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Fractionation of Cellulose-Rich Products from an Empty Fruit Bunch (EFB) by Means of Steam **Explosion Followed by Organosolv Treatment**

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Abstract: In this study an empty fruit bunch (EFB) was subjected to a two-step pretreatment to defragment cellulose-rich fractions as well as lignin polymers from its cell walls. First pretreatment: acid-catalyzed steam explosion (ACSE) pretreatment of EFB was conducted under the temperature range of 180-220 °C and residence time of 5-20 min. The ACSE-treated EFB was further placed into the reactor containing 50% aq. ethanol and NaOH as a catalyst and heated at a temperature of 160 °C for 120 min for the second pretreatment: alkali-catalyzed organosolv treatment (ACO). The mass balance and properties of treated EFB were affected by the residence time. The lowest yield of a solid fraction was obtained when the residence time was kept at 15 min. Xylose drastically decreased, especially under the ACSE pretreatment. However, the crystallinity of cellulose increased by increasing the severity factor of the pretreatment and was 47.8% and 57% udner the most severe conditions. The organosolv lignin fractions also showed the presence of 14 major peaks via their pyrolysis-GC analysis. From here, it can be suggested that this kind of pretreatment can indeed be one potential option for lignocellulosic pretreatment.

Keywords: Biomass; two-step pretreatment; steam explosion; organosolv treatment; empty fruit bunch

1. Introduction

Over the recent decades, the utilization of empty fruit bunch (EFB) to produce renewable energy source has been studied extensively. This, EFB typically, is a leftover of the fresh fruit bunches after their fruit harvesting. Moreover, it is the major downstream residue from the Southeast Asian palm oil industry. This industry, recently, has produced 70 million metric tons of crude palm oil (CPO) just within one production year 2017–2018 amounting their production even up to 35% of the total production of edible vegetable oils [1]. Theoretically, palm oil plantations can produce more than 100 million metric tons of EFB since 1.42–1.88 tons of EFB are generated for every one ton of CPO produced [2]. However, unfortunately, most of these EFB is dumped and pose serious environmental problems. Therefore, it is highly desirable to utilize these biomasses for sustainable energy production.

Biochemical conversion of lignocelluloses involving chemical pretreatment followed by enzymatic hydrolysis and finally anaerobic fermentation is a well-established production line for lignocellulosic bioethanol production. In this classical approach, due to an inherited complex cell wall structure, effective fractionation of major lignocellulosic biomass components (cellulose, hemicellulose, and lignin) is crucial for effective subsequent processing. Undoubtedly, there have been several pretreatment studies involving EFB to deconstruct its native web into its constituents. In this regard, steam



explosion, which uses high-pressure steam to breakdown biomass structure, has been widely adapted strategy [3]. The effects of several factors like biomass particle size, moisture, pressure, residence time, reaction temperature and catalysts on the steam explosion were consistently investigated for several decades [4]. Previously, Choi et al. used alkaline reagent (3% NaOH at 160 °C) to catalyze steam explosion pretreatment and dissolved out C5 sugar-based components as well as lignin components from biomass [5]. Their yields, after enzymatic hydrolysis, for glucose and xylose heightened up to 93% and 78% respectively. In another study, the steam explosion of rose gum tree (Eucalyptus grandis) was carried out under the temperature range of 200–210 °C and residence time of 2–5 min after impregnation with 0.087% and 0.175% (w/w) H₂SO₄ [6]. Their results showed that 0.175% (w/w) H₂SO₄-impregnated chips at 210 °C for 2 min was the optimal condition for hemicellulose extraction. Today steam explosion is seen as one of the most widely employed and cost-effective process for lignocellulose pretreatment, yet the process still needs to be improved to realize industrialization [7]. In addition to this steam explosion strategy, another effective fractionation scheme for lignocelluloses is organosolv treatment, so-called organosolvation. This process, in principle, extracts lignin from lignocellulose with organic solvents, such as alcohols, acetone and organic peracids [8]. Previous studies have shown considerable effects of organosolv treatment (diethylene glycol) of rice straw and EFB as compared to soda pulping by Gonzalez et al. [9] keeping in view the heterogeneous yet complex cell wall structure of EFB, it is highly likely to investigate an appropriate pretreatment strategy for commercial production of biofuels [10]. Therefore, it has to be investigated the proper pretreatment process of EFB. In this study we adapted a two-step pretreatment strategy to fractionate EFB biomass into its sugar and non-sugar components. For this two-step pretreatments, EFB was first subjected to acid-catalyzed steam explosion (ACSE) followed by alkali-catalyzed organosolv treatment (ACO). Pretreatment efficacy was evaluated in terms of yields, crystallinity, and chemical composition of each solid fraction.

