they did not observe a similar change with other extrusion pretreatment conditions. In another study, Zhang et al. (2012a) observed that alkali extrusion of corn stover had no effect on crystallinity index. The above studies confirm that extrusion facilitates the fibrillation without losing energy to destroy the cellulose crystallinity that raises the question of whether cellulose crystallinity is an impeding factor or not.

#### 2.6.4 Pore Size and Quantity

Some of the researchers have supported their finding with scanning electron microscopic (SEM) images to show the topological changes. One such image is presented for control and extrusion pretreated feedstocks in Fig. 2.8. Senturk-Ozer et al. (2011) have provided the evidence in Fig. 2.9 how the topology changes when mixed wood species was pretreated using reactive extrusion process. One can easily notice the increase in pore size as well as the gradual emergence of separated cellulosic fibers in the extruder upon delignification. Recently, Zhang et al. (2012a) reported an increase in porosity from 73 to 148 mg/g when corn stover extruded depending upon the alkali concentration. However, the authors concluded that higher alkali concentrations not necessarily result in more meso and large-scale pores since the porosity/amount of dye absorbed was not in full agreement with sugar recovery.

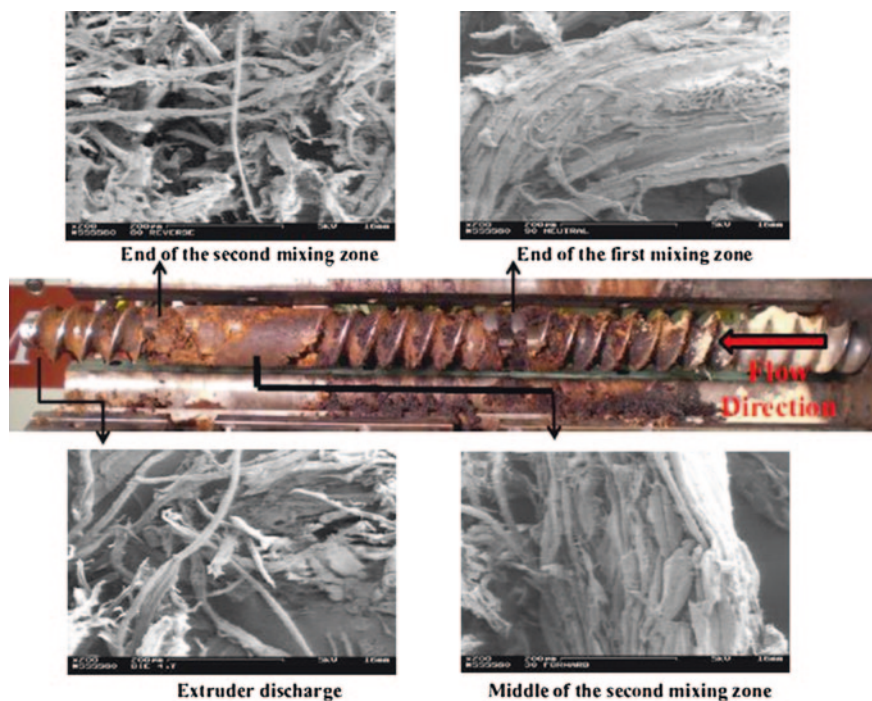




**Fig. 2.8** SEM images of corn stover (Zhang et al. 2012b) and miscanthus (Jurisic 2012) before and after extrusion pretreatment. Reprinted from applied biochemistry and biotechnology, pretreatment of corn stover with twin-screw extrusion followed by enzymatic saccharification, © 2011, Shujing Zhang, 2, with kind permission from Springer Science and Business Media and any original (first) copyright notice displayed with material

### 2.6.5 Washing of Extrudates is Boon or Bane?

Soybean hull and wheat bran were moisture balanced with sodium hydroxide, urea, and thiourea solution (10 % w/w) to achieve 30–35 and 20–25 %, respectively, and then extruded in a twin screw extruder (Lamsal et al. 2010). Extrudates washed extensively with excess water and centrifugation, HCl was used for adjusting pH to 6.5 and finally the samples were dried at 45 °C for overnight. The reducing sugar of 12–18 % and 38–40 % for soybean hull and wheat bran extrudates, respectively, before washing increased to 28–30 % and 63–70 %, respectively. The authors speculated that extensive washing for the removal of solvents and inhibitors that increased sugar recovery without reporting the amount of solvent and inhibitors details before and after washing, further the effect of HCl addition and pore collapsibility details also missing. They also reported that washing of extrudates made with water alone also improved the reducing sugar without providing sufficient details. According to Yoo et al. (2011), unlike acid or alkali hydrolyzed soybean hulls (Lamsal et al. 2010), the extruded soybean hulls (moisture balanced with water) did not require neutralization or washing steps prior to enzymatic hydrolysis.



**Fig. 2.9** SEM micrographs of mixed wood samples collected from different locations in the twin screw extruder (Senturk-Ozer et al. 2011). Reprinted from biomass technology, biomass pretreatment strategies via control of rheological behavior of biomass suspensions and reactive twin screw extrusion processing, 102/19, 2011, Semra Senturk-Ozer, Halil Gevgilili, Dilhan M. Kalyon, 8, with kind permission from Springer Science and Business Media and any original (first) copyright notice displayed with material

Barta et al. (2011) extruded barely straw with alkali (6 % dm) and then washed the solid fraction with tenfold amount of distilled water. They found the washed solid fraction resulted in higher glucose (60–68 %) and xylose recovery (52–59 %) than that of whole slurry (44–50 % glucose and 40–46 % xylose) at different enzyme loading. Duque et al. (2011) also washed the barely straw extruded with alkali and further details were not found in the conference poster.

