




## Review

# An Overview of Extrusion as a Pretreatment Method of Lignocellulosic Biomass

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**Abstract:** Lignocellulosic biomass is both low cost and abundant, and unlike energy crops, can escape associated ethical dilemmas such as arable land use and food security issues. However, their usage as raw material in a biorefinery implies an inherent upstream pretreatment step to access compounds of interest derived from lignocellulosic biomass. Importantly, the efficiency of this step is determinant for the downstream processes, and while many pretreatment methods have been explored, extrusion is both a very flexible and promising technology. Extrusion is well-known in both the polymer and pharmaceutical industries and has been used since the 18th century. However, as a pretreatment method for lignocellulosic biomass, extrusion is relatively new. The first use for this purpose dates back to the 1990s. Extrusion enjoys a high degree of flexibility due to the many available parameters, but an understanding of extrusion requires a knowledge of these parameters and the different relationships between them. In this paper, we present a concise overview of lignocellulosic biomass extrusion by reviewing key extrusion parameters and their associated extruder design components and operating conditions.

**Keywords:** biomass pretreatment; lignocellulosic biomass; extrusion; reactive extrusion



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## 1. Introduction

Petroleum, its derivatives, and more generally fossil materials, have found deep-rooted applications in all sectors of modern life. Gasoline, kerosene, sanitizers, fertilizers, asphalt, textiles, cosmetics, pharmaceuticals, solvents, diluents, plastics, printing inks, vaseline, and rust removers are some of the products that have become an integral part of today's lifestyles [1,2]. Among all these products, those with energy applications (fuels) are of particular importance because they enter into the production process of almost everything produced on an industrial scale.

The problems associated with the use of fossil fuels are well known and their consequences on the environment are increasingly obvious. However, getting out of this dependence on fossil fuels means finding competitive alternatives. Among the renewable energies available today, lignocellulosic biomass is one of those capable of replacing fossil materials in many applications, including energy production [3–6]. Long considered useless or of little interest, lignocellulosic biomass (LCB) is one of the most abundant resources on earth. Global lignocellulosic biomass production is estimated at several billion dry tons per year. In Canada, lignocellulosic residues (forest and agricultural) are estimated between 64 and 561 million dry tons per year, and less than 30 million tons are used in the industry [7].

LCB is an important source of renewable energy. However, many difficulties hinder its use as a raw material in the industry. LCBs must be pretreated before their utilization in a biorefinery process. The goal of this step is to deconstruct the lignocellulosic structure to get access to the desired compound (i.e., glucose, xylose, etc.). It is well documented that pretreatment is the limiting step in the biorefinery context [8–10], at least for two reasons. First, LCBs are recalcitrant to pretreatment. Lignocellulose is a complex matrix, and as the main constituent of plants cells walls, lignocellulose acts in nature as a defense system against microbial, chemical, and physical attacks. This matrix is mainly comprised of cellulose, hemicellulose, and lignin linked to each other by a diversity of strong and weak bonds (ester, ether, hydrogen, Van der Waals, etc.). The second reason is a corollary of the first since several pretreatments methods have been developed to address the complex nature of LCBs, but still need improvements regarding efficiency, cost, and environmental aspects.

LCB pretreatments are classified into four classes: (a) chemical, (b) physical, (c) biological, and (d) physicochemical [11,12]. Class (a) pretreatments include acid hydrolysis, alkaline hydrolysis, ozonolysis, organosolvation, oxidative delignification, ionic liquids, deep eutectic solvents, and natural deep eutectic solvents. Class (b) includes physical treatments such as extrusion, milling, irradiation, microwave, ultrasound, pyrolysis, and pulsed electric fields. Biological pretreatments (i.e., class (c)) are named according to the type of organism involved: fungi, bacteria, and archaea. Class (d) includes physicochemical treatment methods such as steam explosion, liquid hot water, SPORL (sulfite pretreatment to overcome recalcitrance of lignocellulose), AFEX (ammonia fiber explosion), CO<sub>2</sub> explosion, and wet oxidation.

Extrusion, from class (b), is a promising pretreatment method. It presents many key advantages for biomass pretreatment in a biorefinery context and is a complex technology with a simple core principle. It consists of destructuring LCB under high shearing forces through contact with one or two rotative screws into a barrel, or more specifically, an extruder. This technology is particularly adaptable, can be used for diverse purposes outside biomass pretreatment, and possesses several parameters that can be modified according to the desired goal [13]. Short residence time is another advantage of extrusion, usually requiring only a few minutes [14]. Concerning operating conditions, extrusion can be run in batch, fed-batch, and continuous processing, and can be run at a mild temperature with low energy consumption and high solid loadings. This technology is also known for rapid heat transfer and effective mixing. Moreover, extrusion offers the possibility to be coupled with other pretreatments methods, and is also a scalable technology possible to achieve comparable results when transferring from a laboratory scale to pilot and industrial scales [15]. Extrusion has been used in food, polymer, and many other industries for a long time (since 1797), but as a pretreatment method for LCB, extrusion is quite recent (the 1990s), and is receiving increasing attention [16].

The great flexibility of Lignocellulosic Biomass Extrusion (LBE) is an advantage. However, at the same time, this flexibility adds a layer of complexity because of the great number of parameters available. Those parameters are important to better understand how LBE works and for scaling up purposes. Thus, the main purposes of this paper are to present an overview of relevant LBE parameters, to show the influence of extrusion setups on the efficiency of the pretreatment, to give core information about typical operational practices, and to highlight R&D needs.

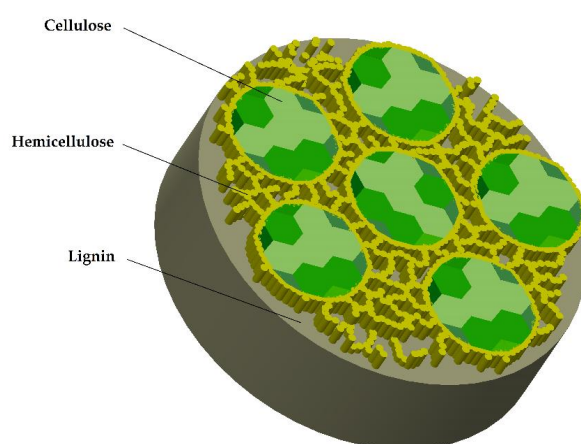
## 2. Lignocellulosic Biomass

### 2.1. Biomass Composition

Since the beginning of biomass extrusion, it has been used for various purposes such as furfural recovery [17], lipid extraction (with microalgae) [18], pigment extraction [19], torrefaction/pelletization [20], biomass briquettes making [21], and composite materials formation [22]. For lignocellulosic biomass pretreatment, sugars recovery (monosaccharides, oligosaccharides, and polysaccharides) remain the preponderant goal so far [9,23,24]. The reasons are that sugars (cellulose and hemicellulose) represent 50 to 80% of LCB and

also because downstream processes utilizing sugar are well mastered today as they have been studied since the beginnings of first-generation biorefinery.

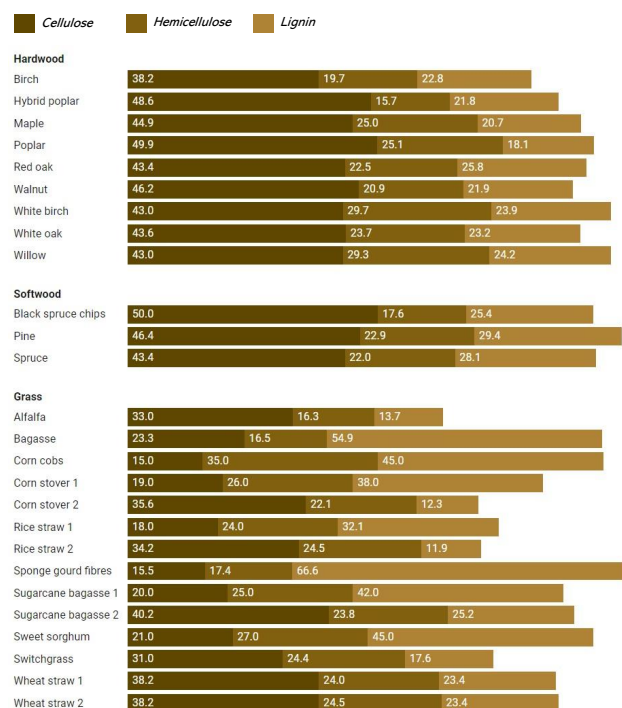
Figure 1 illustrates lignocellulose. Cellulose is the principal constituent of plant cells wall and the most abundant polymer from living organisms [25]. It is a linear D-glucose polymer with  $\beta(1-4)$  glycosidic bonds. In LCB, cellulose occupies between 20% and 50% of all components [26]. Hemicellulose, like cellulose, is a biopolymer. It consists of about 15–35% of LCB on a dry basis [26]. While cellulose is a hexose polymer composed of only one type of monomer, hemicellulose is a heteropolymer (mixtures of pentoses and hexoses). The most abundant monomers in hemicellulose by order are xylose and arabinose for pentoses and mannose, glucose, and galactose for hexoses. Hemicellulose is also a nonlinear polymer with significant short branching sidechains that contribute to the overall cohesion of lignocellulosic structures. This biopolymer is embedded between cellulose fibers and lignin and plays the role of a binder via covalent bonds. Compared to cellulose, the molecular weight of hemicellulose is low, and its structure is easily hydrolyzed.



**Figure 1.** Lignocellulose.

After cellulose, lignin is the most abundant biopolymer on earth and is counted for about 5% to 30% in the composition of LCB [27]. Lignin is a three-dimensional aromatic biopolymer [28]. It is also a plant cell wall component like hemicellulose and cellulose in woody plant tissues. The main role of lignin is to prevent the cell from exterior threats such as microorganism attacks. It is made of three monomers (monolignols): *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which respectively appear in the lignin polymer as Hydroxyphenyl (H lignin), Guaiacyl (G lignin), and Syringyl (S lignin). Softwood is mainly composed of G lignin units while hardwood has essentially both S and G lignin units [29]. Monolignols are linked one to another by alkyl-aryl, alkyl-alkyl, and aryl-aryl bonds. The relative abundance of one of these linkages over the others determines the physicochemical and biological properties of the lignin [30]. Lignin and cellulose are linked both by hydrogen (weak) and covalent (strong) bonds. Figure 2 shows an overview of some LCB compositions (details about data sources are presented in Appendix A). Cellulose, hemicellulose, and lignin form a complex and resistant material (i.e., lignocellulose) whose structure can vary depending on many factors (type of biomass, sources, stage of maturity, plant part, etc.). Generally, agricultural residues require less harsh pretreatment conditions than forest residues. During lignocellulosic biomass extrusion (LBE), the mechanical action of the screws on the extrudate disrupts the lignocellulose material. Covalent and hydrogen bonds are altered and weakened, while the degree of polymerization of cellulose is technically reduced and a part of the lignin layer is removed. As Table 1 shows, so far, studies do not permit to state clearly whether or not there is a significant difference between biomass composition before and after extrusion. The differences observed can be for diverse reasons: A structural change in the biomass during extrusion, the denaturation of certain compound according to the severity of the pretreatment conditions, the fact

of bias related to precision and accuracy of the protocol used for biomass composition estimation, etc.



**Figure 2.** Composition of some lignocellulosic biomass.

**Table 1.** Lignocellulosic biomass composition before and after extrusion.

Biomass	Compounds	Composition (%)		References
		Before Extrusion	After Extrusion	
Bulgur bran	Glucose	36.38 ± 0.32	30.86 ± 0.64	[31]
	Hemicellulose	29.42 ± 0.13	33.18 ± 0.53	
	Total lignin	12.54 ± 0.14	16.24 ± 0.31	
Eucalyptus	Cellulose	46.90 ± 1.21	44.90 ± 1.86	[32]
	Hemicellulose	12.87 ± 0.35	13.71 ± 0.32	
	Lignin	31.15 ± 0.40	32.97 ± 0.86	
	Ash	0.86 ± 0.00	0.57 ± 0.05	
Olive stone	Cellulose	20.8 ± 0.2	18.3 ± 2.8	[33]
	Hemicellulose	25.9 ± 0.1	22.4 ± 0.4	
	Lignin	35.5 ± 0.6	39.0 ± 0.2	
Barley straw	Glucose	32.9	32.80	[34]
	Hemicellulose	26.1	15.53	
	Lignin	18.8	15.71	
	Ash	3.9	2.17	
Corn stover	Cellulose	32.75 ± 0.32	33.98 ± 0.14	[35]
	Hemicellulose	31.08 ± 0.57	30.20 ± 0.28	
	Lignin	10.07 ± 0.91	9.89 ± 0.43	
Oat hull	Cellulose	31.16 ± 1.15	34.32 ± 2.06	[36]
	Hemicellulose	28.72 ± 0.25	26.40 ± 0.53	
	Lignin	18.12 ± 0.63	15.00 ± 1.30	
Wheat straw	Cellulose	37.8 ± 1.9	46.9 ± 0.1	[37]
	Hemicellulose	28.2 ± 0.5	28.7 ± 0.1	
	Lignin	19.8 ± 0.3	15.4 ± 0.1	
	Ash	3.7 ± 0.0	3.3 ± 0.0	
Corn cob	Cellulose	42.0 ± 0.15	34.8 ± 0.23	[13]
	Hemicellulose	45.9 ± 0.90	38.9 ± 0.52	
	Neutral detergent soluble	9.3 ± 0.95	19.0 ± 0.60	

## 2.2. Crystallinity

Usually, in LBE, crystallinity refers to cellulose. Natural cellulose polymers contain both crystalline (D-glucose monomers ordered) and amorphous (D-glucose monomers disordered) sequences [38,39], and the crystallinity index is the overall percentage of the crystalline fraction. That is, it is the relative quantity of crystalline sequence in cellulose. Crystallinity is determined by X-ray diffraction and the following formula:

$$CI = \frac{I_{200} - I_{am}}{I_{200}}, \quad (1)$$

where  $I_{200}$  represent the height of the (200) peak and  $I_{am}$  is the minimum intensity between the (200) and the (110) peaks [40].