2. Materials and Methods

2.1. Feedstock Analysis

As raw biomass for this study, EFB ($\leq 6\%$ moisture) was provided by the Korea Institute of Science and Technology, in a setting of 0.5–2 mm fiber. Holocellulose, lignin, and ash content in the EFB sample were analyzed according to the National Renewable Energy Laboratory (NREL) standard procedures [11–13]. Carbon, hydrogen, and nitrogen contents were measured by using a CHNS-932 analyzer (LECO Corp., St. Joseph, MI, USA) and inorganic elements were analyzed by inductively coupled plasma emission spectroscopy (iCAP7400 Duo, Thermo Fisher Scientific, Waltham, MA, USA) [14]. Thermogravimetric analysis was performed under an inert atmosphere (50 mL/min N₂ flow) at a heating rate of 10 °C/min up to 800 °C with a TGA/DSC 3+ (METTLER TOLEDO, Columbus, OH, USA) [14]. All the results with the corresponding values are listed in Table 1.

Properties	Value
Elemental analysis (wt%)	
Carbon	45.4 ± 0.4
Hydrogen	5.0 ± 0.2
Nitrogen	0.6 ± 0.0
Oxygen ¹	49.0 ± 0.2

Table 1. Chemical and thermal characteristics of empty fruit bunch.

Properties	Value
Component analysis (wt%)	
Holocellulose	70.6 ± 0.2
Arabinose	6.1
Galactose	3.1
Glucose	39.0
Xylose	18.8
Lignin	18.0 ± 0.2
Extractives	4.6 ± 0.1
Ash	6.2 ± 0.3
Inorganic element (ppm)	
Aluminum	1760
Calcium	2170
Iron	2680
Magnesium	790
Potassium	11,930
Phosphorus	750
Silicon	760
Thermogravimetric analysis	
Volatiles (wt%)	80.5
Char (wt%)	19.5
Temperature at max. degradation rate (°C)	318.8

Table 1. Cont.

¹ By difference.

2.2. ACSE-First Pretreatment

Initially, we screened out experimental conditions based on our initial trials and proceeded accordingly as described below for the pretreatment. The complete fractionation processes are delineated in Figure 1. Briefly, for ACSE treatment, EFB was first washed to remove inorganic elements using a method suggested by Moon et al. [15] Later on it was impregnated in distilled water for 120 min with slow stirring, and finally the feedstock was dried in an oven at 75 °C. It was then impregnated in dilute sulfuric acid (0.5, 1, 2 wt%) for 4 h to make it ready for steam explosion pretreatment. The effect of dilute acid concentration on impregnation was examined by the component analysis (holocellulose, lignin, and sugar) [12].

For ACSE experiments, autoclave reactors with 2 L high pressure steam were loaded first with 150 g of raw EFB biomass samples on dry basis as a control. The final temperature in the reactor was applied to reach in the interval of 180–220 °C and the residence time was 5–15 min. After the intended reaction time, a valve was opened to release the pressure immediately. Solid fractions (E-S) from the steam explosion was washed with distilled water, and the resulting aqueous fraction (E-L) was also collected. Then, acid impregnated EFB, with the same solids loading, was steam-treated under the temperature of 220 °C and 20 min of residence time, the most severe conditions that could be stably maintained with the reactor. After the reaction and cooling, solid fraction (EA-S), and aqueous fraction (EA-L) were also collected.