Zhang et al. (2012a) extruded corn stover after moisture balancing to 50 % db with alkali solutions (1–14 % w/w), washed with 44 mL of distilled water/g of corn stover extrudates through vacuum filtration and dried the extrudates at ambient conditions for 3 days. They found the extrudates without washing had higher sugar recovery than that of washed extrudates at lower alkali concentrations (1–3 % w/w), but the observation was opposite at higher alkali concentrations (5–14 % w/w). Higher alkali concentration resulted extrudates with high pH that necessitates the washing to neutralize the samples before enzymatic hydrolysis. The authors also attributed pore collapsibility during air drying might outweighed the washing effect at higher alkali concentrations.

The above researchers have reported washing of the feedstocks after extrusion pretreatment; however, it may not be necessary if the alkali concentration is low enough. Zhang et al. (2012a) also found that corn stover extrudates with no washing resulted higher sugar recovery than that of washed extrudates. According to the Novozymes biomass kit, most of the enzymes have optimum activity between a pH of 4.5–6.5 at 45–70 °C. When switchgrass is soaked with different alkali concentrations, the sample prepared for enzymatic hydrolysis (after adding citrate buffer, DI water, and enzymes) had a pH of 4.8–5.4, which is well within the range of Novozyme's recommendations. The authors recorded a sugar recovery of 35–40 % for alkali soaked feedstocks without washing them, depending upon the type of feedstock, alkali concentration, and particle size. It is better to prepare the hydrolysis sample and check the pH before hydrolysis, if the pH is within the recommended pH of the enzymes then there is no need for washing. Moreover, washing removes solubilized sugars (5–7 %) and increases water consumption also.

### 2.6.6 Fermentation Inhibitors

Compounds like furfural, HMF, acetic acid, and glycerol are formed during feedstock pretreatment depending upon the severities (pretreatment temperature, residence time, and acid concentration); moreover the degradation is proportional to the pretreatment severities. Degradation of pentose and hexose results in formation of furfural and HMF, acetyl content in hemicellulose is hydrolyzed into acetic acid. According to Luo et al. (2002), furfural and HMF inhibits glycolysis and ethanol pathway, protein and RNA synthesis and all these indicate they are potential fermentation inhibitors. Furfural and HMF was not found in any of the extrusion pretreatments employed on different feedstocks with or without alkalis and this makes extrusion pretreatment is better than other leading pretreatments. However, Chen et al. (2011) reported furfural in the range of 0.3–1 g/L when dilute sulfuric acid (1–3 % w/w) added to the rice straw in a twin screw extruder. This indicates that the combination of acidic condition and high temperature leads to furfural formation. Considering this criterion, when sulfuric acid (1.5–3.5 % w/w) added to rape straw pretreated in a twin screw extruder (Choi and Oh 2012) would have resulted in furfural, which was not reported. If the hydrolysate contains furfural in the range of 0.5–8 g/L that would result in an inhibition 21–97 % of ethanol production by *Saccharomyces cerevisiae*, with HMF having a higher threshold level than furfural (Luo et al. 2002; Pienkos and Zhang 2009; Banerjee et al. 1981).

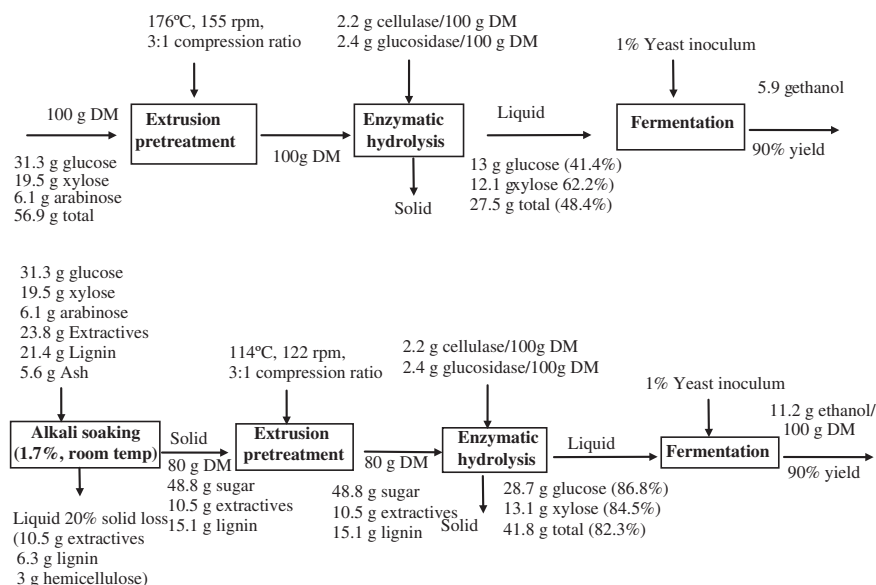
Hydrolysis of the acetyl group present in the hemicellulose is responsible for acetic acid formation as a result of deacetylation. Chemical interference is the mechanism that acetic acid inhibits ethanol production through dissociating in the cytoplasm and causing pH imbalances at high concentration ultimately result in cell growth inhibition or death (Luo et al. 2002). Acetic acid