Hemicellulose and lignin are considered non-crystalline polymers (amorphous polymers) and are both heteropolymers. However, hemicellulose can also be highly crystalline because of multiple ramifications of homopolymers with a crystalline structure (xylans, mannans, arabinans, and galactans) attached to the principal heteropolymer chain [41]. The crystallinity of cellulose is particularly important in LBE when enzymes are involved before, during, or after the processing for enzymatic hydrolysis. This is because the amorphous part of cellulose is more susceptible to saccharification compared to the crystalline part, and can be degraded between five and thirty times more quickly [42,43].

Kuster et al. [44] recorded a decrease from 57% to 54% of the crystallinity index after extrusion of sugarcane bagasse. It could be obvious that the crystallinity index might decrease after extrusion, but many studies showed that it is not always so. For example, Vandebossche et al. [45] extruded four types of biomass (i.e., barley straw, sweet corn, blue agave, and oil palm empty fruit bunch) and found that the crystallinity of all extrudates was higher than for the raw materials (Table 2). Marone et al. [46] came to the same conclusion with corn stover. Fu et al. [47] observed the crystallinity of Douglas fir residuals and found that after extrusion, the crystallinity index slightly increased, which was attributed to effects from both heat and moisture content. Recrystallization can occur in cellulose because, under high temperatures, hydrogen atoms in the amorphous region undergo a realignment [48].

As an indicator of enzymatic hydrolysis yield, cellulose crystallinity is also controversial. Some authors reported a strong correlation between crystallinity and glucose and xylose/mannose yield, while others showed that crystallinity index is not accurate to predict sugar yield [48,49].

**Table 2.** Crystallinity index.

Biomass	Substrate Crystallinity (%)	Extrudate Crystallinity (%)	References
Banana fibers	39	-	[50]
Sugarcane bagasse	48	-	[50]
Sponge gourd fibers	50	-	[50]
Sweet corn	41 ± 3	47 ± 6	[45]
Barley straw	44 ± 8	46 ± 2	[45]
Blue agave bagasse	27 ± 7	52 ± 1	[45]
OPEFB	50 ± 8	51 ± 7	[45]
Corn stover	48 ± 4	51.2 ± 3.4	[46]
Sugarcane bagasse	57.3 ± 1.3	54.0 ± 0.23	[44]

## 2.3. Particle Size

Usually, biomass will undergo a size reduction before its application to the extrusion process. A grinder is used in that case, and this step involves energy consumption and must be included in the energy balance of LBE process. At pilot and industrial scales, biomass size reduction can seriously affect the economic profitability of the LBE. However,



particle size plays an important role in lignin removal, reaction kinetics, hydrolysis rate, rheological properties of the substrate inside the barrel, and sugar yield. A strong correlation between the particle size and the extrusion Specific Mechanical Energy (SME) ( $-0.786$ ), the torque ( $-0.788$ ), the glucose recovery yield ( $-0.813$ ), and the xylose/mannose recovery yield ( $-0.787$ ) has been observed during extrusion of Douglas-fir forest residuals, all with  $p$ -value inferior to 0.01 [48]. This means that when the particle size decreased, the SME, torque, glucose recovery yield, and xylose-mannose recovery yield increased. Additionally, many authors reported a size reduction of the extrudate relatively to the substrate after the extrusion process [51–53]. The reduction of the extrudate particle size increases their specific surface, which has clear advantages with respect to improvements in enzymatic saccharification.

#### 2.4. Morphology

After extrusion, a visual inspection of the extrudate allows a first appreciation of the impact of the extrusion pretreatment on the biomass. Particle size is reduced, the extrudate looks rough, crumbly, and has a broken surface to the touch [46,54]. LCBs' microstructure can be observed by Scanning Electron Microscopy (SEM). Usually, extrudates show a disruptive surface with a lot of clear exfoliations compared to substrates which are compact (bundled) and have smooth surfaces. Important fibrillation in the extrudate has also been reported in the literature. Extrudate microfibrils are twisted, untied, and untangled [55–58]. The disruptive and fibrillation effect of extrusion can be remarkably enhanced when chemicals are used during the extrusion process (reactive extrusion). For example, Han et al. [59] observed a significant disruption and fibrillation in the microstructure of the extrudate (wood powder of pussy willow) when [EMIM]Ac (1-ethyl-3-methylimidazolium acetate) and DMSO (dimethyl sulfoxide) were used as additive during the extrusion process. The chemicals reacted with the water molecules inside the substrate and then created voids (porosity) in the biomass. Byun et al. [58] experienced a similar microstructure with Amur silvergrass. Porosity is also created by water evaporation under mild and high-temperatures extrusion (above 100 °C), but this effect is significantly enhanced with hydrophilic chemical additives. The increase in porosity results in an increase in the specific surface of the extrudate, which is highly beneficial for enzymatic hydrolysis [53]. Karunanithy and Muthukumarappan [60] demonstrated that the efficiency of enzymatic hydrolysis strongly depends on the accessibility of sugars to the enzymes. The greater the accessible surface, the higher the rate of enzymatic hydrolysis. Size reduction also participates in the increase of the specific surface, as highlighted in the preview section. Cellulose microfibrils in Han's extrudate were less than 500 nm in diameter [59].

#### 2.5. Moisture

Substrate moisture is a key parameter for LBE. Most of the time, LCBs after harvest are not immediately pretreated, but rather undergo preparation before extrusion. The storage conditions (i.e., temperature and time) determine the biomass moisture content. Ambient temperature is preferred for storage to reduce energy consumption, and storage can last from a few hours to many months. The biomass is stored until the desired moisture for extrusion is reached. This moisture ranges from 6% to 50% according to the type of biomass (see Table 3). It is important to note that materials above 50% are not sufficiently consistent to be extruded and behave more like a liquid than a solid. Moisture content around 25% seems to be an optimum for high (above 70%) sugar recovery from barley and wheat straw [37,61], but more investigations are required.

#### 2.6. Biomass Preparation before Pretreatment

Biomass preparation is a necessary step for successful extrusion. We investigated twenty-seven LBE studies in order to identify common practices during biomass preparation before extrusion (Table 3). Biomass preparation steps consist of [a] sorting/washing, [b] drying, [c] grinding/milling, [d] sieving, [e] mixing with additives, [f] storing, and

[g] extrusion. The first step (sorting) is an inspection of the sample collected, to remove contaminants (plastic, sand, etc.). Sometimes washing is necessary to remove the contaminants [53]. The drying step has at least two goals. The first one is to restrict microbial activity in the biomass, especially if the biomass is very wet, while the second is to lower the moisture content of the raw material [44]. Grinding/milling steps are for the size reduction of the substrate, and sieving ensures a desired particles size for the substrate [13]. There are two ways to use additives in LBE: after and during the extrusion process. Some prefer the former and run step [e] [59]. Then, the biomass is directly extruded or stored until extrusion [32].

Authors freely adapt these steps to their material and their goal. Table 3 shows that some omit certain steps or change the order. For example, Liu et al. [62] used only [d] (milling) for corn stover preparation; Kuster et al. [44] used steps [b] (drying), [c] (milling), [d] (sieving), and [e] (mixing with additive) to prepare sugarcane bagasse and sugarcane straw for extrusion; while for eucalyptus tree, Duque et al. [32] opted for a [c]-[b]/[f]-[d] sequence. However, generally speaking, all the above steps mentioned remain important for best practices for biomass preparation before extrusion.

**Table 3.** Practices of biomass preparation before extrusion.

Substrate	Source	Steps	Size (mm)	Storage Time	Tempera	Moisture (%)	Additives before Extrusion	Reference
Barleystraw	Research centre	[b]-[c]-[d]-[g]	5	-	-	-	No	[45]
Barley straw	Research centre	[c]-[d]-[f]-[g]	5	Stored until use	-	6	No	[61]
Big bluestem	Farm	[c]-[d]-[f]-[g]	0.4–0.8	Stored until use	RT	-	-	[63]
Big bluestem	Farm	[c]-[d]-[e]/[f]-[g]	2, 4, 6, 8, 10	~8 h	RT	10, 20, 30, 40, 50	Water	[64]
Blue agave	Manufacture	[b]-[c]-[d]-[g]	2	-	-	-	No	[45]
Corn cob	Farm	[b]-[c]-[d]-[g]	2	-	RT	-	No	[13]
Corn stover	Farm	[c]-[b]-[e]-[g]	2	-	RT	22.5, 25, 27.5	No	[49]
Corn stover	Farm	[c]-[b]-[e]-[f]-[g]	2	8 h	RT	50	NaOH	[15]
Corn stover	Farm	[c]-[g]	2–5	0 h	-	-	No	[62]
Corn stover	Farm	[c]-[d]-[e]/[f]-[g]	2, 4, 6, 8, 10	~8 h	RT	10, 20, 30, 40, 50	Water	[64]
Eucalyptus trees	Research centre	[c]-[b]/[f]-[d]-[g]	60–190	2 months	-	20	No	[32]
Hardwood biomass (oak, fir, and pine sawdust)	-	[e]-[g]	1	-	RT	21–28	NaOH	[55]
Miscanthus	Farm	[c]-[d]-[g]	3	-	7	-	No	[65]
Olive tree pruning	Farm	[b]-[c]-[e]-[g]	1–4	-	RT	10	No	[66]
OPEFB	Manufacture	[b]-[c]-[d]-[f]	2	-	-	-	No	[45]
Prairie cordgrass	Farm	[c]-[d]-[e]/[f]-[g]	2, 4, 6, 8, 10	~8 h	RT	10, 20, 30, 40, 50	Water	[64]
Rape straw	Research centre	[c]-[d]-[g]	1.4–2.36	24 h	45 ± 5	6.44	No	[67]
Rice hull	Manufacture	[a]-[b]-[c]-[d]-[g]	25.4	24 h	60	-	No	[53]
Soybean hulls	Manufacture	[b]-[d]-[g]	1.041	24 h	RT	40, 45, 50	No	[68]
Sugarcane bagasse	Mill	[b]-[c]-[d]-[e]-[f]-[g]	0.2–2	24 h	Cold room	10.4 ± 0.36 8.9 ± 0.30	Water, Glycol, Ethylene glycol, Tween 80	[44]
Sugarcane bagasse	Manufacture	[c]-[d]-[e]-[g]	0.425–1.000	-	40	10	[EMIM]Ac	[69]
Sugarcane straw	Mill	[b]-[c]-[d]-[e]-[f]-[g]	0.2–2	24 h	Cold room	12.05 ± 0.36 10.34 ± 0.26	Water, Glycol, Ethylene glycol, Tween 80	[44]

Table 3. Cont.

Substrate	Source	Steps	Size (mm)	Storage Time	Tempera	Moisture (%)	Additives before Extrusion	Reference
Sweet corn	Manufacture	[b]-[c]-[d]-[g]	6	-	-	-	No	[45]
Switchgrass	Farm	[c]-[d]-[e]-[f]-[g]	2, 4, 6, 8, 10	~8 h	RT	10, 20, 30, 40, 50	water	[64]
Switchgrass (matured)	Farm	[c]-[d]-[f]-[g]	0.3–1.2	Stored until use	RT	-		[63]
Wheat straw	-	[c]-[f]-[g]	5	Stored until use	40	6	No	[37]
Wood powder of pussy willow	-	[d]-[b]-[f]-[e]-[g]	25.4	24 h	40	-	[EMIM]Ac, DMSO, [EMIM]Ac/DMSO	[59]

### 3. Extruder

An extruder is a thermomechanical device composed of different parts, with the most important being the barrel (inside which are one or more screws) and the die. These two parts are generally temperature controlled by a system of heating and cooling. Most often, extruders are equipped with one or more liquid injection points (Figure 3). The first patent of an extruder was filled by Joseph Bramah in 1797. Today, several types of extruders are available according to the number of screws. However, single-screw extruders and twin-screw extruders are both widely used for LBE, although twin-screw designs are more common. These screws rotate around their axis thanks to a drive motor and exert a significant mechanical force on the biomass, which is caught between the screws and between the screws and the wall.