Figure 1. Schematic diagram of the two-step fractionation process of empty fruit bunches (EFB) by (acid-catalyzed) steam treatment followed by alkali-catalyzed organosolv treatment.

2.3. ACO Second Pretreatment

Organosolv treatment experiments, as a 2nd treatment for both the E-S & EA-S solid fractions obtained from 1st treatment, were performed as follows: both the solid fractions were placed, one by one, in a solvent-circulating reactor with a solvent of a 50:50% (w/w) ethanol:water mixture maintaining a (10:1 (w/w) solvent:solid ratio) along with a 2 wt% of NaOH as a catalyst. The reaction was carried out at a temperature of 160 °C and 120 min residence time. After the desired reaction time, cellulose-rich solid fractions were collected and labelled as E-S-CS and EA-S-CS and liquid fractions were labelled as E-S-OL and EA-S-OL corresponding to E-S and EA-S biomass samples, respectively. The organosolv lignin was precipitated from E-S-OL and EA-S-OL by acidification with a 2 M of hydrochloric acid maintaining pH = 2. The precipitated organosolv lignin was freeze-dried and collected as a powder and saved for further experiments.

2.4. Analysis

Yields of each solid fraction were calculated using the following equation:

Yield (%) = weight of a solid fraction (g)/weight of dry feedstock (g) \times 100

Holocellulose, lignin, and sugar content in each solid fraction were analyzed by the same process mentioned in Section 2.1. X-ray powder diffraction patterns (XRD) were analyzed by a Bruker D8 Advance with DAVINCI using Cu K α radiation ($\lambda = 1.5418$ Å), operated at 40 kV and 40 mA with a scan speed of 0.5 s/min in a range of 2–50 degrees (2 thetas). Chemical compounds in liquid fraction were quantified and qualified using gas chromatography-mass spectrometry systems (5975C Series GC/MSD System, Agilent Technologies, Santa Clara, CA, USA) [14]. Organosolv lignin was analyzed by a coil-type CDS Pyroprobe 5000 (CDS Analytical Inc., Oxford, PA, USA) [16].

3. Results and Discussion

3.1. Mass Balance

3.1.1. Effect of Residence Time and Temperature on Fractionation

The effects of residence time and temperature on the fractionation process were studied at various intervals (residence time 5, 10, 15 min and temperature 180, 200, 220 °C). Figure 2 shows the mass distribution of solid fractions obtained from EFB at various temperatures and residence time conditions.



Figure 2. Yields of the solid fractions from steam explosion and organosolv treatment of EFB under different temperatures and residence times.

Mass composition of the fraction was affected by residence time. At all temperature conditions, E-S from the steam explosion, and its subsequent, E-S-CS from organosolv treatment decreased with increasing residence time. For example, at 200 °C and in the range of 5–15 min, yields of E-S and E-S-CS decreased from 79.0 wt% and 73.8 wt% to 68.3 wt% and 61.2 wt%, respectively. The lowest yield was obtained when the residence time was kept for 15 min, regardless of reaction temperatures. The effect of temperature was not much clear as that of residence time. Under the same residence time condition, the yield of E-S and E-S-CS decreased only 3–8 wt%. The combined effect of temperature (T) and residence time (t) can be expressed as severity factor ($\log_{10} (R_0)$) [$R_0 = t \times \exp((T-100)/14.75)$) [17]. The severity factor obtained ranged from 3.1 to 4.7. There was a scant negative correlation between the severity factor and the solid fraction yield, showing that increasing temperature and residence time results in the removal of compounds from solid fractions.

