

Screw Extrusion Pretreatments to Enhance the Hydrolysis of Lignocellulosic Biomass

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Abstract

The conversion of biomass to biofuels begins with biomass pretreatment. Most traditional pretreatment methods are chemical or physical. Each method has a specific effect on cellulose, hemicellulose, and lignin fractions. The main goal of pretreatment is to remove or weaken the tight linkages among cell wall components, thus increasing enzyme accessibility and improving the hydrolysis of cellulose. In recent studies, the use of the extrusion process has been described as a new, potentially viable development in the pretreatment of lignocellulosic materials and the hydrolysis of cellulose. The hypothesis is that extruder screw speed and barrel temperature may disturb biomass structure, thereby increasing accessibility of cellulose for hydrolysis. This manuscript aims to provide an overview of the major representative progress and development on the use of the extrusion process for biomass pretreatment and cellulose hydrolysis. Extrusion can be used as a physical pretreatment method in biofuel production.

Keywords: Screw extrusion; Pretreatment; Lignocellulose; Bioenergy

Introduction

Biomass materials are the most abundant renewable resources on Earth. Recently, extensive research has been carried out to produce commercially useful products from lignocellulose, such as biofuels, biochemical products, and so on [1].

A lignocellulosic material is regarded as the recalcitrance of the substrate. An additional pretreatment step is required because the lignocellulosic structure is very complex, highly crystalline, and resistant to enzymatic hydrolysis in its natural state. Various chemical, physical, physicochemical, and biochemical pretreatment methods have been investigated to break down the structural integrity of lignocellulosic biomass and to enhance enzymatic action on cellulose. These methods include acid hydrolysis, alkali hydrolysis, steam explosion, ammonia fiber explosion (AFEX), and hot water treatment, among others. These pretreatment strategies can alter the natural structure of lignocelluloses, or disrupt their cell wall structure to reduce cellulose crystallinity, thus increasing lignocelluloses' surface area and porosity, or making them accessible to enzymes. Each pretreatment method has its own advantages and disadvantages. For example, dilute acid pretreatment achieves more than 90% sugar yield, but requires corrosion-resistant equipment and neutralization prior to the biological steps. The high temperature in hydrothermal pretreatment leads to sugar degradation. Alkalis are too expensive, and difficult to recover and reuse during biomass pretreatment. The cost of ammonia and its recovery are important factors in AFEX pretreatment [1,2].

The extrusion process is a novel and promising physical pretreatment method for biomass conversion to ethanol production. Single-screw and twin-screw extruders are widely used extrusion techniques in the snack food, feed, and plastic industries. Although both single-screw and twin-screw extruders are used in extrusion processes, twin-screw extruders are being increasingly favored over single-screw ones. The main reasons for this preference are the extended control of residence time distribution and mixing, as well as superior heat and mass transfer capabilities. Twin-screw extruders, according to their specific characteristics, can tackle more complex tasks such as homogenizing, alloying, dispersing pigments and additives, reactive compounding, concentrating, devolatilizing, and polymerizing, among others. The single-screw extruder is currently used for simpler jobs such as melting,

plasticizing, and discharging melt. The major difference between single-screw and twin-screw extruder is the conveying mechanism. Single-screw machines depend on frictional forces in the solid conveying zone and on viscous forces in the melt-pumping zone. Twin-screw extruders are largely dependent on the screw's geometrical configuration and positive displacement character. The relative merits and performance of twin-screw extruders have received more interests [3-5].

Extrusion is characterized by low cost, good monitoring of temperature and screw speed, high shear, and excellent processing ability. It is a process in which ingredients are subjected to simultaneous heating, mixing, and shearing, resulting in physical and chemical changes as the material is conveyed along the extruder barrel. The foremost advantage of extrusion over other pretreatment methods such as hydrothermal (190°C to 210°C), compressed liquid hot water (180°C to 230°C), steam pretreatment (190°C to 210°C), and steam explosion

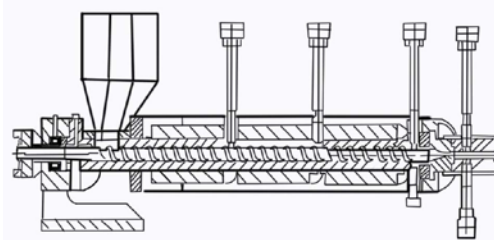


Figure 1: Sketch showing extruder components [6].