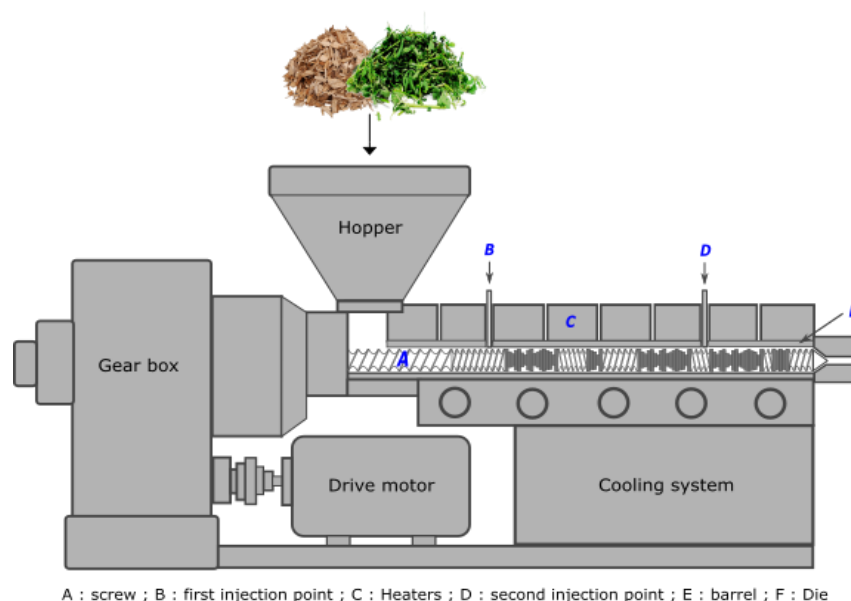


Figure 3. Extruder.

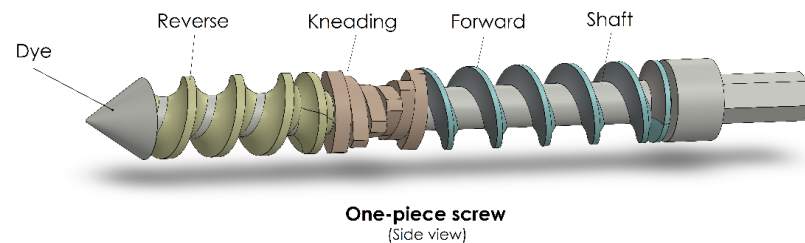
#### 3.1. Screw Type

Screws have two principal functions: convey and disrupt. The lignocellulosic substrate is conveyed from the feeding zone (zone under the hopper) to the die. During transport, the substrate undergoes high shearing forces as a consequence of protrusions of the screws, which results in the disorganization of the lignocellulose complex, with a part of the lignin layer removed while the cellulose crystallinity is technically assumed to decrease.

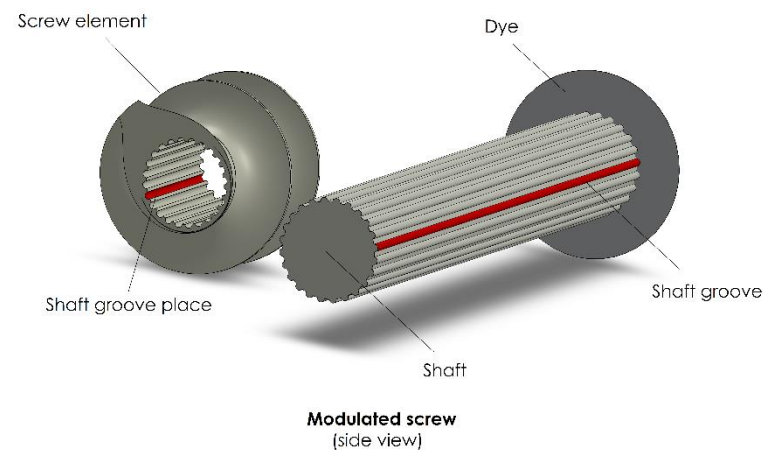
An extruder screw is made of a non-corrosive and resistant (high shearing forces) metal [67], and consists of a shaft surmounted by different shapes of protrusion, with two typical screw types: the one-piece screw and the modulated screw. The one-piece screw is a full bar on which protrusions are made directly on the shaft (Figure 4). In the case



of a modulated screw, this consists of a bar ridged lengthwise on which modules (screw elements) are mounted (Figure 5). Contrary to one-piece screws, modulated screws offer more flexibility because the configuration of the screw can be changed by using different modules [55]. In the case of LBE, modulated screws are better suited, as most of the time the screw configuration must be changed according to the type of biomass.

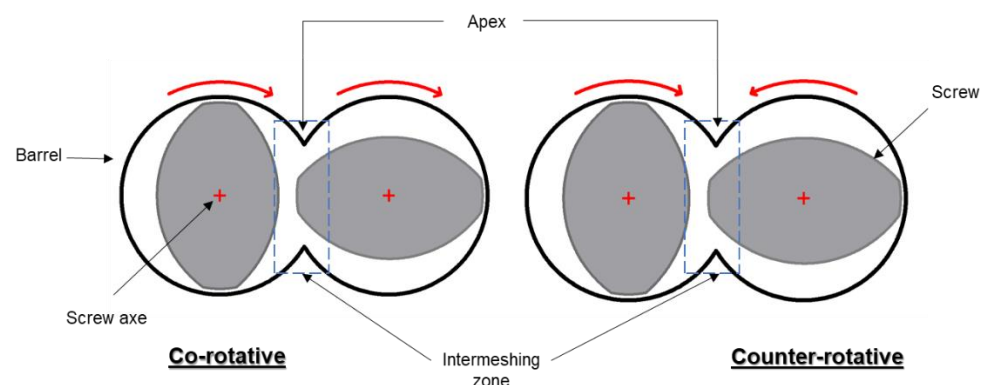


**Figure 4.** One-piece screw.



**Figure 5.** Modulated screw.

Similarly, twin-screws have more than one configuration and can be co-rotative (turn in the same direction) or counter-rotative (turn in opposite directions). Furthermore, counter-rotative screws can be intermeshing or non-intermeshing (Figure 6). Conversely, co-rotative screws are always intermeshing and provide better mixing than counter-rotative configurations [70,71].



**Figure 6.** Co- and counter-rotative extruder screws.

Screws can also take different longitudinal geometries. Cylindrical, conical, and mixed-shape screw configurations are the best known. For a typical cylindrical screw design, the diameter is the same along the screw from the beginning to the end of the screw, and this is the most common design for LBE. For conical screw designs, the diameter constantly

decreases (or increases) from one end to the other, and this kind of design is used for biomass briquetting [72]. Mixed-shape screw designs feature two different screw diameters linked by a conical compression zone, which facilitates a transition from one diameter to the next. Such compression zone designs can be both considered soft (long) or strong (short). Conical and mixed-shape screws have been explored in studies for materials such as thermoplastic polyurethane, polyvinyl chloride (PVC), and plastic composites [73–75].

The choice of the screw type is made when the extruder is purchased, and generally, the operators do not have much freedom for modification afterwards.

### 3.2. Screw Configuration

Lignocellulosic Biomass Extrusion (LBE) efficiency is strongly dependent on the screw configuration [76]. Screw configuration is the final layout obtained from the arrangement of screw elements on the shaft. Contrary to screw type, authors have full control of overall screw configuration.

LBE screw configuration is formed by transport elements (forward and reverse) and mixing elements (kneading). Gatt and Vandenbossche [14] proposed the following screw configuration for LBE: F-T-M-R-M-R-M-T; where F = forward transport element (with more spaced spirals than T), T = transport element (forward), M = mixing element (kneading), and R = reverse transport element. Although screw configuration differs from one user to another, the T-M pattern is almost always present at the beginning of a screw configuration [14,77–79].

Wahid et al. [80] investigated the effect of screw configuration on the pretreatment of wheat straw and deep litter in order to produce biogas. They tested many screw configurations by using a starting screw configuration only composed of forward screw elements, and they changed some of these forward screw elements by kneading or reverse screw elements to get a new configuration. Five screw configurations were then obtained. These are (a) mild kneading (medium length kneading block replacing some forward screw elements); (b) long kneading (a long block of kneading screw elements replacing some forward screw elements); (c) reverse (a block of reverse screw elements replacing some forward screw elements); (d) kneading and reverse (a block of kneading screw element and a block of reverse screw elements replacing some forward screw element on the same shaft. However, these two blocks are separated from each other by some forward screw elements; and (e) kneading with reverse (the same configuration as the previous but here the two blocks are contiguous). Configuration (a) was found suitable for deep litter (soft texture) and configuration (d) for wheat straw because they gave the best compromise between energy consumption, sugar availability, and methane yield. As for configuration (b), it was found unproductive because of important energy consumption for both LCBs. The authors have also demonstrated that the energy consumption increases as reverse and/or kneading elements are added to the screw configuration and at the same time, these elements enhance the disruptive effect of the screw on the biomass (like with the (d) configuration). In the same perspective, Kuster et al. [44] pre-treated sugarcane biomass and observed that the glucose recovery yield was improved when reverse elements are placed just after the last kneading zone. With a similar screw configuration, Negro et al. [66] reported an increase in the overall sugar yield with olive-tree prunings.

Thus, a screw configuration starting with T-M followed by a reverse element after one or two kneading elements, including the last kneading element, should be optimal to improve the sugar recovery yield. However, more investigations are required to confirm this assertion.

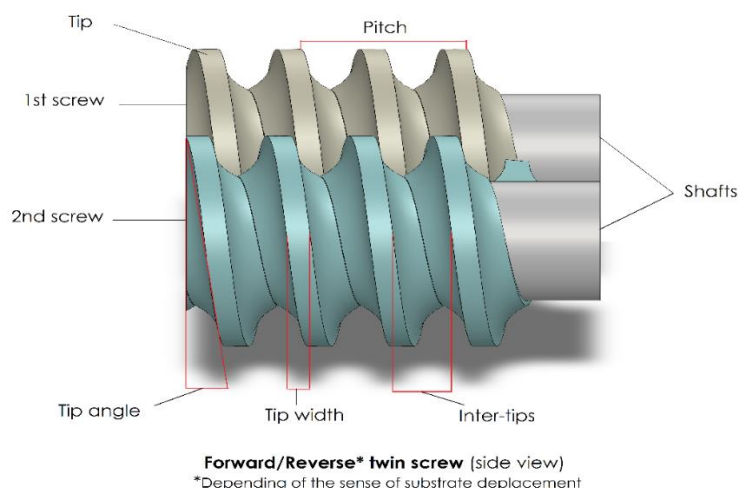
### 3.3. Screw Elements

Each screw element type has a geometry that defines its function, and this geometric variation will systematically affect extrusion performance. Furthermore, lignocellulose composition differs from one type of biomass to another (wood, agricultural residues, etc.) as well as variability within a specific biomass type according to different factors

(age, maturity stage, etc.), and this also affects screw element selection. Thus, an ideal geometry exists according to each specific biomass to be pre-treated. However, from a practical perspective, this can prove to be difficult because of downtime associated with reconfiguration, which can limit productivity.

### 3.3.1. Forward Screw Element

The Forward Screw Element (FSE) is an elliptical screw element designed to convey the substrate forward while turning around its axis on a rotor force. It appears at the beginning of the screw, under the feeding zone of the extruder. FSE are selected for extrusion processing according to their depth, length of the pitch, and flight angle. Figure 7 shows a side view of FSE. The geometry and orientation of the design is important for performance. For instance, as the tip angle increases, the speed at which the substrate is conveyed also increases. Similarly, increasing pitch, in turn, translates to a larger available volume in the FSE. Finally, increasing the screw tip width increases the clearance surface (between tip and barrel) and reduces the available volume in the FSE.



**Figure 7.** Intermeshing forward/reverse twin-screw elements.

FSE has an impact on the resulting extrudate properties, and this was demonstrated by Djuric and Kleinebudde [81] by wet granulation of lactose monohydrate with a twin-screw extruder. Wet granulation is one of the ways to make solid oral forms (tablets, capsules) in the pharmaceutical industry [82], where fine powder particles are agglomerated together to form larger compounds. Djuric and Kleinebudde [81] tested the porosity and the friability of the extrudate obtained after using different FSE pitches and found that the friability of the extrudate increased with the pitch length. With respect to LBE, depending on the rheological behavior of the substrate, excessively small pitches can lead to extra flow resistance in the barrel, while increasing the FSE pitch may lead to substrate friability; the substrate has insufficient viscosity to ensure a suitable fluidity inside the barrel. Usually, FSE with greater pitch are set directly under the feeding zone, while those with lower pitch are placed downstream from the feeding zone. Kohlgrüber et al. [83] considered a pitch range 1.5–2 times that of the screw diameter as the most suitable for FSE under the feeding zone.

### 3.3.2. Reverse Screw Element

A Reverse Screw Element (RSE) has the same design as a FSE, but with opposite flights (Figure 7). Set together on the same shaft as an FSE, an RSE is an obstacle to the forward displacement of the substrate, and thus an RSE represents a high zone of resistance. The goal of RSE in LBE is to increase pressure on the substrate and also to reach a steady state, especially with small pitches [84]. Similar to FSE, a side view section of an RSE shows the same behavior with respect to tip angle and tip width, with an additional particularity: as

the pitch decreases, the resistance generated by RSE highly increases, which controls the back pressure and increases the specific mechanical energy.