In general, both mechanical and chemical effects take place when an acetyl group derived from hemicellulose acts as an acid at high temperature during the steam explosion [18]. These effects play important roles in the hydrothermal degradation of holocellulose. Hemicellulose and lignin are isolated by the high temperature in the steam condition. Organosolv treatment, however, on the other hand, solubilize lignin and provide holocellulose by using organic solvent mixture and inorganic catalysts [7]. Therefore, holocellulose and lignin compositions of solid fractions were also analyzed to examine the fractionation efficiency of the process.

Holocellulose and lignin contents of E-S and E-S-CS were calculated for each experiment (Table 2). Percentage of holocellulose composition decreased with increasing severity of steam explosion. A maximum of 24.1 wt% of holocellulose (220-15) was dissolved in E-L. On the contrary, the percentage of lignin composition increased with increasing severity factor. It can be anticipated that lignin melts under a high temperature and pressure, then condensed with other compounds like extractives or ash while cooling. Solid fractions which have undergone organosolvation showed an unremarkable change

of holocellulose contents. In addition, a considerable amount of lignin content still remained in the solids. Maximum 7.5% of lignin (220-15) was solubilized in 50% ethanol mixture. Lignin fractionation efficiency of organosolv treatment from EFB was falling short of our expectation because of its low lignin removal. These results showed EFB presents a high level of recalcitrance to the fractionation process. Thus, dilute acid pretreatment to level down the EFB recalcitrance had considerable effects and the results are discussed in Section 3.1.2.

		Holocellulose (wt%)	Lignin (wt%)
Rav	v EFB	70.6 ± 0.2	18.0 ± 0.2
	180-5	70.2 ± 0.1	23.3 ± 0.0
	180-10	69.3 ± 0.2	22.9 ± 0.1
	180-15	70.8 ± 0.2	25.1 ± 0.2
	200-5	71.2 ± 0.1	24.2 ± 1.0
E-S	200-10	69.9 ± 0.1	27.9 ± 0.8
	200-15	71.6 ± 0.4	29.3 ± 0.8
	220-5	68.3 ± 0.1	29.4 ± 0.8
	220-10	67.5 ± 0.0	33.7 ± 0.1
	220-15	67.9 ± 0.3	34.6 ± 0.2
	180-5	80.8 ± 0.3	20.1 ± 0.1
	180-10	80.3 ± 0.2	20.2 ± 0.1
	180-15	81.1 ± 0.2	21.6 ± 0.3
	200-5	83.6 ± 0.1	20.6 ± 0.1
E-S-CS	200-10	80.2 ± 0.2	22.8 ± 0.5
	200-15	81.5 ± 0.1	22.9 ± 0.9
	220-5	83.8 ± 0.2	21.5 ± 0.6
	220-10	74.9 ± 0.8	24.6 ± 0.5
	220-15	76.2 ± 0.1	22.8 ± 0.2

 Table 2. Component analysis of pretreated EFB solid fractions under different temperatures and residence times.

E-S: solid fraction obtained from steam explosion treatment of EF. E-S-CS: cellulose rich solid fraction obtained from alkali catalyzed organosolv treatment of E-S fraction.

3.1.2. Effect of Dilute Acid Impregnation on Fractionation

Acid impregnation has been considered to play a vital role for steam explosion treatment [4,19]. Keeping this in view, the effects of dilute acid on the fractionation process was studied with the feedstock impregnation in dilute sulfuric acid (0.5, 1, 2 wt%) for 4 h. Steam explosion process was further operated at residence time of 20 min and temperature of 220 °C, which showed the highest severity score so that the effect of dilute acid concentration can be compared clearly. Figure 3 shows the mass distribution of solid fractions obtained from EFB at various acid concentrations.

Mass composition of EA-S did not affect by the acid concentration clearly until the concentration reaches 2.0%. Moreover, at 0.5 and 1.0% dilute acid concentrations, EA-S from ACSE also showed no remarkable changes in the mass distribution. In the range of 0%–1.0% dilute acid concentration, yields of EA-S decreased from 73.0 to 70.8 wt%. However, EA-S-CS from ACO decreased with an increase in the acid concentration. In the same range of 0%–1.0% dilute acid concentration, EA-S-CS decreased from 59.0 to 45.9 wt%. At 2.0% dilute acid concentration, EA-S and EA-S-CS decreased with an increase in the acidity.