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(193°C to 230°C), is the use of low barrel temperature. Extrusion prevents carbohydrate degradation and lignin oxidation, which would otherwise result in potential fermentation inhibitors. Extrusion has the potential to become a viable biomass pretreatment method. Extrusion is practical and easy to adopt in large-scale productions because it is a continuous pretreatment process. Moreover, no liquid fraction is produced during extrusion; therefore, no effluent disposal or treatment problem, no solid loss, and no safety issues are involved. A typical extruder consists of three zones, namely, the feed, the transition/compression, and the metering. A feed hopper, screw, barrel, die, and drive are the major components of an extruder, as shown in Figure 1 (Redrawn from [6] with permission from Springer). Screw design strongly influences optimum temperature profile, work done on the material, and amount of frictional heat generated. Karunanithy and Muthukumarappan [2,6] reported that extruder parameters, such as compression ratio, screw speed, and barrel temperature, are important factors that influence sugar recovery from the biomass. The compression ratio has a direct impact on shear development within the extruder barrel that affects sugar release from the biomass because of the process of plasticization occurring in the compression zone. Compression can be achieved in several ways such as varying the screw and barrel configuration, increasing the root diameter, decreasing the pitch or barrel diameter with constant root diameter, decreasing the screw pitch in a decreasing barrel diameter, and introducing restrictions. A gradual decrease of flight depth in the direction of the discharge and a decrease in the pitch in the compression section are the most common ways to achieve compression. Extruder barrel temperature facilitates the melting or softening/plasticizing of the feed [2,4,6-8].

Most traditional pretreatment technologies have inefficiencies related to batch processing, small capacity, and low solid loading. Extrusion processing can provide a unique continuous reactor environment for a combination of thermomechanical and chemical pretreatment of lignocellulosic biomass at higher throughput and solid

levels. This review showed that there is scope to explore extrusion as one of the feasible lignocellulosic pretreatment methods [9,10]. Table 1 summarizes different lignocelluloses pretreated by screw extrusion technologies and the hydrolysis results.

Extrusion pretreatment of wheat bran and soybean hull

Commonly available agricultural coproducts, wheat bran and soybean hull, were the model substrates used in this study to compare particle size reduction in two physical pretreatment methods, grinding and thermomechanical extrusion, as alternatives to traditional biomass pretreatments for lignocellulosic ethanol. Extrusion led to a higher reduction in sugar yield compared with grinding for wheat bran, but not for soybean hulls. A combination of lower temperature and high residence time (low screw speed) or higher temperature and low residence time (high screw speed) led to higher sugar yield. The best combination of extrusion screw speed and maximum barrel temperature were 7 Hz/150°C and 3.7 Hz/110°C. The use of a solvent mixture (sodium hydroxide, urea, and thiourea) and calcium chloride solution combined with the extrusion treatment did not lead to an improvement in sugar yield reduction. Lamsal's research showed that the use of chemical treatment combined with extrusion does not result in an improvement in the hydrolysis of lignocellulosic substrates [9].