was the most common inhibitors found in low concentrations in the extrusion pretreatments. The hydrolyzate of extruded soybean hull had acetic acid concentration of 1.12–1.42 g/L (Yoo et al. 2012). The authors found acetic acid in the range of 0.04–0.26 g/L for corn stover, 0.03–0.43 g/L for switchgrass (Karunanithy and Muthukumarappan 2011b), 0.05–0.18 g/L for big bluestem (Karunanithy and Muthukumarappan 2012b), and 0.04–0.20 g/L for prairie cord grass (Karunanithy and Muthukumarappan 2011d) when pretreated in a single screw extruder. Similarly, the authors found acetic acid concentration of 0.06–0.17, 0.07–0.16, 0.06–0.1, and 0.07–0.18 g/L, respectively, for corn stover (Karunanithy and Muthukumarappan 2011e), switchgrass grass (Karunanithy and Muthukumarappan 2012b), big bluestem (Karunanithy and Muthukumarappan 2011g), and prairie cord grass (Karunanithy and Muthukumarappan 2011h) when extruded after alkali soaking. However, Karunanithy et al. (2012) reported there was no acetic acid found in the hydrolyzate of extruded pine chips. Chen et al. (Chen et al. 2011) reported higher acetic acid concentration (2.0–5.9 g/L) for rice straw extruded with sulfuric acid than other extrusion studies. If the hydrolyzate contains 1.4–7.5 g/L of acetic acid that would inhibit 50–80 % of ethanol production by *Sacchromyces cerevisiae*; however, the effect is pH dependent (higher inhibition at lower pH) (Olsson and Hanh-Hägerdal 1996; Maiorella et al. 1983; Phowchinda et al. 1995; Pampulha and Loureiro 1989). The concentration of acetic acid found in most of the extrusion studies [extrusion of rice with acid] was far lower than the inhibition limit (5 g/L) (Taherzadeh et al. 1997).

Glycerol is a by-product and it is not directly toxic to yeast. If the glycerol concentration is greater than 100 g/L then it generates osmotic stress in the cells thereby inhibits ethanol fermentation (Maiorella et al. 1983). Extrusion pretreatment of corn stover, switchgrass, big bluestem, and prairie cord grass resulted in a glycerol concentration of 0.02–0.18 g/L (Karunanithy and Muthukumarappan 2010a, b). When these feedstocks subjected to alkali soaking followed by extrusion, a glycerol concentration of 0.04–0.16 g/L was found only for switchgrass (Karunanithy and Muthukumarappan 2012b). Yoo et al. (2012) reported a higher glycerol concentration of 0.24–0.69 g/L for the hydrolyzate of extruded soybean hull. Jurisic (2012) reported byproducts in the range of 0.2–5.1 % on dry matter basis when *miscanthus* pretreated in a single screw extruder. Yoo et al. (2012) reported a significant increase in acetic acid and glycerol concentration between hydrolyzate and fermentation broth of extruded soybean hull. They also found high concentration of lactic acid (7.2–9.3 g/L) only in fermentation broth. Hence, these observations necessitate the fermentation trials of extrusion pretreated feedstocks to ensure extrusion's merit.

### 2.6.7 Mass Balance Analysis

Mass balance provides details on how the pretreatment changes the solid fraction, change in composition of the feedstocks, and degradation/formation of byproducts



**Fig. 2.10** Mass balance diagram of extrusion pretreated switchgrass (Karunanithy and Muthukumarappan 2011b). Reprinted from industrial crops and products, optimization of switchgrass and extruder parameters for enzymatic hydrolysis using response surface methodology, 2011, 33/1, C. Karunanithy, K. Muthukumarappan, 12, with kind permission from Springer Science+Business Media and any original (first) copyright notice displayed with material

if any. Figure 2.10 shows the mass balance of extruded switchgrass with and without alkali soaking. As noticed from the figure, alkali soaking resulted in a solid loss of 20 % including small amount of hemicellulose. Preservation of hemicellulose is one of the criteria for an effective pretreatment. The hemicellulose loss can be avoided in the above study if the authors would have used alkali solution for moisture balancing of switchgrass. Mass balance analysis is an important tool for economic reasons; therefore, researchers should report the mass balance analyses of extrusion employed on different feedstocks.

## 2.7 Comparison of Extrusion with Other Pretreatments

A few researchers have compared different pretreatments with extrusion using the same feedstocks. The authors compared alkali soaking of different feedstocks with extrusion and they found the performance of extrusion (48–57 %) was better than alkali soaking (35–39 %) as shown in Fig. 2.5. However, when alkali soaked feedstocks pretreated in an extruder increased the sugar recovery to 86–95 %. Similarly Zhang et al. (2012a, b) compared extrusion with alkali-extrusion of corn stover and found alkali-extrusion had better glucose (87 %) and xylose (51 %) than that of extrusion alone (49 % glucose and 25 % xylose). A possible reason



for increase in sugar recovery is a combination of delignification due to alkali soaking/incorporation and extrusion. The sugar recovery from soybean hull through extrusion pretreatment (155 %) was better than dilute acid (70 %) and alkali (129 %) pretreatments (Yoo et al. 2011, 2012) compared to control. Ng et al. (2011) compared extrusion (50 °C, 100, rpm, 1 straw: 2 water), alkali-extrusion (50 °C, 100 rpm, 4 % NaOH, 1 straw: 2 water), and steam explosion (190 °C, 10 min, 11.6 bars; 220 °C, 10 min, 22.2 bars) of wheat straw. They concluded that low temperature extrusion (32 %) alone yields with 14 % glucose lower in comparison to highest yield from severe steam explosion (46 %). They also reported that alkali-extrusion (42 %) had a comparable glucose yield to severe steam explosion (46 %) and better than steam explosion (40 %). They were in the opinion that temperature would increase the degree of fractionation in extrusion; however, high pretreatment temperature (>200 °C) would generate fermentation inhibitors, thus one has to strike a balance between sugar recovery and inhibitors.