Figure 3. Yields of the solid fractions from acid catalyzed steam explosion (ACSE) and alkali-catalyzed organosolv treatment (ACO) of EFB.

Table 3 shows the holocellulose and lignin contents of EA-S and EA-S-CS calculated for each experimental run. The total amount of holocellulose harshly decreased with increasing dilute acid concentration. At 0.5% dilute acid concentration, 41.3 and 26.8 wt% of holocellulose still remained in EA-S and EA-S-CS, respectively. When the concentration increased to 2.0%, however, only 28.1 and 16.0 wt% of holocellulose remained in EA-S and EA-S-CS, respectively. Lignin exhibited somewhat different behavior in mass decrease. The amount of lignin did change slightly by the steam treatment. Hwoever, after ACO, 4.3%–6.7% of lignin was removed from the solid fractions. The removal efficiency of lignin between 0.5% and 2.0% acid concentration respectively. Similar studies were reported for the dilute acid treatment of rice straw [20] and corn stover [21]. However, the proper acid concentration or removal efficiencies of hemicellulose and lignin were different by feedstock properties. Since the purpose of this experiments is to lower only hemicellulose and lignin contents in EFB, so a high acid concentration was not adapted to avoid the loss of holocellulose contents.

		Holocellulose (wt%)	Lignin (wt%)
Raw	EFB	70.6 ± 0.2	18.0 ± 0.2
	220-20	69.0 ± 0.2	24.4 ± 0.8
EA C	0.5%	56.7 ± 0.2	33.7 ± 0.2
EA-S	1.0%	52.0 ± 0.1	38.0 ± 0.1
	2.0%	45.6 ± 0.1	45.9 ± 0.8
	220-20	64.1 ± 0.1	23.2 ± 0.8
	0.5%	56.5 ± 0.4	25.3 ± 0.4
EA-3-C3	1.0%	49.3 ± 0.3	27.9 ± 0.4
	2.0%	42.8 ± 0.1	30.1 ± 0.3

Table 3. Component analysis of acid pretreated EFB solid fractions.

EA-S: solid fraction obtained from acid catalyzed steam explosion treatment of acid impregnated EFB. EA-S-CS: cellulose rich solid fraction obtained from alkali catalyzed organosolv treatment of EA-S fraction.

3.1.3. Sugars Quantification

Tables 4 and 5 show the total sugar contents of each product fractions (EA-S, EA-S-CS, EA-L, and EA-S-OL). Glucose content in the solid fractions showed no significant change while lignin content increased compared to the raw material. It means that the glucose in the EFB took limited damage by the steam explosion process and the organosolv treatment. It is possible that long reaction times increased the accumulation of degradation by-products and mass losses by volatilization [22]. As the

acid concentration increased, however, the amount of glucose in the solid steadily decreased. When the acid concentration increased to 2.0%, the glucose amount decreased from 415 to 380 mg/g fraction. In contrast, concentration of glucose in EA-L dropped with 0.5 wt% acid pretreatment but increased by increasing acid concentration. Xylosyl groups were the most affected hemicellulose components during acid impregnation and the pretreatment process. The amount of xylose in the solid drastically decreased with increasing dilute acid concentration. As a result, concentration of xylose in the liquid fraction increased to twice of the control (10.1–21.9 mg/mL liquid). At 2.0% dilute acid concentration, more than 70% of the xylan in the EFB was hydrolyzed during two-step pretreatments. Arabinosyl, galactosyl, and mannosyl residues were removed from the solids by steam explosion with more than 0.5% acid concentration (Table 5).