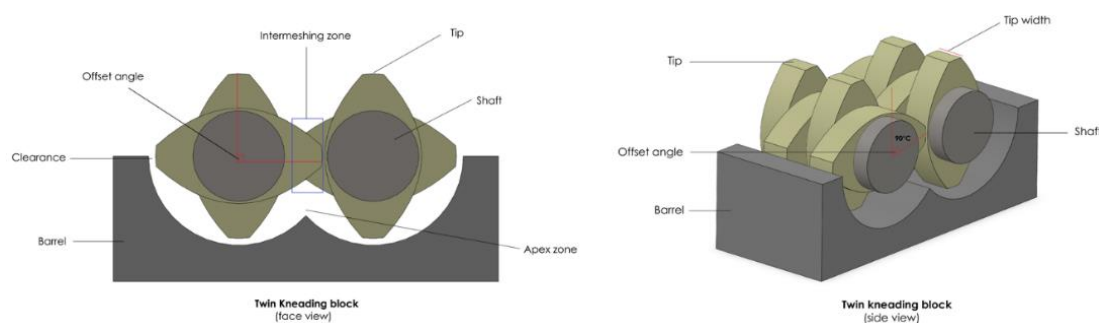
RSE has an impact on the LBE efficiency, as Gu et al. [48] have shown through their investigation of glucose and xylose/mannose yield obtained during an LBE of Douglas-fir residues. Using a twin-screw divided into six zones, they found a significant increase in the glucose and xylose/mannose yield next to the RSE due to high shearing forces. Kuster et al. [44] reported similar results on sugarcane biomass, with the insertion of a RSE increasing the yield of lignocellulose hydrolysis. Zheng et al. [78] investigated height screw configuration to find the best one for xylose separation from steam-exploded corncobs and found that xylose recovery was higher using configurations containing one or more RSE. They also found that while xylose yield varied with configurations containing RSE, these outcomes were always superior to a configuration without RSE. However, regardless of how a RSE improves LBE pretreatment, attention must be paid to the specific mechanical energy.

### 3.3.3. Kneading Element

Kneading elements (KE) play a disruptive and distributive effect on the substrate, and can also act as mild flow-restricting elements [14,85]. A screw configuration for LCB pretreatment will typically contain at least one kneading block comprised of two or more juxtaposed KE. During LBE a kneading block is ideally set immediately downstream of the first FSE [14,77,78]. Furthermore, Kuster et al. [44] demonstrated that the best place for a RSE is just after a kneading block because of the additional back pressure and resistance provided by the RSE.

Kneading blocks geometry depends on the angles between KE, KE staggering, tip thickness, and clearance. Figure 8 presents both facing and lateral views of a kneading block. As KE tip thickness increases, the kneading surface also increases, while reducing the available volume in the kneading block. Furthermore, creating an offset angle between the KE will improve the distributive function of the kneading block. The optimum offset angle ( $\alpha$ ) as a function of the number of KE ( $n_{KE}$ ) is given by:

$$\alpha = \frac{180}{n_{KE}} \quad (2)$$



**Figure 8.** Kneading blocks (front-facing and lateral view).

All the KE presented in Figure 8 are vertical and then have no conveying function, only disruptive and distributive function. However, sometimes a KE is staggered either because a conveying function or an increase or decrease of shearing forces on the substrate in the kneading zone is needed. Shearing forces increase when the staggering of the kneading block is opposite to the displacement direction of the substrate and decrease when the staggering is in the same direction [55,86]. The choice of the staggering angle of the kneading block should be related to the extrusion purpose [44].

Usually, kneading blocks are composed of 4–8 KE. The length of a kneading block influences the LBE. During their experiment on wheat straw and deep litter, Wahid et al. [80] found that a longer kneading block improved the biodegradability of the extruded biomass better than a shorter one. As for Fu et al. [47], they recorded a 7% increase in the glucose

yield when the number of KE was increased. Therefore, it may seem interesting to lengthen the kneading block to maximize the biodegradability of the extrudate. However, the authors pointed out that long kneading blocks increase the temperature, the residence time, and the specific mechanical energy, and this must be taken into consideration before lengthening the kneading block, especially for bioextrusion, as enzyme degradation can result in excessive kneading effects or a rise in temperature. A good alternative is to use both KE and RSE instead of a long kneading block, which is more favorable. The first solution is better than the second in terms of temperature control (due to reduced shearing forces), specific mechanical energy saving, and screw length shortening [80].

### 3.4. Die Shape

The die is the end of the screw through which the substrate exits the extruder, and its diameter is consistently lower than the inner barrel diameter. Similar to the screws and the barrel, the die is generally heated. It is an important part of the extruder because it influences the back pressure inside the barrel and in turn the overall efficiency of the LBE process [48]. The die entry is a high-pressure zone, as the substrate inside the barrel is conveyed by the screws and forced to pass through the die which has a smaller diameter [75,87].

Different shapes of dies are available, but a typical common design for a LBE is a cone entry followed by a cylinder at the end (Figure 3). Patil et al. [88] studied the influence of this shape over the pressure in the barrel, and both the entry angle ( $2\alpha$ ) and the length-to-die diameter ratio ( $L/D_{\text{die}}$ ) were found to be correlated with the internal pressure. For entry angles ( $2\alpha$ ) up to  $30^\circ$ , the pressure linearly increased with a slope of 0.5. With respect to  $L/D_{\text{die}}$  ratio, the relation has a slope of 0.6. Understanding this relationship, a given die design can be used to regulate the extrusion pressure [55]. Moreover, a larger die requires a lower specific mechanical energy than a smaller one because the pressure at the die entry for a larger die entry is lower and requires less mechanical energy.

Sometimes extrusion is run without a die for many different reasons. The principal reason for LBE operation without a die is reports of serious packing at the die entrance due to insufficient fluidity of the substrate (lack of solvent or catalyst) [59,89].

### 3.5. Torque

The torque (i.e., moment or moment of a force) is the capacity of a force to turn an object around its axis. For an extruder, the torque is the aptitude of the screws to turn around their axis, and it is an indicator of the efficiency of the extruder [90]. Torque also plays a role in the determination of the specific mechanical energy and is correlated to other extrusion parameters. For example, substrate moisture is inversely correlated with torque [68]. The torque increases when the barrel temperature and the screw speed are lowered [86,91,92]. Adding Reverse Screw Elements (RSE) to the screw configuration tends to increase the torque [93,94]. Concerning the particle size of the substrate, there is no evidence about its impact on the torque [64].

Importantly, torque influences the sugar recovery yield. Higher torque leads to sugar recovery improvement. Gu et al. [48] recorded an increase from 27% up to 43% of glucose yield and from 13% to 21% for xylose/mannose yield when the torque was increased from 15 Nm to 70 Nm. However, there is no specific torque range for LBE extrusion because it can differ from one extruder to another, according to the type of biomass and the extrusion conditions [86]. However, one approach to lower the torque and still reach good sugar recovery yield is to use additives (solvent or catalyst), especially those with a great affinity towards cellulose such as ethylene glycol and glycerol [40].

### 3.6. Specific Mechanical Energy

The specific mechanical energy (SME) is an input parameter that is expressed in Watt-hour per kilogram (Wh/kg) or Joule per kilogram (J/kg). The SME is the energy supplied for one kilogram of extrudate obtained. It is an indicator of the stability and capacity



of the extrusion process, as a rapid change of the SME usually relates to instability in the flow [14,32].

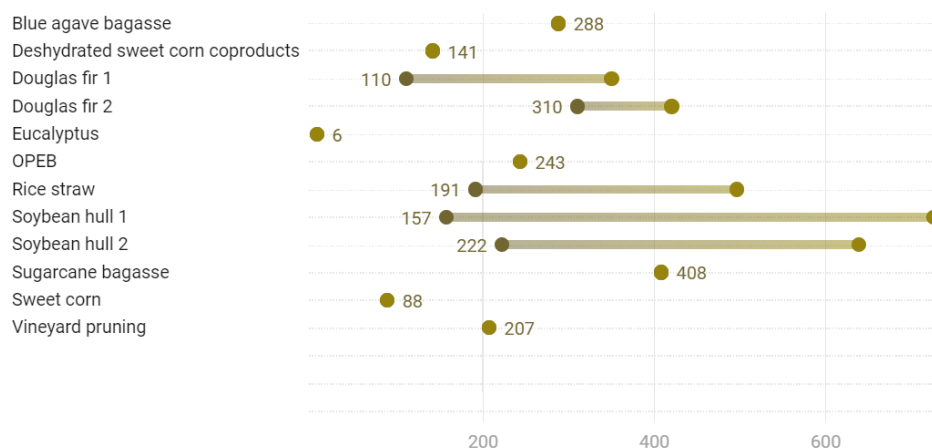
SME is a function of the torque, the mass flow, the power of the extruder motor, and the screw speed, as outlined in the following formula:

$$SME = \frac{(Total\ torque - friction\ Torque) \times N \times (P_m)}{(max_t) \times (max_{ss}) \times m_f}, \quad (3)$$

where  $N$  is the screw speed (rev/min),  $m_f$  is the mass flow rate (kg/s),  $max_t$  is the maximum allowable torque,  $max_{ss}$  is the maximum allowable screw speed, and  $P_m$  is the power of the drive motor at a rated speed of  $max_{ss}$ . Gu et al. [48] found that the SME is correlated with the median particles size and the crystallinity of the substrate respectively with  $r = -0.79$  and  $r = -0.87$ . Furthermore, it has been reported that the viscosity of the substrate influences the SME as less viscous substrates require higher SME [95].

Zheng et al. [78] studied the role of the SME in xylose recovery yields and found that mass flow higher than 1.45 kg/h negatively affected the xylose recovery yield. However, when the additive flow (water) was increased, they recorded an improvement in the xylose recovery yield while the SME decreased concurrently, which was attributed to lower friction in the barrel due to increased moisture content. These results show that additives can be used to lower the SME in LBE and improve the sugar recovery results.

Energy consumption is one of the main concerns of biomass pretreatment. The goal is to recover the highest among of the desired compound under the least energy consumption possible. Thus, the SME should be set in the optimum range for a given LBE. For example, Lamsal et al. [79] tested SME values from 222 to 639 Wh/kg and found that 416,6 Wh/kg was optimum for wheat bran. Figure 9 gives an overview of some SME for LBE (details about data sources are presented in Appendix B). In cases where the SME is an output, the value can be predicted with a highly accurate model ( $R^2 = 0.978$ ) developed by Lei et al. [93] for a twin-screw extruder.



**Figure 9.** Specific mechanical energy for some lignocellulosic biomass extrusion (Wh/kg).

Comparing power consumption between pretreatment methods is complicated and somewhat unnecessary. Indeed, the pre-treatment method must be evaluated with regard to the profitability of the product which allows it to manufacture at the end of the chain (ethanol, biogas, biodiesel, enzymes, resin, etc.). Kazi et al. [96] used an ASPEN Plus model to simulate the profitability (on short-term economic viability) of four LCB pretreatment methods for ethanol production. The pretreatment methods were dilute acid, 2-stage dilute acid, ammonia fiber explosion (AFEX), and hot water. Corn stover was the raw biomass for all of them. Results showed the dilute acid pretreatment as the best pretreatment method as it gave the lowest product value (1.36 dollars of gasoline-equivalent). On the other hand, Yoo et al. [97] compared the profitability (for a year) of dilute acid and extrusion pretreat-



ment in the production of ethanol. The Monte Carlo model was used for this purpose and soybean hulls were the substrate. Extrusion pretreatment was the best pretreatment as it produced 23.4% more ethanol than the dilute acid pretreatment. The main reason was the high conversion of cellulose to glucose, achieved with extrusion pretreatment [98].

In practice, in order to lower the energy balance of the whole extrusion pretreatment, good practices are:

- Avoid the use of a thermal source during biomass preparation, instead privilege room temperature or solar heat.
- Use kneading screw elements and reverse screw elements sparingly in the screw configuration. As highlighted in Section 3.2, these two elements enhance the disruptive effect of screws on biomass, but at the same time, they increase the energy consumption [66,80]. The operator must find a compromise according to the objectives of their extrusion pretreatment.
- Opt for continuous extrusion to avoid unnecessary energy consumption and also because starting up the extruder is time-consuming and energy-intensive. Therefore, plan each extrusion well and prepare everything before starting.
- Make sure the moisture of the substrate is sufficient to ensure smooth transport of the substrate in the barrel, as dry matter content and extruder electricity consumption are strongly linked ( $R^2 = 0.73$ ) [99]. This practice also helps to avoid the overloading of the barrel and the jamming of the screws.
- Limit to the strict minimum the number of passes of the biomass in the extruder. This number may vary from one type of biomass to another. For this, preliminary tests are necessary. As highlighted in Section 5.2, several studies have shown that beyond a certain number of passes, there is no longer any significant improvement in the sugar recovery rate [44,69].

#### 4. Additives

Reactive extrusion is performed in an extruder where one or more additives chemically react with the biomass to achieve a change in composition and structure of the lignocellulose. Reactive extrusion is very common in LBE. Usually, the additive is a catalyst, a solvent, an enzyme (bioextrusion), or a combination of them. Additives can also be acid, alkali, organosolv, mineral, etc. Water, sodium hydroxide (NaOH), ethylene glycol, lime (CaOH), sulphuric acid ( $H_2SO_4$ ), Tween 80 (polysorbate 80) as surfactant, and [EMIM]Ac (1-Ethyl-3-methylimidazolium acetate) as ionic liquid are the most used. Reactive extrusion presents a key advantage because LCBs have poor flow capabilities. The aim of using additives is to enhance the flowability of the substrate in the barrel and facilitate saccharification via hydrolysis of the chemicals over the substrate. Reactive extrusion can be performed via two methods: mixing the additive with the substrate during the preparation step or adding the additive during the extrusion process.