## 2.8 Torque and Specific Mechanical Energy

The amount of energy required to run the extruder screw is called torque that provides insight into the extruder operation. The motor provides power to turn the screw. Torque relates to the power consumption of the extruder. Torque is related to extruder speed, fill, and viscosity of the material in the screw channel (Harper 1989). Several factors extruder parameters such as screw speed, temperature, compression ratio, and feedstock parameters such as moisture content and particle size are contributing to the net torque. In general, high screw speed and low temperature led to greater torque thereby specific mechanical energy (SME). SME is defined as the mechanical energy input required obtaining unit weight of extrudate. In order to calculate SME, one should know throughput of the feedstock ( $\dot{m}$  kg/h).

$$\text{SME (Wh/kg)} = P(W) \times \dot{m}(\text{kg/h}) \quad (2.1)$$

$$P(W) = 220 \text{ V} \times I(A) \times \text{Screw speed (rpm)}/\text{Rated screw speed (rpm)} \times 0.95 \quad (2.2)$$

$$\text{Torque, } \tau \text{ (Nm)} = 9550 \times P \text{ (kW)}/\text{Screw Speed (rpm)} \times (1/2) \quad (2.3)$$

In  $P(W)$  formula,  $P(W)$  represents the power consumption,  $I(A)$  is the electrical intensity through the driving motor. In torque formula, 9550 is the conversion factor,  $P(kW)$  is the measured power, and  $1/2$  represents the twin-screw (if it is single screw extruder, this term becomes one).

A certain optimum level of torque and SME is necessary to achieve maximum sugar recovery, beyond which negative effects, such as re-condensation of lignin (Karunanithy and Muthukumarappan 2010c) and degradation of sugars (Lamsal et al. 2010; Yoo et al. 2011), might become significant. Lee et al. (2009) found torque as the most effective parameter for fibrillation, compared to the operation

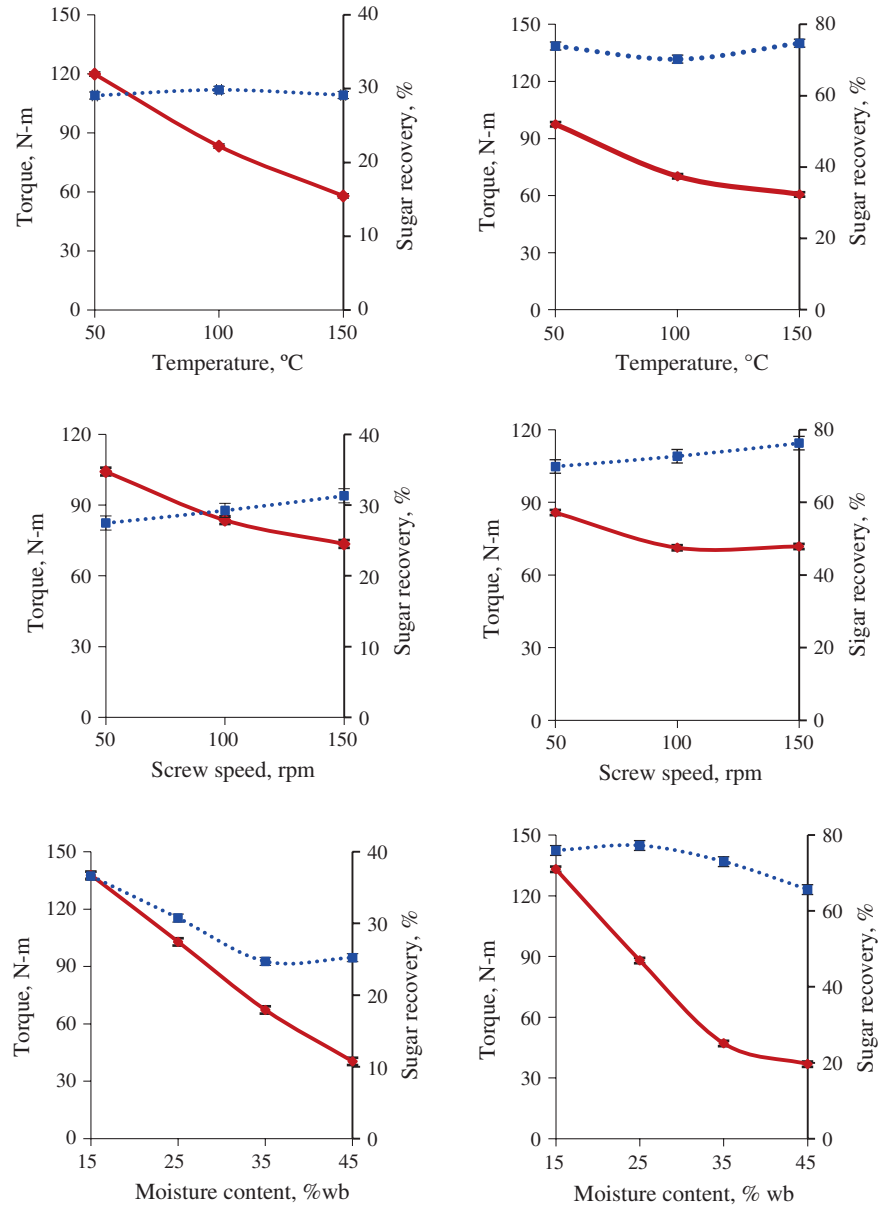
temperature and the swelling effect of agents, within the results obtained in this study. They achieved a high torque (~60–75 Nm) at operating temperature of 40 °C in counter rotating twin screw extrusion of Douglas fir led to the highest glucose recovery. The authors compared torque requirement of different feedstocks and correlated with total sugar recovery as depicted in Fig. 2.11. Chen et al. (2011) reported a similar range of torque requirement (107–202 Nm) for extrusion pretreatment of rice straw with acid. Recently, Karunanithy et al. (2012) found the torque requirement as 180–320 Nm for pine chips. In general, the torque requirement/SME is high at low screw speed (Chen et al. 2011; Karunanithy and Muthukumarappan 2011i, 2012a), barrel temperature (Lee et al. 2009; Karunanithy and Muthukumarappan 2011i, 2012a) and feedstock moisture content (Yoo et al. 2012; Karunanithy and Muthukumarappan 2011i, 2012a). However, Yoo et al. (2012) reported an increase in torque with screw speed for soybean hull pretreatment. The authors reported varying optimum ranges of torque requirement during extrusion for maximum sugar recovery from switchgrass (85–100 Nm), corn stover (52–70 Nm), prairie cord grass (27–42 Nm), and big bluestem (53–84 Nm) (Karunanithy and Muthukumarappan 2011i). They also reported the torque requirement depends upon the lignin content of the feedstocks.