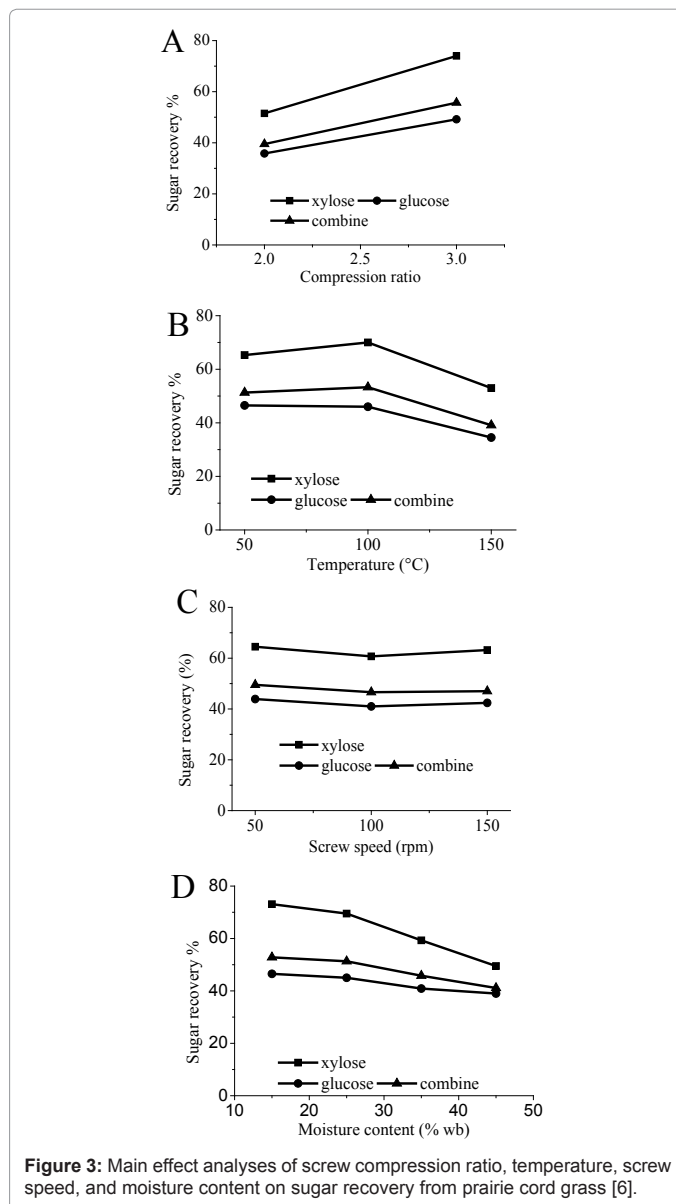
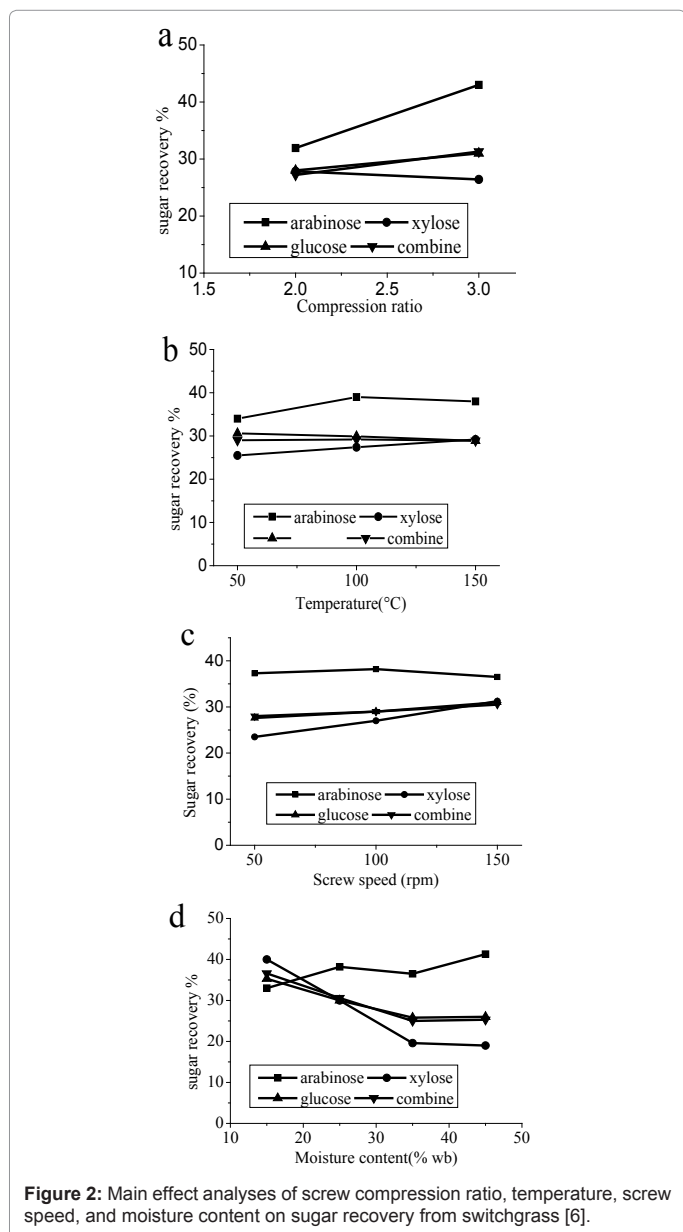
Extrusion pretreatment of switchgrass and prairie cord grass