##### 4.1. Addition before Extrusion

Adding additives to the biomass before extrusion (i.e., during biomass preparation) modifies the biomass moisture and this has certain advantages for reactive extrusion. In particular, this approach allows for a more precise control of the moisture content and mixing is optimal for maximum contact with the additive. Furthermore, when the mixture is stored in the presence of reactive additives, delignification can start during this period, weakening the lignocellulose structure and subsequently facilitating extrusion flow. Many studies have demonstrated that using additives before the extrusion process can be a very good practice, and the application of different kinds of additives has been investigated. Kuster et al. [44] studied the effect of water, glycerol, Tween 80, and ethylene glycol on sugar recovery with sugarcane bagasse and sugarcane straw, and water was found to be the best additive for both biomasses as evidenced by sugar recovery yield. However, this also led to problems with flow during extrusion. Under the pretreatment conditions tested (i.e., long residence time of the substrate inside the barrel, high shearing forces, and temperature),

the substrate began to dry and then blocked the screws. Glycerol, as an additive, achieved a slightly lower glucose recovery yield, but substantially improved the flow conditions. On the other hand, with willow and [EMIM]Ac as additives, Han et al. [59] achieved recovery yield for glucose and xylose of 99% and 99.5%, respectively. Da Silva et al. [69] applied the same solvent on sugarcane bagasse, and achieved 90% glucose recovery yield at 25 wt.% for 8 min extrusion. Zhang et al. [15] obtained 86.8% of glucose recovery yield and 50.5% of xylose recovery yield with dry corn stover combined with NaOH.

#### 4.2. Addition during Extrusion

Adding reagents during extrusion involves the use of a pump with a controllable flow rate. Some extruders are equipped with one or two additive pumps, wherein a first additive is injected in the screw zone located after the biomass hopper (Figure 3). Subsequently, another reagent is added downstream in the extruder to neutralize the first additive (in the case of alkali). The two flows and their respective concentration must be correctly adjusted. If not, the first additive action will not be optimal, or a poor neutralization can occur, negatively affecting further treatment of the extrudate. Extrusion performed this way saves time and energy compared to the case when the biomass and additives are mixed before extrusion and is well adapted to continuous extrusion. These advantages are crucial, especially at pilot and industrial scales. However, the mixing time for biomass and additive is reduced, and the sugar recovery yield can be affected [59,77,100]. Choi and Oh [67] pretreated ripe straw with sulphuric acid without a neutralization reagent. Only 43% of glucan (glucose) at 3.5% *w/v* H<sub>2</sub>SO<sub>4</sub> was recovered. Thus, the application of additives before or during the extrusion process must consider the objectives of the experiments, as well as energy consumption, and scale up implications. Sometimes, LBE is coupled with other pretreatments methods [101]. In that case, the second pretreatment method must be taken into account during the decision-making process.

### 5. Working Parameters

#### 5.1. Temperature

Extrusion is defined as a high-temperature technology [102]. In fact, there are three ranges of temperature for LBE: under 100 °C (low temperatures), between 100 °C and 150 °C (mild temperatures), and above 150 °C (high temperatures) [47,103].

The temperature inside the extruder barrel results from the heat generated by both external and internal sources. The external source is coming from the heating system of the extruder, while the internal source is the heat generated by the effect of shear forces inside the extruder (viscous dissipation) [104]. Some extruders offer the possibility to impose a temperature profile along the screw. For example, Montiel et al. [100] pretreated blue agave bagasse using an extruder with four screw sections with different temperatures: 22 °C in the feeding zone, 50 °C in deconstruction zone, 25 °C in the neutralization zone, and 25 °C in the filtration zone. In this case, a higher temperature in the neutralization zone, such as 50 °C in the deconstruction zone, can denature the neutralization agent. This is a good example of how a temperature profile across the extruder design is advantageous for setting the optimum temperature for each screw zone.

It is unclear which temperature range (low, mild, or high) is suitable for a better sugar recovery. For Karunanithy et al. [105], single-extruded pine wood ran at different temperatures (100 °C, 150 °C, and 180 °C) achieved bests recovery results at 180 °C with 66.1% of total sugar recovery. Zheng et al. [78] experienced similar results after a twin-screw extrusion of sweet corn, with xylose recovery yield increasing with temperature (65–100 °C). At higher temperatures, biomass moisture loss is important, which can cause a powerful disturbance in the biomass structure due to shearing forces and elevated thermal action. Higher temperatures can have additional negative impacts on the extrusion process, as the substrate releases volatile organic compounds which can hinder downstream processes (enzymatic saccharification, fermentation, etc.) [104,106,107]. Gu et al. [48] used a twin-screw extruder to pre-treat Douglas fir residuals. The screws had five sections (T1 to T5)

along with the screws, with the following temperature profile: T1 and T2 (25 °C), T3 (50 °C), T4 and T5 (50, 100, or 150 °C). The results showed that glucose and xylose/mannose yield decreased when the temperature increased in sections T4 and T5, where the conditions ranged from 50 °C to 150 °C. They attributed this result to the fact that moisture evaporation is pronounced in T4 and T5 at high temperatures, leading to particle agglomeration, an increase in particle size, and cellulose recrystallization.

### 5.2. Residence Time

The biomass residence time in extrusion is considered a particular advantage for this process, as it is very short compared to other pretreatment methods. For LBE, the timespan is on the scale of minutes, with residence times around 1 min 30 s being achieved by Karunanithy et al. [105] and Vaidya et al. [56]. However, there are no standard residence times for laboratory studies, as residence times between 1 and 10 min are common [86]. On the other hand, a short residence time could be a problem, especially in the case of bioextrusion (extrusion with enzymes) or in reactive extrusion, when additives are added during the processing, both of which would require longer times for the necessary reactions to take place.

The residence time is the consequence of many factors. For example, screw design can play a role, as cylindrical screws generate longer residence time than conical screws for the same screw length [108]. Depending on screw speed and the screw configuration, the residence time can be lengthened or shortened. Screw configurations containing more KE, RSE, and short pitches elements lengthen the residence time, while more FSE and larger pitches elements tend to shorten the residence time [80,109,110]. On the other hand, many authors found that the screw speed is inversely proportional to the residence time [32,48,111]. Generally speaking, flow resistance inside the barrel translates into longer residence times. Furthermore, an extruder without a die at the end of the barrel results in shortened residence times. The length to diameter ratio (L/D) of the screws also influences the residence time, with higher ratios increasing the residence time [86].

So far, there is no evidence about the role of other parameters such as liquid/solid ratio on the residence time. Based on current knowledge, it can be assumed that a higher ratio will shorten the residence time because adding additives enhances the substrate flowability.

It has been reported that long residence times enhance sugar recovery yield as the effects of the shearing forces and all the other pretreatment conditions over the substrate are exerted over a longer period. However, long residence times also raise the SME [78,112]. Usually, operators increase the residence time by recirculating the extrudate into the extruder as many times as needed (i.e., number of passes). The number of passes can be up to ten or more. Da Silva et al. [69] investigated the effect of the number of passes on saccharification yield for sugarcane bagasse with an ionic liquid as the additive. The results showed that the glucose and xylose recovery increased after the first pass, but additional passes did not significantly increase the yields of glucose and xylose recovery compared to the first pass. Kuster et al. [44] experimented with 10 extrusion passes with both sugarcane bagasse and straw. As previously mentioned, a slight improvement of the glucose recovery yield was observed for each pass (after the first). However, for bagasse after 3 passes and 7 for straw, no improvement was recorded. Additionally, multi passes did not affect the crystallinity index, as no significant variation of the index was observed after the first pass.

### 5.3. Screw Speed

From the initial development of extrusion as a processing step, even in the case of LCB pretreatment, screw speed has been considered as an important parameter [80,113,114]. Screw speed is measured in rotations per minute (rpm) and usually ranges from 30 to 200 rpm in laboratory LBE settings. Screw speeds less than 100 rpm are considered low and those above 120 rpm are considered high. In particular cases, it can be set very low (down to 5 rpm), or very high (up to 420 rpm) [59,68,115,116]. As noted in the preview

sections, screw speed influences the torque, the SME, the barrel temperature, the residence time, and the substrate flow rate.

Screw speed is one of the most documented parameters in LBE. Like temperature, screw speed alone cannot guarantee the efficiency of the extrusion pretreatment [49,79,86]. It must be related to other extrusion parameters. For example, Karunanithy and Muthukumarappan [117] extruded switchgrass, while Heredia et al. [118] extruded Brewers' spent grain. Both studies recorded opposite behavior about screw speed over the glucose recovery yield. While Karunanithy and Muthukumarappan [117] found the best result by decreasing the screw speed from 150 to 50 rpm, Heredia et al. [118] obtained their best results by increasing the screw speed from 100 up to 200 rpm. However, it is important to notice that Heredia et al. [118] ran the extrusion under 20% moisture at 50 °C, while Karunanithy and Muthukumarappan [117] worked at 15% moisture content and 150 °C. It is also possible to vary the screw speed between high and low settings during the extrusion process. In that case, a way to overcome the rise of the SME is to lower the torque at high screw speeds [64,78]. Nevertheless, this processing requires more complex design and controls to operate.

## 6. Challenges, Limitations, and Future Prospects

Reactive extrusion is an interesting technology due to the advantages it has over other pretreatment methods, and the traditional disadvantages from which it is freed. These are: the high risk of corrosion of the equipment, the use of large quantities of water during or after pretreatment, the appearance of inhibitors, the pollution and toxicity linked to the use of certain chemical products, and the length of the pre-treatment time which can last several days for example in the case of biological pre-treatments (fungi, bacteria, termites, etc.) [24,119]. On the other hand, the challenges related to extrusion as a method of LCB pretreatment can essentially be summarized in four points: the initial investment cost, the energy consumption, the post-purchase flexibility of the design parameters, and the process scale-up.

Although on a medium and long-term basis extrusion is a commercially attractive solution and far better than many other pretreatment methods, the investment costs in this technology are high [97,98]. The high prices of extruders hinder the democratization of their use. In this case, it might be interesting to diversify the use of the extruder. For example, the same extruder could be used to manufacture composite materials whose commercialization could allow a faster return on investment. Concerning energy consumption, extruders need a heat source and a cooling system in addition to a power supply. These are made possible through the use of electricity. The consequence is a non-negligible energy consumption. It is possible from several practical techniques, such as those presented in Section 3.6, to save energy or improve the energy efficiency of the extruder, but less energy-consuming extruders are of essential needs to accelerate the return on investment in the case where the extruder is exclusively used for LCB pretreatment. Another important aspect is the relatively small leeway of the extruder holders for the modification of the screw elements. Extruder owners in most cases have to refer to the equipment supplier for modifications, which add delays and affect the productivity of the extruder. Although technically very difficult, the design of adaptable screw elements according to the desired shapes, inclinations, and diameters or the development of an extruder capable of variably housing one, two, or three screws could revolutionize the use of extruders for maximum destruction of the lignocellulosic complex but also for many other applications. The limits of extrusion are those of mechanical pretreatments in general. They necessarily require an external energy source. Moreover, with mechanical pretreatments, it is impossible to be selective and to target, for example, the types of chemical bonds in the biomass that we would like to break, as this is the case with most chemical pretreatments. Thus, biomass fractionation (separation into its three major components) with extrusion requires coupling with another pretreatment method such as Organosolv [120].

Regarding future prospects, in addition to solving the challenges mentioned above, it is about finding an interesting coupling of extrusion with another method of pretreatment. The idea would be to benefit from the many advantages offered by extrusion while mitigating its disadvantages. So far, several coupling ideas have been studied in the literature. For example, extrusion has been coupled with liquid hot water for eucalyptus and aspen pretreatment [121], with Steam explosion for corncob pretreatment [122], Ultrasonication for rice hull pretreatment [53], Ionic Liquid (IL) for pussy willow and sugar bagasse pretreatment [59], and with Organosolv method for prairie cordgrass pretreatment [122]. As extrusion is one of the most used methods in pretreatment couplings, it is of great interest to investigate, in a review, each of the couplings extrusion has been implicated in, in order to highlight their efficiency, their advantages and disadvantages, their need for improvement, and if possible to advise possible interesting coupling ideas based on lessons learned from existing couplings.

Extrusion optimization and scaling up is also an aspect that is attracting more and more interest. Indeed, experimental designs with response surfaces have been and continue to be used for optimization. The problem is that they take time and are sometimes very expensive. Today, new computational techniques (therefore faster and less expensive) are in development. A genetic algorithm method is one that currently focuses attention. Nastaj and Wilczynski's work [123] entitled "optimization and scale-up for polymer extrusion" is a rich source of information on this subject.

## 7. Conclusions

Extrusion is a very flexible method of lignocellulosic biomass pretreatment due to the many parameters available, with optimal conditions for a given process, and can include extruder design, biomass type, additives, and operating conditions. While some parameters related to the extruder design are limited to initial design plans, several other parameters can be adopted as needed by operators to customize for a process' given needs. Most of these parameters are correlated, and clear identification of the purpose of the extrusion and the downstream treatments, as well as the possibility to scale up the process, are important when selecting the extrusion settings. Particular attention should be paid to the energy consumption during the biomass preparation and the extrusion process, with settings leading to satisfactory sugar recovery with the lowest energy consumption as a focus.