SME for soybean hull and wheat bran was reported in the range of 566–2615 and 800–2300 kJ/kg, respectively (Lamsal et al. 2010; Yoo et al. 2012). However, addition of chemicals (solution) during extrusion pretreatment of soybean hull and wheat bran reduced the SME 240–540 kJ/kg (Lamsal et al. 2010) due to increase in feedstock moisture content. Rice straw pretreatment in a twin screw extrusion with acid had a SME in the range of 192–496 Wh/kg. The relationship between sugar recovery and torque/SME may not be linear since other factors such as residence time, degree of hydration, degree of fill, and any adverse changes in the substrate would affect the process (Yoo et al. 2012). In order to establish and confirm the relationship between sugar recovery and torque, further investigations are required.

## 2.9 Extrusion Involved in Sequential Pretreatments

According to Lee et al. (2010), mechanical kneading alone may not be sufficient for exposing cellulose in submicro/nanoscale for complete enzymatic hydrolysis. With the aim of complete hydrolysis, first Douglas fir and eucalyptus were subjected to hot-compressed water treatment (140–180 °C for 30 min excluding come up time), followed by water washing and then fed to twin screw extruder at room temperature with a screw speed of 45–120 rpm. The glucose yield of sequential pretreated Douglas fir was about 5 times (18–26 wt %) higher than that of hot-compressed water treatment (<5 wt %) alone. Sequential pretreatment resulted in a higher glucose yield for Eucalyptus than for Douglas fir due to the higher hot-compressed water treatment effect in Eucalyptus. Extrusion of Douglas fir with ethylene glycol had a glucose yield of 62.4 % (Lee et al. 2009)





**Fig. 2.11** Effect of independent variables on torque requirement (\_\_\_\_) and sugar recovery (.....) from switchgrass and corn stover (Karunanithy and Muthukumarappan 2012a). Reprinted from BioEnergy research, a comparative study on torque requirement during extrusion pretreatment of different feedstocks, © 2011, Chinnadurai Karunanithy, 5, with kind permission from Springer Science+Business Media and any original (first) copyright notice displayed with material

and this sequential pretreatment had a glucose yield of 67.2 % (Lee et al. 2010). The authors attributed that hot-compressed water treatment facilitated the partial removal of hemicellulose and lignin resulted in loosening the structure in turn the fibrillation (about 20 nm) and hydrolysis. Advantage of this sequential pretreatment is that the extruder can be operated at room temperature with less torque requirement since the feedstock structure was already loosened. Was it worth that the energy spent in the sequential pretreatment for an increase of 5 % glucose yield? Or in other words, is it economical considering only 5 % increase in glucose yield.

In order to increase sugar concentration and overall sugar recovery from rice straw Chen et al. (2011) explored the sequential pretreatment consisting of extrusion with dilute sulfuric acid followed by hot water extraction using saturated steam (130–160 °C) for 10–30 min. They found that enzymatic yield of 19–33 % and 50–61 %, respectively, for only extrusion and sequential extrusion-hot water extraction. The increase in yield was attributed to increase in surface area and decrease in mean particle diameter from 2.8 to 4.0 m<sup>2</sup>/g and 400–500 μm (only extrusion)/g to 7–10 m<sup>2</sup>/g and 90–300 μm (sequential pretreatment), respectively.

We are exploring different sequential pretreatments consisting microwave or ozone in the front or back end of extrusion and the results are yet to be published. We expect about 20–30 % increase in sugar recovery depending upon the pretreatment conditions.