Karunanithy and Muthukumarappan [2,6,11] reported that extrusion has the potential to be a viable continuous pretreatment method for switchgrass and prairie cord grass. Their study investigated the effects of compression ratio, screw speed, moisture contents, and barrel temperature on sugar recovery from switchgrass and prairie cord grass using a single-screw extruder. The pretreated samples were subjected to enzymatic hydrolysis for sugar recovery measurement. The compression ratio, screw speed, temperature, and moisture content (as independent variables) significantly contributed to glucose,

Lignocellulose	Extruder	Extrusion condition	Enzymatic hydrolysis	Sugar yield	Reference
Switchgrass	Single-screw	Barrel temperature 176°C, screw speed 155 rpm, moisture content 20% wb, particle size 8 mm	Cellulase 15 FPU/g and β -glucosidase 60 CBU/g of dry matter	Glucose 41.4%, xylose 62.2%	[2]
Switchgrass	Single-screw	Barrel temperature 180°C, screw speed 118 rpm, alkali concentration 2%, particle size 6 mm	Cellulase 15 FPU/g and β -glucosidase 60 CBU/g of dry matter	Glucose 90.5%, xylose 81.5 %	[11]
Corn stover	Single-screw	75 rpm and 125°C, moisture content 21%	Cellulase 15 FPU/g and β -glucosidase 60 CBU/g of dry matter	Glucose 75%, xylose 49%	[4]
Prairie cord grass	Single-screw	Barrel temperature 114°C, screw speed 122 rpm, alkali concentration 1.70%, particle size 8 mm	Cellulase 15 FPU/g and β -glucosidase 60 CBU/g of dry matter	Glucose 86.8%, xylose 84.5%	[11]
Corn stover	Single-screw	Barrel temperature 125°C, screw speed 75 rpm	Cellulase 15 FPU/g and β -glucosidase 60 CBU/g of dry matter	Glucose 75%, xylose 49%	[4]
Corn stover	Twin-screw	Screw speed 80 rpm, moisture content 27.5%	0.3 g enzyme/g cellulose	Glucose 48.79%, xylose 24.98%	[7]
Wheat bran	Twin-screw	Screw speed/barrel temperature 7 Hz/150°C, moisture content 25%	47 mg cellulase/g substrate	Reducing sugar 60% to 73%	[9]
Soybean hull	Twin-screw	Screw speed/barrel temperature 3.7 Hz/110°C, moisture content 25%	47 mg cellulase/g substrate	Reducing sugar 25% to 36%	[9]
Rice straw	Twin-screw	Screw speed 40 rpm, temperature 120°C with 3% H ₂ SO ₄	20 FPU/g cellulose	Xylan 83.7% , saccharification 80%	[12]
Douglas fir	Twin-screw	Treated with hot-compressed water at 170°C followed with screw speed 45 rpm to 120 rpm at room temperature	10 FPU/g cellulose	Glucose 27.72%, xylose 1.07%	[13]
Douglas fir	Twin-screw	Treated with hot-compressed water at 180°C, followed with screw speed 45 rpm to 120 rpm at room temperature	10 FPU/g cellulose	Glucose 34.32%, xylose 3.69%	[13]