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## Appendix A

**Table A1.** Specific mechanical energy for some lignocellulosic biomass extrusion (Wh/kg).

Substrate	Value or Range (Wh/kg)	References
Blue agave bagasse	288	[84]
Deshydrated sweet corn coproducts	141	[84]
Douglas fir 1	110–350	[78]
Douglas fir 2	310–420	[47]
Eucalyptus	6	[84]
OPEB	243	[84]
Rice straw	191–496	[92]
Soybean hull 1	157–726	[68]
Soybean hull 2	222–639	[79]
Sugarcane bagasse	408	[84]
Sweet corn	88	[84]
Vineyard pruning	207	[84]



## Appendix B

**Table A2.** Composition of some lignocellulosic biomass.

N°	Substrate	Composition (%)			References
		Cellulose	Hemicellulose	Lignin	
Hardwood					
1.	Birch	38.2	19.7	22.8	[124]
2.	Hybrid poplar	48.6	15.7	21.8	[42]
3.	Maple	44.9	25	20.7	[42]
4.	Poplar	49.9	25.1	18.1	[42]
5.	Red oak	43.4	22.5	25.8	[42]
6.	Walnut	46.2	20.9	21.9	[42]
7.	White birch	43	29.7	23.9	[39]
8.	White oak	43.6	23.7	23.2	[42]
9.	Willow	43	29.3	24.2	[124]
Softwood					
1.	Black spruce chips	50	17.6	25.4	[39]
2.	Pine	46.4	22.9	29.4	[124]
3.	Spruce	43.4	22	28.1	[124]
Grasses					
1.	Alfalfa	33	16.3	13.7	[39]
2.	Bagasse	23.33	16.52	54.87	[50]
3.	Corn cobs	15	35	45	[125]
4.	Corn stover 1	19	26	38	[126]
5.	Corn stover 2	35.6	22.1	12.3	[124]
6.	Rice straw 1	18	24	32.1	[125]
7.	Rice straw 2	34.2	24.5	11.9	[124]
8.	Sponge gourd fibres	15.46	17.44	66.59	[50]
9.	Sugarcane bagasse 1	20	25	42	[127]
10.	Sugarcane bagasse 2	40.2	23.8	25.2	[42]
11.	Sweet sorghum	21	27	45	[127]
12.	Switchgrass	31.0	24.4	17.6	[42]
13.	Wheat straw 1	38.2	24	23.4	[124]
14.	Wheat straw 2	38.2	24.5	23.4	[42]

## References

- Gupta, R.; Sharma, M.; Jangir, V.; Gautam, A.K.; Chandra, A.; Arya, R.K. A theoretical and mathematical study on the importance of petroleum derivatives in the production of sanitizer based products. *Mater. Today Proc.* **2022**, in press. [\[CrossRef\]](#)
- Al-Samhan, M.; Al-Fadhli, J.; Al-Otaibi, A.M.; Al-Attar, F.; Bouresli, R.; Rana, M.S. Prospects of refinery switching from conventional to integrated: An opportunity for sustainable investment in the petrochemical industry. *Fuel* **2022**, *310*, 122161. [\[CrossRef\]](#)
- Braga, A.; Faria, N. Biotechnological production of specialty aromatic and aromatic-derivative compounds. *World J. Microbiol. Biotechnol.* **2022**, *38*, 80. [\[CrossRef\]](#) [\[PubMed\]](#)
- Reshmy, R.; Paulose, T.A.P.; Philip, E.; Thomas, D.; Madhavan, A.; Sirohi, R.; Binod, P.; Kumar Awasthi, M.; Pandey, A.; Sindhu, R. Updates on high value products from cellulosic biorefinery. *Fuel* **2022**, *308*, 122056. [\[CrossRef\]](#)
- Liu, K.; Du, H.; Zheng, T.; Liu, H.; Zhang, M.; Zhang, R.; Li, H.; Xie, H.; Zhang, X.; Ma, M.; et al. Recent advances in cellulose and its derivatives for oilfield applications. *Carbohydr. Polym.* **2021**, *259*, 117740. [\[CrossRef\]](#)
- Peter, S.; Lyczko, N.; Gopakumar, D.; Maria, H.J.; Nzihou, A.; Thomas, S. Nanocellulose and its derivative materials for energy and environmental applications. *J. Mater. Sci.* **2022**, *57*, 6835–6880. [\[CrossRef\]](#)
- Antar, M.; Lyu, D.; Nazari, M.; Shah, A.; Zhou, X.; Smith, D.L. Biomass for a sustainable bioeconomy: An overview of world biomass production and utilization. *Renew. Sustain. Energy Rev.* **2021**, *139*, 110691. [\[CrossRef\]](#)
- Hoang, A.T.; Nizetic, S.; Ong, H.C.; Mofijur, M.; Ahmed, S.F.; Ashok, B.; Bui, V.T.V.; Chau, M.Q. Insight into the recent advances of microwave pretreatment technologies for the conversion of lignocellulosic biomass into sustainable biofuel. *Chemosphere* **2021**, *281*, 130878. [\[CrossRef\]](#)
- Zhang, J.; Zou, D.; Singh, S.; Cheng, G. Recent developments in ionic liquid pretreatment of lignocellulosic biomass for enhanced bioconversion. *Sustain. Energy Fuels* **2021**, *5*, 1655–1667. [\[CrossRef\]](#)



10. Xu, H.; Kong, Y.; Peng, J.; Song, X.; Liu, Y.; Su, Z.; Li, B.; Gao, C.; Tian, W. Comprehensive analysis of important parameters of choline chloride-based deep eutectic solvent pretreatment of lignocellulosic biomass. *Bioresour. Technol.* **2021**, *319*, 124209. [\[CrossRef\]](#)
11. Kumar, P.; Barrett, D.M.; Delwiche, M.J.; Stroeve, P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Ind. Eng. Chem. Res.* **2009**, *48*, 3713–3729. [\[CrossRef\]](#)
12. Galbe, M.; Zacchi, G. Pretreatment of lignocellulosic materials for efficient bioethanol production. *Adv. Biochem. Eng. Biotechnol.* **2007**, *108*, 41–65. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Pérez-Rodríguez, N.; García-Bernet, D.; Domínguez, J.M. Extrusion and enzymatic hydrolysis as pretreatments on corn cob for biogas production. *Renew. Energy* **2017**, *107*, 597–603. [\[CrossRef\]](#)
14. Gatt, E.; Rigal, L.; Vandenbossche, V. Biomass pretreatment with reactive extrusion using enzymes: A review. *Ind. Crops Prod.* **2018**, *122*, 329–339. [\[CrossRef\]](#)
15. Zhang, S.; Keshwani, D.R.; Xu, Y.; Hanna, M.A. Alkali combined extrusion pretreatment of corn stover to enhance enzyme saccharification. *Ind. Crops Prod.* **2012**, *37*, 352–357. [\[CrossRef\]](#)
16. Morales-Huerta, J.C.; Hernández-Meléndez, O.; Hernández-Luna, M.G.; Manero, O.; Bárzana, E.; Vivaldo-Lima, E. An experimental and modeling study on the pretreatment and alkaline hydrolysis of blue agave bagasse in twin-screw extruders. *Ind. Eng. Chem. Res.* **2021**, *60*, 12449–12460. [\[CrossRef\]](#)
17. Zhang, H.; Yang, W.; Roslan, I.I.; Jaenicke, S.; Chuah, G.-K. A combo Zr-HY and Al-HY zeolite catalysts for the one-pot cascade transformation of biomass-derived furfural to  $\gamma$ -valerolactone. *J. Catal.* **2019**, *375*, 56–67. [\[CrossRef\]](#)
18. Li, Q.; Zhou, Z.; Zhang, D.; Wang, Z.; Cong, W. Lipid extraction from *nannochloropsis oceanica* biomass after extrusion pretreatment with twin-screw extruder: Optimization of processing parameters and comparison of lipid quality. *Bioprocess Biosyst. Eng.* **2020**, *43*, 655–662. [\[CrossRef\]](#)
19. Pan-Utai, W.; Iamtham, S. Physical extraction and extrusion entrapment of C-phycoerythrin from *Arthrospira platensis*. *J. King Saud Univ.—Sci.* **2019**, *31*, 1535–1542. [\[CrossRef\]](#)
20. Sarker, T.R.; Azargohar, R.; Stobbs, J.; Karunakaran, C.; Meda, V.; Dalai, A.K. Complementary effects of torrefaction and pelletization for the production of fuel pellets from agricultural residues: A comparative study. *Ind. Crops Prod.* **2022**, *181*, 114740. [\[CrossRef\]](#)
21. Ahiduzzaman, M.; Islam, A.S. Development of biomass stove for heating up the barrel of rice husk briquette machine. *Procedia Eng.* **2013**, *56*, 777–781. [\[CrossRef\]](#)
22. Rowell, R.M. Challenges in biomass–Thermoplastic composites. *J. Polym. Environ.* **2007**, *15*, 229–235. [\[CrossRef\]](#)
23. Guiao, K.S.; Tzoganakis, C.; Mekonnen, T.H. Green mechano-chemical processing of lignocellulosic biomass for lignin recovery. *Chemosphere* **2022**, *293*, 133647. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Zhang, Y.; Ni, S.; Wu, R.; Fu, Y.; Qin, M.; Willför, S.; Xu, C. Green fractionation approaches for isolation of biopolymers and the critical technical challenges. *Ind. Crops Prod.* **2022**, *177*, 114451. [\[CrossRef\]](#)
25. Li, T.; Chen, C.; Brozena, A.H.; Zhu, J.Y.; Xu, L.; Driemeier, C.; Dai, J.; Rojas, O.J.; Isogai, A.; Wagberg, L.; et al. Developing fibrillated cellulose as a sustainable technological material. *Nature* **2021**, *590*, 47–56. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Kumar, D.; Singh, V. Bioethanol Production From Corn. In *Corn*; AACC International Press: Washington, DC, USA, 2019; pp. 615–631.
27. Niu, N.; Feng, L.; Lin, Y.; Li, X.; Zhang, D.; Yao, S. The sources of dechlorane plus (DP) in surface sediment from Bohai sea and the northern part of the yellow sea, China: Evidence from the fractional abundance of anti-DP (fanti) combined with lignin biomarker. *Reg. Stud. Mar. Sci.* **2020**, *39*, 101437. [\[CrossRef\]](#)
28. Fernández-Rodríguez, J.; Erdocia, X.; Sánchez, C.; González Alriols, M.; Labidi, J. Lignin depolymerization for phenolic monomers production by sustainable processes. *J. Energy Chem.* **2017**, *26*, 622–631. [\[CrossRef\]](#)
29. Ahvazi, B.; Wojciechowski, O.; Ton-That, T.M.; Hawari, J. Preparation of lignopolyols from wheat straw soda lignin. *J. Agric. Food Chem.* **2011**, *59*, 10505–10516. [\[CrossRef\]](#)
30. Garlapati, V.K.; Chandel, A.K.; Kumar, S.P.J.; Sharma, S.; Sevda, S.; Ingle, A.P.; Pant, D. Circular economy aspects of lignin: Towards a lignocellulose biorefinery. *Renew. Sustain. Energy Rev.* **2020**, *130*, 109977. [\[CrossRef\]](#)
31. Yağcı, S.; Sutay Kocabaş, D.; Çalışkan, R.; Özbek, H.N. Statistical investigation of the bioprocess conditions of alkali combined twin-screw extrusion pretreatment to enhance fractionation and enzymatic hydrolysis of bulgur bran. *J. Sci. Food Agric.* **2022**, early view. [\[CrossRef\]](#)
32. Duque, A.; Manzanares, P.; González, A.; Ballesteros, M. Study of the application of alkaline extrusion to the pretreatment of eucalyptus biomass as first step in a bioethanol production process. *Energies* **2018**, *11*, 2961. [\[CrossRef\]](#)
33. Doménech, P.; Duque, A.; Higuera, I.; Iglesias, R.; Manzanares, P. Biorefinery of the olive tree—Production of sugars from enzymatic hydrolysis of olive stone pretreated by alkaline extrusion. *Energies* **2020**, *13*, 4517. [\[CrossRef\]](#)
34. Duque, A.; Doménech, P.; Álvarez, C.; Ballesteros, M.; Manzanares, P. Study of the bioprocess conditions to produce bioethanol from barley straw pretreated by combined soda and enzyme-catalyzed extrusion. *Renew. Energy* **2020**, *158*, 263–270. [\[CrossRef\]](#)
35. Wang, Z.; He, X.; Yan, L.; Wang, J.; Hu, X.; Sun, Q.; Zhang, H. Enhancing enzymatic hydrolysis of corn stover by twin-screw extrusion pretreatment. *Ind. Crops Prod.* **2020**, *143*, 111960. [\[CrossRef\]](#)
36. Debiagi, F.; Faria-Tischer, P.C.S.; Mali, S. A green approach based on reactive extrusion to produce nanofibrillated cellulose from oat hull. *Waste Biomass Valoriz.* **2021**, *12*, 1051–1060. [\[CrossRef\]](#)