## 2.10 Future Directions

Extrusion pretreatments of different feedstocks clearly demonstrate that it is one of the continuous methods ready for scaling up. However, fermentation results of the extrusion pretreated feedstocks are missing. Fermentation trials of extrusion pretreated soybean hull revealed the presence of lactic acid, though it was not present in the hydrolyzate, but no furfural or HMF presents either in the hydrolyzate or fermentation broth. Hence, in order to prove extrusion pretreatment capability, extruded feedstock should be subjected to fermentation trials to check types of inhibitors and their levels and effects. Though torque requirements of different feedstocks gives fair idea about extrusion pretreatment, energy analysis is missing. Providing complete energy analysis of the extrusion pretreatment of different feedstocks would help the biorefinery industry. The literature survey reveals that extrusion pretreatment alone is capable of getting a sugar recovery in the range of 50–65 %. This indicates sequential pretreatment would be viable option. Considering the cost economics of chemicals and effluent treatment, hot water/steam pretreatment in the front (preferably) or back end of extrusion would be explored for different feedstocks. Hot water pretreatment in the front end would reduce the torque requirement remarkably during extrusion pretreatment thereby one can save energy cost. In addition, we have indicated several research opportunities in different sections on this chapter.

## References

- Akdogan H (1996) Pressure, torque, and energy responses of a twin screw extruder at high moisture contents. *Food Res Int* 29(5–6):423–429
- Baillif M, Oksman K (2009) The effect of processing on fiber dispersion, fiber length, and thermal degradation of bleached sulfite cellulose fiber polypropylene composites. *J Thermoplast Compos Mat* 22(2):115–133
- Banerjee N, Bhatnagar R, Viswanathan L (1981) Inhibition of glycolysis by furfural in *Saccharomyces cerevisiae*. *Eur J Appl Microbiol Biotech* 11:226–228
- Barta Z, Duque A, Oliva JM, Manzanares P, González A, Ballesteros M, Réczey K (2011) Improving enzymatic hydrolysis of alkali-extruded barley straw by varying the dosage and ratio of hemicellulases and cellulases ITALIC6 Italian meeting on lignocellulosic chemistry final workshop cost FP0602 workshop cost FP0901 5–8 September 2011. Viterbo, Italy
- Cadoche L, Lopez GD (1989) Assessment of size reduction as a preliminary step in the production of ethanol from lignocellulosic wastes. *Biol Waste* 30(2):153–157
- Carr ME, Doane WM (1984a) Modification of wheat straw in a high shear mixer. *Biotech Bioeng* 26:1252–1257
- Carr ME, Doane WM (1984b) Pretreatment of wheat straw in a twin screw compounder. *Biotech Bioeng Symp* 14:187–195
- Chang VS, Kaar WE, Burr B, Holtzapple MT (2001) Simultaneous saccharification and fermentation of lime-treated biomass. *Biotechnol Lett* 23(16):1327–1333
- Chen S, Wayman M (1989) Continuous production of ethanol from aspen cellulose by co-immobilized yeast and enzymes. *Process Biochem* 24(10):204
- Chen FL, Wei YM, Zhang B, Ojokoh AO (2010) System parameters and product properties response of soybean protein extruded at wide moisture range. *J Food Eng* 96:208–213
- Chen W-H, Xu Y-Y, Hwang W-S, Wang J-B (2011) Pretreatment of rice straw using an extrusion/extraction process at bench-scale for producing cellulosic ethanol. *Bioresour Technol* 102:10451–10458
- Choi CH, Oh KK (2012) Application of a continuous twin screw-driven process for dilute acid pretreatment of rape straw. *Bioresour Technol* 110:349–354
- Chundawat SPS, Venkatesh B, Dale BE (2007) Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility. *Biotech Bioeng* 96(2):219–231
- Dale MC, Tyson G, Zhao C, Lei S (1995) The Xylan delignification process for biomass conversion to ethanol. Report DOE/CE/15594-78/Conf-950587-3
- Dale BE, Weaver J, Byers FM (1999) Extrusion processing for ammonia fiber explosion (AFEX). *Appl Biochem Biotech* 77:35–45
- de Vrije T, de Haas GG, Tan GB, Keijsers ERP, Claassen PAM (2002) Pretreatment of miscanthus for hydrogen production by *Thermotoga elfii*. *Intl J Hydrogen Energy* 27(11–12):1381–1390
- Desari RK, Bersin RE (2007) The effect of particle size on hydrolysis reaction rates and rheological properties in cellulosic slurries. *Appl Biochem Biotech* 136–140(1–12):289–299
- Draanen AV, Mello S (1997) Production of ethanol from biomass. US Patent No. 5677154
- Duque A, Manzanares P, Ballesteros I, Negro MJ, Oliva JM, Gonzalez A, Ballesteros M (2011) Extrusion process for barley straw fractionation
- Gibbons WR, Westby CA, Dobbs TL (1986) Intermediate-scale, semicontinuous solid phase fermentation process for production of fuel ethanol from sweet sorghum. *Appl Environ Microbiol* 51(1):115–122
- Gould JM (1984) Alkaline peroxide delignification of agricultural residues to enhance enzymatic saccharification. *Biotech Bioeng* 26:46–52
- Gould JM (1985) Enhanced polysaccharide recovery from agricultural residues and perennial grasses treated with alkaline peroxide. *Biotech Bioeng* 27:893–896
- Gould JM, Jasberg BK, Fahey GC Jr, Berger LL (1989) Treatment of wheat straw with alkaline hydrogen peroxide in a modified extruder. *Biotech Bioeng* 33(2):233–235