Table 1: Summary of screw extruder pretreatment technologies on the sugar yield of lignocellulose hydrolysis.

xylose, and combined sugar recovery. Statistical analyses revealed that a 3:1 screw compression ratio (compared with 2:1) increased glucose recovery by 12% and 8%, and combined sugar recovery by 37% and 40% for switchgrass and prairie cord grass, respectively (Figure 2 and 3, both Redrawn from [6] with permission from Springer). Statistical analyses also revealed that glucose recovery increased by 12% and 8%, and combined sugar recovery increased by 37% and 40% at a 3:1 screw compression ratio compared with 2:1 for switchgrass and prairie cord grass, respectively. The highest sugar recovery for switchgrass (45.2%) was obtained at the lowest screw speed (50 rpm), the highest temperature (150°C), and a moisture content of 15%. The highest glucose, xylose, and combined sugar recovery of 61.4%, 84.3%, and 65.8% were recorded. Prairie cord grass can be extruded at a lower temperature and screw speed (50°C and 50 rpm) with a 25% moisture content for better glucose, xylose, and combined sugar recovery (61.4%, 84.3%, and 65.8%, respectively). In addition, sugar recovery from prairie cord grass can be improved by combining with alkali soaking. There can be



improved sugar recovery from Prairie cord grass by combining with alkali soaking. The optimal pretreatment conditions of 114°C barrel temperature, 122 rpm screw speed, 1.70% alkali concentration, and 8 mm particle size resulted in maximum glucose, xylose, and combined sugar recovery of 86.8%, 84.5%, and 82%, respectively, using enzymatic hydrolysis.

Extrusion pretreatment of corn stover

Karunanithy and Muthukumarappan (2010) [4] investigated the single screw extruder extrusion pretreatment of corn stover. The objective of this study was to evaluate the effects of barrel temperature and screw speed on sugar recovery from corn stover, and to select a suitable enzyme combination with a corresponding ratio. When different enzymes and ratios were employed during hydrolysis, the hypothesis that screw speed, barrel temperature, and their combinations significantly thereby influencing sugar recovery was confirmed. Based on the highest glucose (75%), xylose (49%), and combined sugar recovery (61%), corn stover could be pretreated at a screw speed of 75

rpm with a barrel temperature of 125°C. These pretreatment conditions yielded the highest glucose and xylose recovery with a cellulase and β -glucosidase ratio of 1:4 during hydrolysis, which was 1.96 and 2.0 times higher than the control sample, respectively.

Zhang et al. [7] investigated the twin-screw extruder extrusion pretreatment of corn stover. This study examined the effect of extrusion as a pretreatment method for corn stover using a continuous twin-screw extruder to improve sugar yield and to shed light on the intrinsic factors contributing to the improvement. The highest glucose, xylose, and combined sugar yields were 48.79%, 24.98%, and 40.07%, respectively. The enzymatic hydrolysis was found to be 27.5% with a screw speed of 80 rpm and an enzyme dosage of 0.028 g enzyme/g dry corn stover (Figure 4 Redrawn from [7] with permission from Springer). The values were respectively 2.2, 6.6, and 2.6 times higher than those of untreated corn stover. X-ray diffraction analysis showed that crystallinity index was not the main property underlying the improvement. Nevertheless, the specific surface area of biomass was found to be closely related to enhanced sugar yield, revealing that twin-screw extrusion can open cell walls at the microscopic scale. This process was enough for efficient enzyme adsorption on cellulose especially favorable on sugar yield.