37. Coimbra, M.C.; Duque, A.; Saéz, F.; Manzanares, P.; Garcia-Cruz, C.H.; Ballesteros, M. Sugar production from wheat straw biomass by alkaline extrusion and enzymatic hydrolysis. *Renew. Energy* **2016**, *86*, 1060–1068. [\[CrossRef\]](#)
38. Park, S.; Baker, J.O.; Himmel, M.E.; Parilla, P.A.; Johnson, D.K. Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulase performance. *Biotechnol. Biofuels* **2010**, *3*, 10. [\[CrossRef\]](#)
39. Chen, J.; Adjallé, K.; Lai, T.T.; Barnabé, S.; Perrier, M.; Paris, J. Effect of mechanical pretreatment for enzymatic hydrolysis of woody residues, corn stover and alfalfa. *Waste Biomass Valorization* **2019**, *11*, 5847–5856. [\[CrossRef\]](#)
40. Lee, S.H.; Teramoto, Y.; Endo, T. Enzymatic saccharification of woody biomass micro/nanofibrillated by continuous extrusion process I—effect of additives with cellulose affinity. *Bioresour. Technol.* **2009**, *100*, 275–279. [\[CrossRef\]](#)
41. Ansell, M.P.; Mwaikambo, L.Y. The structure of cotton and other plant fibres. In *Handbook of Textile Fibre Structure*; Woodhead Publishing: Sawston, UK, 2009; pp. 62–94.
42. Zhao, X.; Zhang, L.; Liu, D. Biomass recalcitrance. Part I: The chemical compositions and physical structures affecting the enzymatic hydrolysis of lignocellulose. *Biofuels Bioprod. Bioeng.* **2012**, *6*, 465–482. [\[CrossRef\]](#)
43. Ghaemi, F.; Abdullah, L.C.; Ariffin, H. Lignocellulose structure and the effect on nanocellulose production. In *Lignocellulose for Future Bioeconomy*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 17–30.
44. Moro, M.K.; Teixeira, R.S.S.; da Silva, A.S.; Fujimoto, M.D.; Melo, P.A.; Secchi, A.R.; da Silva Bon, E.P. Continuous pretreatment of sugarcane biomass using a twin-screw extruder. *Ind. Crops Prod.* **2017**, *97*, 509–517. [\[CrossRef\]](#)
45. Vandenbossche, V.; Brault, J.; Vilarem, G.; Hernández-Meléndez, O.; Vivaldo-Lima, E.; Hernández-Luna, M.; Barzana, E.; Duque, A.; Manzanares, P.; Ballesteros, M.; et al. A new lignocellulosic biomass deconstruction process combining thermo-mechano chemical action and bio-catalytic enzymatic hydrolysis in a twin-screw extruder. *Ind. Crops Prod.* **2014**, *55*, 258–266. [\[CrossRef\]](#)
46. Marone, A.; Trably, E.; Carrère, H.; Prompsy, P.; Guillon, F.; Joseph-Aimé, M.; Barakat, A.; Fayoud, N.; Bernet, N.; Escudié, R. Enhancement of corn stover conversion to carboxylates by extrusion and biotic triggers in solid-state fermentation. *Appl. Microbiol. Biotechnol.* **2018**, *103*, 489–503. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Fu, Y.; Gu, B.-J.; Wang, J.; Gao, J.; Ganjyal, G.M.; Wolcott, M.P. Novel micronized woody biomass process for production of cost-effective clean fermentable sugars. *Bioresour. Technol.* **2018**, *260*, 311–320. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Gu, B.J.; Dhumal, G.S.; Wolcott, M.P.; Ganjyal, G.M. Disruption of lignocellulosic biomass along the length of the screws with different screw elements in a twin-screw extruder. *Bioresour. Technol.* **2019**, *275*, 266–271. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Zhang, S.; Xu, Y.; Hanna, M.A. Pretreatment of corn stover with twin-screw extrusion followed by enzymatic saccharification. *Appl. Biochem. Biotechnol.* **2012**, *166*, 458–469. [\[CrossRef\]](#) [\[PubMed\]](#)
50. Guimarães, J.L.; Frollini, E.; da Silva, C.G.; Wypych, F.; Satyanarayana, K.G. Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil. *Ind. Crops Prod.* **2009**, *30*, 407–415. [\[CrossRef\]](#)
51. Zheng, J.; Choo, K.; Rehmann, L. The effects of screw elements on enzymatic digestibility of corncobs after pretreatment in a twin-screw extruder. *Biomass Bioenergy* **2015**, *74*, 224–232. [\[CrossRef\]](#)
52. Kang, K.E.; Han, M.; Moon, S.-K.; Kang, H.-W.; Kim, Y.; Cha, Y.-L.; Choi, G.-W. Optimization of alkali-extrusion pretreatment with twin-screw for bioethanol production from miscanthus. *Fuel* **2013**, *109*, 520–526. [\[CrossRef\]](#)
53. Zhang, Y.; Li, T.; Shen, Y.; Wang, L.; Zhang, H.; Qian, H.; Qi, X. Extrusion followed by ultrasound as a chemical-free pretreatment method to enhance enzymatic hydrolysis of rice hull for fermentable sugars production. *Ind. Crops Prod.* **2020**, *149*, 112356. [\[CrossRef\]](#)
54. Rashed, G.I.; Chong, L.; Zhiyuan, S.; Hongzhen, F.; Chen, C.; Junjie, L.; Qiao, L.; Jianhui, D.; Huazheng, C.; Hongmei, W.; et al. Effect of a promising CSESE pretreatment on the morphological structure and properties of jute fibers. *E3S Web Conf.* **2021**, *252*, 02049. [\[CrossRef\]](#)
55. Senturk-Ozer, S.; Gevgilili, H.; Kalyon, D.M. Biomass pretreatment strategies via control of rheological behavior of biomass suspensions and reactive twin screw extrusion processing. *Bioresour. Technol.* **2011**, *102*, 9068–9075. [\[CrossRef\]](#) [\[PubMed\]](#)
56. Vaidya, A.A.; Gaugler, M.; Smith, D.A. Green route to modification of wood waste, cellulose and hemicellulose using reactive extrusion. *Carbohydr. Polym.* **2016**, *136*, 1238–1250. [\[CrossRef\]](#) [\[PubMed\]](#)
57. Debiagi, F.; Faria-Tischer, P.C.S.; Mali, S. Nanofibrillated cellulose obtained from soybean hull using simple and eco-friendly processes based on reactive extrusion. *Cellulose* **2019**, *27*, 1975–1988. [\[CrossRef\]](#)
58. Byun, J.; Cha, Y.-L.; Park, S.-M.; Kim, K.-S.; Lee, J.-E.; Kang, Y.-G. Lignocellulose pretreatment combining continuous alkaline single-screw extrusion and ultrasonication to enhance biosugar production. *Energies* **2020**, *13*, 5636. [\[CrossRef\]](#)
59. Han, S.-Y.; Park, C.-W.; Endo, T.; Febrianto, F.; Kim, N.-H.; Lee, S.-H. Extrusion process to enhance the pretreatment effect of ionic liquid for improving enzymatic hydrolysis of lignocellulosic biomass. *Wood Sci. Technol.* **2020**, *54*, 599–613. [\[CrossRef\]](#)
60. Karunanithy, C.; Muthukumarappan, K. Thermo-mechanical pretreatment of feedstocks. In *Green Biomass Pretreatment for Biofuels Production*; Gu, T., Ed.; Springer: Dordrecht, The Netherlands, 2013; pp. 31–65.
61. Duque, A.; Manzanares, P.; Ballesteros, I.; Negro, M.J.; Oliva, J.M.; Saez, F.; Ballesteros, M. Optimization of integrated alkaline-extrusion pretreatment of barley straw for sugar production by enzymatic hydrolysis. *Process Biochem.* **2013**, *48*, 775–781. [\[CrossRef\]](#)
62. Liu, C.; Van Der Heide, E.; Wang, H.; Li, B.; Yu, G.; Mu, X. Alkaline twin-screw extrusion pretreatment for fermentable sugar production. *Biotechnol. Biofuels* **2013**, *6*, 97. [\[CrossRef\]](#)

63. Karunanithy, C.; Muthukumarappan, K.; Gibbons, W.R. Sequential extrusion-microwave pretreatment of switchgrass and big bluestem. *Bioresour. Technol.* **2014**, *153*, 393–398. [\[CrossRef\]](#)
64. Karunanithy, C.; Muthukumarappan, K. Influence of extruder and feedstock variables on torque requirement during pretreatment of different types of biomass—A response surface analysis. *Biosyst. Eng.* **2011**, *109*, 37–51. [\[CrossRef\]](#)
65. Cha, Y.-L.; Yang, J.; Seo, S.-i.; An, G.H.; Moon, Y.-H.; You, G.-D.; Lee, J.-E.; Ahn, J.-W.; Lee, K.-B. Alkaline twin-screw extrusion pretreatment of Miscanthus with recycled black liquor at the pilot scale. *Fuel* **2016**, *164*, 322–328. [\[CrossRef\]](#)
66. Negro, M.J.; Duque, A.; Manzanares, P.; Sáez, F.; Oliva, J.M.; Ballesteros, I.; Ballesteros, M. Alkaline twin-screw extrusion fractionation of olive-tree pruning biomass. *Ind. Crops Prod.* **2015**, *74*, 336–341. [\[CrossRef\]](#)
67. Choi, C.H.; Oh, K.K. Application of a continuous twin screw-driven process for dilute acid pretreatment of rape straw. *Bioresour. Technol.* **2012**, *110*, 349–354. [\[CrossRef\]](#) [\[PubMed\]](#)
68. Yoo, J.; Alavi, S.; Vadlani, P.; Amanor-Boadu, V. Thermo-mechanical extrusion pretreatment for conversion of soybean hulls to fermentable sugars. *Bioresour. Technol.* **2011**, *102*, 7583–7590. [\[CrossRef\]](#)
69. Da Silva, A.S.A.; Teixeira, R.S.S.; Endo, T.; Bon, E.P.S.; Lee, S.-H. Continuous pretreatment of sugarcane bagasse at high loading in an ionic liquid using a twin-screw extruder. *Green Chem.* **2013**, *15*, 1991. [\[CrossRef\]](#)
70. Shah, A.; Gupta, M. Comparison of the flow in co-rotating and counter-rotating twinscrew extruders. *ANTEC* **2004**, *5*, 443–447.
71. Cantine, O. PEO Hot Melt Extrudates for Controlled Drug Delivery. Ph.D. Thesis, Université Lille, Lille Cedex, France, 2017.
72. Solano, D.; Vinyes, P.; Arranz, P. *The Biomass Briquetting Process: A Guideline Report*; UNDP-CEDRO Publication: Beirut, Lebanon, 2016.
73. Zhang, X.; Zhang, W.; Su, J.; Wang, M.; Lu, C. Preparation, characterization, and properties of polyethylene composites highly filled with calcium carbonate through co-rotating conical twin-screw extrusion. *J. Vinyl Addit. Technol.* **2014**, *20*, 108–115. [\[CrossRef\]](#)
74. Leng, J.; Wu, J.; Chen, N.; Xu, X.; Zhang, J. The development of a conical screw-based extrusion deposition system and its application in fused deposition modeling with thermoplastic polyurethane. *Rapid Prototyp. J.* **2019**, *26*, 409–417. [\[CrossRef\]](#)
75. Vera-Sorroche, J.; Kelly, A.L.; Brown, E.C.; Gough, T.; Abeykoon, C.; Coates, P.D.; Deng, J.; Li, K.; Harkin-Jones, E.; Price, M. The effect of melt viscosity on thermal efficiency for single screw extrusion of HDPE. *Chem. Eng. Res. Des.* **2014**, *92*, 2404–2412. [\[CrossRef\]](#)
76. Kelly, A.L.; Brown, E.C.; Coates, P.D. The effect of screw geometry on melt temperature profile in single screw extrusion. *Polym. Eng. Sci.* **2006**, *46*, 1706–1714. [\[CrossRef\]](#)
77. Duque, A.; Manzanares, P.; Ballesteros, I.; Negro, M.J.; Oliva, J.M.; Gonzalez, A.; Ballesteros, M. Sugar production from barley straw biomass pretreated by combined alkali and enzymatic extrusion. *Bioresour. Technol.* **2014**, *158*, 262–268. [\[CrossRef\]](#) [\[PubMed\]](#)
78. Zheng, J.; Choo, K.; Rehmann, L. Xylose removal from lignocellulosic biomass via a twin-screw extruder: The effects of screw configurations and operating conditions. *Biomass Bioenergy* **2016**, *88*, 10–16. [\[CrossRef\]](#)
79. Lamsal, B.; Yoo, J.; Brijwani, K.; Alavi, S. Extrusion as a thermo-mechanical pre-treatment for lignocellulosic ethanol. *Biomass Bioenergy* **2010**, *34*, 1703–1710. [\[CrossRef\]](#)
80. Wahid, R.; Hjorth, M.; Kristensen, S.; Møller, H.B. Extrusion as pretreatment for boosting methane production: Effect of screw configurations. *Energy Fuels* **2015**, *29*, 4030–4037. [\[CrossRef\]](#)
81. Djuric, D.; Kleinebudde, P. Impact of screw elements on continuous granulation with a twin-screw extruder. *J. Pharm. Sci.* **2008**, *97*, 4934–4942. [\[CrossRef\]](#)
82. Fülöp, G.; Domokos, A.; Galata, D.; Szabó, E.; Gyürkés, M.; Szabó, B.; Farkas, A.; Madarász, L.; Démuth, B.; Lendér, T.; et al. Integrated twin-screw wet granulation, continuous vibrational fluid drying and milling: A fully continuous powder to granule line. *Int. J. Pharm.* **2021**, *594*, 120126. [\[CrossRef\]](#)
83. Kohlgrüber, K.; Ullrich, M.; Hepperle, J.; Rudolf, R.; König, T.; Liesenfelder, U.; Bierdel, M.; Kirchhoff, J.; Lechner, F.; Sämann, H.-J.; et al. *Co-Rotating Twin-Screw Extruders Fundamentals, Technology, and Applications*; Hanser Publications: Munich, Germany, 2008. [\[CrossRef\]](#)
84. Vandenbossche, V.; Brault, J.; Vilarem, G.; Rigal, L. Bio-catalytic action of twin-screw extruder enzymatic hydrolysis on the deconstruction of annual plant material: Case of sweet corn co-products. *Ind. Crops Prod.* **2015**, *67*, 239–248. [\[CrossRef\]](#)
85. Choudhury, G.S.; Gautam, A. Screw configuration effects on macroscopic characteristics of extrudates produced by twin-screw extrusion of rice flour. *J. Food Sci.* **1999**, *64*, 479–487. [\[CrossRef\]](#)
86. Duque, A.; Manzanares, P.; Ballesteros, M. Extrusion as a pretreatment for lignocellulosic biomass: Fundamentals and applications. *Renew. Energy* **2017**, *114*, 1427–1441. [\[CrossRef\]](#)
87. Abeykoon, C.; Kelly, A.L.; Brown, E.C.; Coates, P.D. The effect of materials, process settings and screw geometry on energy consumption and melt temperature in single screw extrusion. *Appl. Energy* **2016**, *180*, 880–894. [\[CrossRef\]](#)
88. Patil, P.D.; Feng, J.J.; Hatzikiriakos, S.G. Constitutive modeling and flow simulation of polytetrafluoroethylene (PTFE) paste extrusion. *J. Non-Newton. Fluid Mech.* **2006**, *139*, 44–53. [\[CrossRef\]](#)
89. Ai, B.; Li, W.; Woome, J.; Li, M.; Pu, Y.; Sheng, Z.; Zheng, L.; Adediji, A.; Ragauskas, A.J.; Shi, J. Natural deep eutectic solvent mediated extrusion for continuous high-solid pretreatment of lignocellulosic biomass. *Green Chem.* **2020**, *22*, 6372–6383. [\[CrossRef\]](#)
90. Guha, M.; Ali, S.Z.; Bhattacharya, S. Twin-screw extrusion of rice flour without a die: Effect of barrel temperature and screw speed on extrusion and extrudate characteristics. *J. Food Eng.* **1997**, *32*, 251–267. [\[CrossRef\]](#)