- Guo G-L, Chen W-H, Chen W-H, Men L-C, Hwang W-S (2008) Characterization of dilute acid pretreatment of silvergrass for ethanol production. *Bioresour Technol* 99(14):6046–6053
- Harper JM (1981) Extrusion of foods, vol. I. CRC Press, Inc., Boca Raton. ISBN 0-8493-5203-3
- Harper JM (1989) Food extruders and their applications. In Mercier C, Linko P, Harper JM (eds) Extrusion cooking. American Association of Cereal Chemists, St. Paul, p 1e15
- Hayashi N, Hayakawa I, Fujio Y (1992) Hydration of heat-treated soy protein isolate and its effect on the molten flow properties at an elevated temperature. *Intl J Food Sci Tech* 27(5):565–571
- Helmig O, Arnold G, Rzehak H, Fahey GC Jr, Berger LL, Merchen NR (1989) Improving the nutritive value of lignocellulosics: the synergistic effects between alkaline hydrogen peroxide and extrusion treatments. *Biotech Bioeng* 33:237–241
- Hu Z, Wang Y, Wen Z (2008) Alkali (NaOH) pretreatment of switchgrass by radio frequency-based dielectric heating. *Appl Biochem Biotech* 148(1–3):71–81
- Jurisc V (2012) Optimization of high shear extrusion pretreatment of grass from genus *miscanthus* as raw material in bioethanol production. PhD thesis, submitted to University of Zagreb, Croatia
- Jurisc V, Karunanithy C, Julson JL (2009) Effect of extrusion pretreatment on enzymatic hydrolysis of *Miscanthus*. ASABE Paper no. 097178. St. Joseph, Mich: ASABE
- Karunanithy C, Muthukumarappan K (2010a) Effect of extruder parameters and moisture content of corn stover and big bluestem on sugar recovery. *Biol Eng* 2(2):91–113
- Karunanithy C, Muthukumarappan K (2010b) Effect of extruder parameters and moisture content of switchgrass, prairie cord grass on sugar recovery from enzymatic hydrolysis. *Appl Biochem Biotech* 162:1785–1803
- Karunanithy C, Muthukumarappan K (2010c) Influence of extruder temperature and screw speed on sugar recovery from corn stover through enzymatic hydrolysis while varying enzymes and their ratios. *Appl Biochem Biotech* 162:264–279
- Karunanithy C, Muthukumarappan K (2011a) Optimization of corn stover and extruder parameters for enzymatic hydrolysis using response surface methodology. *Biol Eng* 3(2):73–95
- Karunanithy C, Muthukumarappan K (2011b) Optimization of switchgrass and extruder parameters for enzymatic hydrolysis using response surface methodology. *Ind Crops Prod* 33(1):188–199
- Karunanithy C, Muthukumarappan K (2011c) Optimization of big bluestem and extruder parameters for enzymatic hydrolysis using response surface methodology. *Inter J Agric Biol Eng* 4(1):61–74
- Karunanithy C, Muthukumarappan K (2011d) Optimization of extruder and prairie cord grass parameters for maximum sugar recovery through enzymatic hydrolysis. *J Biobased Mat Bioenergy* 5(4):520–531
- Karunanithy C, Muthukumarappan K (2011e) Chapter 14: application of response surface methodology to optimize the alkali concentration, corn stover particle size and extruder parameters for maximum sugar recovery. In: MA Dos Santos Bernardes (ed) *Biofuel production-recent development and prospects*, pp 343–374. ISBN:978-953-307-478-8
- Karunanithy C, Muthukumarappan K (2011f) Optimization of alkali concentration, switchgrass particle size and extruder parameters for maximum sugar recovery using response surface methodology. *Chem Eng Tech* 34(9):1413–1426
- Karunanithy C, Muthukumarappan K (2011g) Optimization of alkali concentration, big bluestem particle size and extruder parameters for maximum sugar recovery using response surface methodology. *BioResources* 6(1):762–790
- Karunanithy C, Muthukumarappan K (2011h) Optimization of alkali concentration and extruder parameters for maximum sugar recovery from prairie cord grass using response surface methodology. *Biochem Eng J* 54:71–82
- Karunanithy C, Muthukumarappan K (2011i) Influence of extruder and biomass variables on torque requirement during pretreatment of different biomasses—a response surface analysis. *Biosyst Eng* 109(1):37–51
- Karunanithy C, Muthukumarappan K (2012a) A comparative study of torque requirement during extrusion pretreatment for different biomasses. *BioEnergy Res* 5:265–276