Extrusion pretreatment of rice straw

A combination of twin-screw extrusion and acid-catalyzed hot water extraction processes was performed at a bench-scale. The influences of the screw speed (30 rpm to 150 rpm), barrel temperature (80°C to 160°C), and the corresponding specific mechanical energy of the extruder on the structural properties of the pretreated rice straw, as well as its sugar concentration and conversion, were investigated. The optimal condition for the extrusion step was determined to be 40 rpm with 3% H₂SO₄ at 120°C. The optimal condition for the extraction step was determined to be 130°C for 20 min. After pretreatment under optimal conditions, 83.7% of the xylan was converted into monomeric xylose, and concentration levels reached 53.7 g/L. Finally, an 80% yield of the total saccharification was obtained after subsequent enzymatic hydrolysis [12].

Extrusion pretreatment of woody biomass

An extrusion process involving a twin-screw extruder was employed to compensate for the limitations of the hot-compressed water (HCW) treatment and to improve enzymatic saccharification yield. Monosaccharide production yield was improved by extrusion after HCW treatment for both Douglas fir and eucalyptus wood. Partial removal of hemicellulose and lignin by HCW treatment effectively improved fibrillation by extrusion. Only HCW treatment produced glucose less than 5 weight percent (wt%) in Douglas fir in a temperature range of 140°C to 180°C by enzymatic hydrolysis. Glucose production

yields of 18 wt% and 26 wt% were obtained after HCW treatment at 170°C and 180°C, respectively, in eucalyptus wood. The use of extrusion after HCW treatment drastically improved monosaccharide production yield in both woods. In the case of Douglas fir, the obtained values were 5 times higher than those obtained by HCW treatment alone. Total monosaccharide production yield was higher in eucalyptus wood than in Douglas fir. The extruded production had a fine fibrous morphology on a submicro/nanoscale. This result shows the great potential of the extrusion process after HCW treatment as a cost-effective pretreatment method for enzymatic saccharification of woody biomass [13].

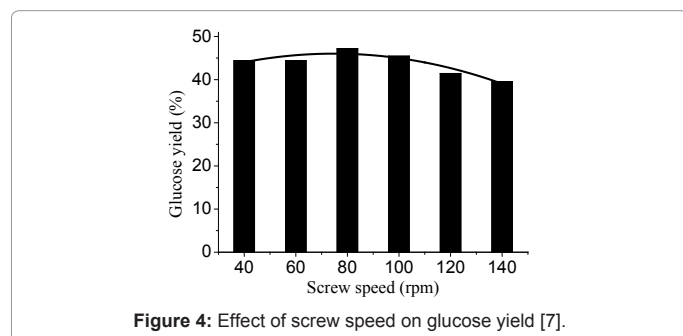
Conclusions and Perspectives

Lignocellulosic biomass has been projected to be one of the main resources for economically attractive second-generation bioethanol production. Although new technologies have substantially improved bioethanol production, a number of challenges still need further investigation. These challenges include developing more efficient pretreatment technologies for lignocellulosic biomass and integrating optimal components into economic ethanol production systems. This review studied thermomechanical extrusion as a pretreatment method for the structural modification of grass and woody biomass. The review was undertaken to understand the influence of extruder barrel temperature, screw speed, moisture content, and biomass types on cellulose hydrolysis and sugar recovery. Different extrusion pretreatment factors for lignocellulosic materials were described and widely studied to improve sugar recovery. All these factors could make lignocellulose accessible to enzymatic reactions. The crystallinity of cellulose, its accessible surface area, lignin and hemicellulose disposal are the main substrate-related factors affecting enzymatic hydrolysis. Although the successful thermomechanical pretreatment of biomass is composition-specific, this relatively novel and continuous technique has great potential for increasing the efficiency of ethanol production from lignocellulosic substrates. Thermomechanical extrusion was shown to be a feasible pretreatment method for lignocellulosic biofuel production.

From a basic research point of view, understanding the fundamentals of screw extrusion pretreatment processes is a critical need. More research should be done to analyze the dynamics of the screw extrusion pretreatment process and its by-products to design a cost-competitive process. Further investigation can help make a suitable choice in improving extruder design depending on the characteristics of the biomass substrate and the hydrolysis process to reduce the cost of the conversion of lignocellulosic biomass to ethanol.

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