91. Akdogan, H. Pressure, torque, and energy responses of a twin screw extruder at high moisture contents. *Food Res. Int.* **1996**, *29*, 423–429. [\[CrossRef\]](#)
92. Chen, W.H.; Xu, Y.Y.; Hwang, W.S.; Wang, J.B. Pretreatment of rice straw using an extrusion/extraction process at bench-scale for producing cellulosic ethanol. *Bioresour. Technol.* **2011**, *102*, 10451–10458. [\[CrossRef\]](#)
93. Lei, H.; Fulcher, R.G.; Ruan, R.; van Lengerich, B. Empirical modeling of die pressure, shaft torque, sme, and product temperature of rice flour in a corotating twin-screw extruder. *Cereal Chem. J.* **2005**, *82*, 582–587. [\[CrossRef\]](#)
94. Harmann, D.V.; Harper, J.M. Effect of extruder geometry on torque and flow. *Trans. ASAE* **1973**, *16*, 1175–1178. [\[CrossRef\]](#)
95. Godavarti, S.; Karwe, M.V. Determination of specific mechanical energy distribution on a twin-screw extruder. *J. Agric. Eng. Res.* **1997**, *67*, 277–287. [\[CrossRef\]](#)
96. Kazi, F.K.; Fortman, J.A.; Anex, R.P.; Hsu, D.D.; Aden, A.; Dutta, A.; Kothandaraman, G. Techno-economic comparison of process technologies for biochemical ethanol production from corn stover. *Fuel* **2010**, *89*, S20–S28. [\[CrossRef\]](#)
97. Yoo, J. *Technical And Economical Assessment of Thermo-Mechanical Extrusion Pretreatment for Cellulosic Ethanol Production*; Kansas State University: Manhattan, KS, USA, 2011.
98. Zheng, J.; Rehmann, L. Extrusion pretreatment of lignocellulosic biomass: A review. *Int. J. Mol. Sci.* **2014**, *15*, 18967–18984. [\[CrossRef\]](#)
99. Hjorth, M.; Gränitz, K.; Adamsen, A.P.S.; Møller, H.B. Extrusion as a pretreatment to increase biogas production. *Bioresour. Technol.* **2011**, *102*, 4989–4994. [\[CrossRef\]](#)
100. Montiel, C.; Hernández-Meléndez, O.; Vivaldo-Lima, E.; Hernández-Luna, M.; Bárzana, E. Enhanced bioethanol production from blue agave bagasse in a combined extrusion–saccharification process. *BioEnergy Res.* **2016**, *9*, 1005–1014. [\[CrossRef\]](#)
101. Beisl, S.; Biermair, F.; Friedl, A.; Mundigler, N.; Miltner, A. Sequential extrusion and organosolv pretreatment for wheat straw valorization. *Chem. Eng. Trans.* **2017**, *61*, 853–858.
102. Merci, A.; Urbano, A.; Grossmann, M.V.E.; Tischer, C.A.; Mali, S. Properties of microcrystalline cellulose extracted from soybean hulls by reactive extrusion. *Food Res. Int.* **2015**, *73*, 38–43. [\[CrossRef\]](#)
103. Appels, L.; Degreve, J.; Van der Bruggen, B.; Van Impe, J.; Dewil, R. Influence of low temperature thermal pre-treatment on sludge solubilisation, heavy metal release and anaerobic digestion. *Bioresour. Technol.* **2010**, *101*, 5743–5748. [\[CrossRef\]](#)
104. Formela, K.; Zedler, L.; Hejna, A.; Tercjak, A. Reactive extrusion of bio-based polymer blends and composites—Current trends and future developments. *Express Polym. Lett.* **2018**, *12*, 24–57. [\[CrossRef\]](#)
105. Karunanithy, C.; Muthukumarappan, K.; Gibbons, W.R. Extrusion pretreatment of pine wood chips. *Appl. Biochem. Biotechnol.* **2012**, *167*, 81–99. [\[CrossRef\]](#)
106. Formela, K.; Wołosiak, M.; Klein, M.; Wang, S. Characterization of volatile compounds, structural, thermal and physico-mechanical properties of cross-linked polyethylene foams degraded thermo-mechanically at variable times. *Polym. Degrad. Stab.* **2016**, *134*, 383–393. [\[CrossRef\]](#)
107. Espert, A.; de las Heras, L.A.; Karlsson, S. Emission of possible odourous low molecular weight compounds in recycled biofibre/polypropylene composites monitored by head-space SPME-GC–MS. *Polym. Degrad. Stab.* **2005**, *90*, 555–562. [\[CrossRef\]](#)
108. Seifert, S. Comparison of parallel and conical twin screw extruders from the processing point of view. *Plast. Rubber Compos.* **2013**, *34*, 134–142. [\[CrossRef\]](#)
109. Raquez, J.-M.; Narayan, R.; Dubois, P. Recent advances in reactive extrusion processing of biodegradable polymer-based compositions. *Macromol. Mater. Eng.* **2008**, *293*, 447–470. [\[CrossRef\]](#)
110. Gogoi, B.K.; Oswalt, A.J.; Choudhury, G.S. Reverse screw element(s) and feed composition effects during twin-screw extrusion of rice flour and fish muscle blends. *J. Food Sci.* **1996**, *61*, 590–595. [\[CrossRef\]](#)
111. da Silva, A.S.; Sobral Teixeira, R.S.; de Oliveira Moutta, R.; Santana, V.; de Barros, R.D.R.O.; Antonieta, M.; da Silva Bo, E.P. Sugar-cane and woody biomass pretreatments for ethanol production. In *Sustainable Degradation of Lignocellulosic Biomass—Techniques, Applications and Commercialization*; Books on Demand: Norderstedt, Germany, 2013.
112. Duque, A.; Álvarez, C.; Doménech, P.; Manzanares, P.; Moreno, A.D. Advanced bioethanol production: From novel raw materials to integrated biorefineries. *Processes* **2021**, *9*, 206. [\[CrossRef\]](#)
113. Guo, Y.; Chung, C.I. Dependence of melt temperature on screw speed and size in extrusion. *Polym. Eng. Sci.* **1989**, *29*, 415–419. [\[CrossRef\]](#)
114. Chung, C.I. Maximum pressure developed by solid conveying force in screw extruders. *Polym. Eng. Sci.* **1975**, *15*, 29–34. [\[CrossRef\]](#)
115. Choi, W.-I.; Oh, K.-K.; Park, J.-Y.; Lee, J.-S. Continuous sodium hydroxide-catalyzed pretreatment of empty fruit bunches (EFB) by continuous twin-screw-driven reactor (CTSR). *J. Chem. Technol. Biotechnol.* **2014**, *89*, 290–296. [\[CrossRef\]](#)
116. Endersen, P.G.; Lechner, F. Co-rotating fully intermeshing twin-screw compounding: Advancements for improved performance and productivity. *Plast. Eng.* **2012**, *64*, 32–38. [\[CrossRef\]](#)
117. Karunanithy, C.; Muthukumarappan, K. Effect of extruder parameters and moisture content of switchgrass, prairie cord grass on sugar recovery from enzymatic hydrolysis. *Appl. Biochem. Biotechnol.* **2010**, *162*, 1785–1803. [\[CrossRef\]](#)
118. Heredia-Olea, E.; Pérez-Carrillo, E.; Serna-Saldívar, S.O. Effect of extrusion conditions and hydrolysis with fiber-degrading enzymes on the production of C5 and C6 sugars from brewers' spent grain for bioethanol production. *Biofuel Res. J.* **2015**, *2*, 203–208. [\[CrossRef\]](#)

119. Zhao, L.; Sun, Z.-F.; Zhang, C.-C.; Nan, J.; Ren, N.-Q.; Lee, D.-J.; Chen, C. Advances in pretreatment of lignocellulosic biomass for bioenergy production: Challenges and perspectives. *Bioresour. Technol.* **2022**, *343*, 126123. [[CrossRef](#)]
120. Brudecki, G.; Cybulska, I.; Rosentrater, K. Integration of extrusion and clean fractionation processes as a pre-treatment technology for prairie cordgrass. *Bioresour. Technol.* **2013**, *135*, 672–682. [[CrossRef](#)] [[PubMed](#)]
121. Tian, D.; Shen, F.; Yang, G.; Deng, S.; Long, L.; He, J.; Zhang, J.; Huang, C.; Luo, L. Liquid hot water extraction followed by mechanical extrusion as a chemical-free pretreatment approach for cellulosic ethanol production from rigid hardwood. *Fuel* **2019**, *252*, 589–597. [[CrossRef](#)]
122. Zhang, H.-J.; Fan, X.-G.; Qiu, X.-L.; Zhang, Q.-X.; Wang, W.-Y.; Li, S.-X.; Deng, L.-H.; Koffas, M.A.G.; Wei, D.-S.; Yuan, Q.-P. A novel cleaning process for industrial production of xylose in pilot scale from corncob by using screw-steam-explosive extruder. *Bioprocess Biosyst. Eng.* **2014**, *37*, 2425–2436. [[CrossRef](#)] [[PubMed](#)]
123. Nastaj, A.; Wilczyński, K. Optimization and Scale-Up for Polymer Extrusion. *Polymers* **2021**, *13*, 1547. [[CrossRef](#)]
124. Jørgensen, H.; Kristensen, J.B.; Felby, C. Enzymatic conversion of lignocellulose into fermentable sugars: Challenges and opportunities. *Biofuels Bioprod. Bioeng.* **2007**, *1*, 119–134. [[CrossRef](#)]
125. Prasad, S.; Singh, A.; Joshi, H.C. Ethanol as an alternative fuel from agricultural, industrial and urban residues. *Resour. Conserv. Recycl.* **2007**, *50*, 1–39. [[CrossRef](#)]
126. Zhu, Y.; Lee, Y.Y.; Elander, R.T. Optimization of dilute-acid pretreatment of corn stover using a high-solids percolation reactor. *Appl. Biochem. Biotechnol.* **2005**, *124*, 1045–1054. [[CrossRef](#)]
127. Kim, M.; Day, D.F. Composition of sugar cane, energy cane, and sweet sorghum suitable for ethanol production at Louisiana sugar mills. *J. Ind. Microbiol. Biotechnol.* **2011**, *38*, 803–807. [[CrossRef](#)]