- Karunanithy C, Muthukumarappan K (2012b) Extrusion pretreatment of biomass towards bioethanol production. LAP LAMBERT Academic Publishing GmbH & Co, Saarbrücken. ISBN 978-3-8473-4262-5
- Karunanithy C, Muthukumarappan K, Gibbons WR (2012) Extrusion pretreatment of pine wood chips. *Appl Biochem Biotechnol*. doi:[10.1007/s12010-012-9662-3](https://doi.org/10.1007/s12010-012-9662-3)
- Kerley MS, Fahey GC Jr, Berger LL, Gould JM, Baker FL (1985) Alkaline hydrogen peroxide treatment unlocks energy in agricultural by-products. *Science* 203:820–822
- Kerley MS, Fahey GC Jr, Berger LL, Gould JL, Merchen NR, Gould JM (1986) Effects of alkaline hydrogen peroxide treatment of wheat straw on site and extent of digestion in sheep. *J Animal Sci* 63:868–878
- Kim SB, Lee YY (2002) Diffusion of sulfuric acid within lignocellulosic biomass particles and its impact on dilute acid treatment. *Bioresour Technol* 83(2):165–171
- Lamsal B, Yoo J, Brijwani K, Alavi S (2010) Extrusion as a thermo-mechanical pre-treatment for lignocellulosic ethanol. *Biomass Bioenergy* 34:1703–1710
- Laser M, Schulman D, Allen SG, Lichwa J, Antal MJ Jr, Lynd LR (2002) A comparison of liquid hot water and steam pretreatments of sugarcane bagasse for bioconversion to ethanol. *Bioresour Technol* 81(1):33–44
- Lee SH, Teramoto Y, Endo T (2009) Enzymatic saccharification of woody biomass micro/nanofibrillated by continuous extrusion process: I: effect of additives with cellulose affinity. *Bioresour Technol* 100(1):275–279
- Lee SH, Inoue S, Teramoto Y, Endo T (2010) Enzymatic saccharification of woody biomass micro/nanofibrillated by continuous extrusion process II: effect of hot-compressed water treatment. *Bioresour Technol* 101:9645–9649
- Lewis SM, Kerley MS, Fahey GC Jr, Berger LL, Gould JM (1987) Use of alkaline hydrogen peroxide-treated wheat straw as an energy source for the growing ruminant. *Nutr Rep Int* 35:1093–1104
- Luo C, Brink D, Blanch W (2002) Identification of potential fermentation inhibitors in conversion of hybrid poplar hydrolyzate to ethanol. *Biomass Bioenergetics* 22:125–138
- Maioresella B, Blanch HW, Wilke CR (1983) By-product inhibition effects on ethanolic fermentation by *Saccharomyces cerevisiae*. *Biotechnol Bioeng* 25:103–121
- Miller S, Hester R (2007) Concentrated acid conversion of pine softwood to sugars Part I: Use of a twin-screw reactor for hydrolysis pretreatment. *Chem Eng Comm* 194(1):85–102
- N'Diaye S, Rigal L, Larocque P, Vidal PF (1996) Extraction of hemicelluloses from poplar, *Populus tremuloides*, using an extruder-type twin screw reactor: a feasibility study. *Bioresour Technol* 57:61–67
- National Research Council (2000) Biobased industrial products—priorities of research and commercialization. National Academy Press, Washington, DC
- Ng TH, Song J, Tarverdi K (2011) Cereal straw pre-treatment for bio-fuel application: comparison between extrusion and conventional steam explosion In: ResCon'11, 4th annual research student conference, pp 14–17, 20–22 June 2011
- Noon R, Hochstetler T (1982) Production of alcohol fuels via acid hydrolysis extrusion technology. *Fuel Alcohol U S A* 4(7):14–23
- Olsson L, Hanh-Hägerdal B (1996) Fermentation of lignocellulosic hydrolysates for ethanol production. *Enzym Microb Tech* 18:312–331
- Pampulha ME, Loureiro V (1989) Interaction of the effect of acetic acid and ethanol on inhibition of fermentation in *Saccharomyces cerevisiae*. *Biotechnol Lett* 11:269–274
- Phowchinda O, Delia-Dupuy ML, Strehaiano P (1995) Effect of acetic acid on growth and fermentation activity of *Saccharomyces cerevisiae*. *Biotechnol Lett* 17:237–242
- Pienkos PT, Zhang M (2009) Role of pretreatment and conditioning processes on toxicity of lignocellulosic biomass hydrolysates. *Cellulose* 16:743–762
- Senturk-Ozer S, Gevgilili H, Kalyon DM (2011) Biomass pretreatment strategies via control of rheological behavior of biomass suspensions and reactive twin screw extrusion processing. *Bioresour Technol* 102:9068–9075

- Taherzadeh MJ, Niklasson C, Lidén G (1997) Acetic acid—friend or foe in anaerobic batch conversion of glucose to ethanol by *Saccharomyces cerevisiae*? Chem Eng Sci 52(15):2653–2659
- Tyson G (1993) Evaluation of alternate pretreatment and biomass fractionation process. NREL report on contract XAW-3-11181-05-104840
- Williams BA, van der Poel AFB, Boer H, Tamminga S (1997) The effect of extrusion conditions on the fermentability of wheat straw and corn silage. J Sci Food Agric 74(1):117–124
- Yang B, Wyman CE (2008) Pretreatment: the key to unlocking low-cost cellulosic ethanol. Biofuels, Bioprod Biorefin 2:26–40
- Yang C, Shen Z, Yu G, Wang J (2008) Effect and aftereffect of  $\gamma$ -radiation pretreatment on enzymatic hydrolysis of wheat straw. Bioresour Technol 99(14):6240–6245
- Yeh A-I, Jaw Y-M (1998) Modeling residence time distributions for single screw extrusion process. J Food Eng 35(2):211–232
- Yoo J, Alavi S, Vadlani P, Vincent AB (2011) Thermo-mechanical extrusion pretreatment for conversion of soybean hulls to fermentable sugars. Bioresour Technol 102:7583–7590
- Yoo J, Alavi S, Vadlani P, Behnke KC (2012) Soybean hulls pretreated using thermo-mechanical extrusion—hydrolysis efficiency, fermentation inhibitors, and ethanol yield. Appl Biochem Biotechnol. doi:[10.1007/s12010-011-9449-y](https://doi.org/10.1007/s12010-011-9449-y)
- Zhang S, Keshwani DR, Xu Y, Hanna MA (2012a) Alkali combined extrusion pretreatment of corn stover to enhance enzyme saccharification. Ind Crops Prod 37:352–357
- Zhang S, Xu Y, Hanna MA (2012b) Pretreatment of corn stover with twin-screw extrusion followed by enzymatic saccharification. Appl Biochem Biotechnol 166:458–469

Green Biomass Pretreatment for Biofuels Production

Gu, T. (Ed.)

2013, IX, 153 p., Softcover

ISBN: 978-94-007-6051-6