		Total Sugar (mg/g Fraction)			Lignin		
		Glucose	Xylose	Arabinose	Galactose	Mannose	(mg/g Fraction)
	220-20	483	170	23	10	4	244
EA-S	0.5%	433	104	-	-	-	337
	1.0%	421	76	-	-	-	380
	2.0%	373	33	-	-	-	459
EA-S-CS	220-20	447	161	20	8	5	232
	0.5%	426	89	-	-	-	253
	1.0%	405	50	-	-	-	279
	2.0%	380	48	-	-	-	301

Table 4. Sugar content of pretreated EFB solid fractions under different temperatures and residence times.

Table 5. Sugar content of acid pretreated EFB liquid fractions.

		Total Sugar (mg/mL Liquid)			Lignin		
		Glucose	Xylose	Arabinose	Galactose	Mannose	(mg/mL Liquid)
	220-20	12.2	10.1	3.6	0.3	-	n.d.
EAT	0.5%	0.3	13.4	0.7	0.3	-	n.d.
EA-L	1.0%	1.4	20.6	0.8	0.4	0.2	n.d.
	2.0%	7.9	21.9	1.1	0.7	1.0	n.d.
220-2	220-20	-	2.2	3.0	-	0.4	38.2
EAROI	0.5%	0.8	3.2	-	-	-	19.0
EA-5-OL	1.0%	0.1	1.4	-	-	-	20.5
	2.0%	-	2.4	-	-	-	12.2

EA-L: liquid fraction obtained from acid catalyzed steam explosion treatment of acid impregnated EFB. EA-S-OL: organosolv liquor obtained from alkali catalyzed organosolv treatment of EA-S fraction.

3.2. Cellulose Crystallinity

The change of cellulose crystallinity as a result of the steam explosion and organosolv treatment was determined by analyzing the x-ray diffraction patterns (Figure 4 and Table 6). By the XRD peak height method, crystallinity index was calculated from the ratio of the height of the 002 peaks (22.7°) and the height of the minimum (18.3°) between the 002 and the 101 peaks [23]. The crystallinity of EFB fiber decreased due to the steam explosion and organosolv treatment. The lowest crystallinity was shown in E-S-CS under the condition of 180-10 (35.9%). The crystallinity of EFB increased by increasing the severity factor. This might be caused by the removal of the amorphous structure of cellulose or components like hemicellulose.

Cellulose crystallinity after the dilute acid impregnation followed by two-step pretreatment was determined by analyzing the X-ray diffraction patterns. The crystallinity of EFB fiber also decreased by both ACSE process and ACO. There was little change of crystallinity, however, between the raw and organosolv treatment.



Figure 4. X-ray diffraction of (A) E-S-CS and (B) EA-S and follow-up EA-S-CS.

		Crystallinity Index (%)
	Raw	58.3
	180-10	35.9
E-S-CS	200-10	47.8
	220-10	60.0
	EA-S 2.0%	47.8
	EA-S-CS 2.0%	57.0

Table 6. X-ray diffraction of (A) E-S-CS and (B) EA-S and follow-up	> EA-S-CS
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3.3. Chemical Properties of Organosolv Lignin

Qualitative and quantitative analysis of obtained organosolv lignins from E-S-OL were performed via pyrolysis-GC-MS analysis, and the results are listed in Table 7. Organosolv lignin obtained under steam explosion conditions of 200 °C and 5–10 min exhibited more than 14 peaks. Phenolic compounds, such as toluene (1), phenol (2), guaiacol (5), syringol (8), and isoeugenol (10), were the major compounds. As shown in Table 7, the number of chemical compounds and the overall peak size in the organosolv lignin decreased by increasing residence time. This might be explained by the fact that the lignin compounds can be condensed in harsher conditions and less decomposed by heat.

Table 7. Qualitative and quantitative analysis of chemical compounds in the organosolv lignin from E-S-OL.

No	Compound	Concentration (Area/IS Area)		
110.		220-5	220-10	
1	Toluene	0.45	0.15	
2	Phenol	4.66	1.67	
3	o-Cresol	0.44	0.16	
4	<i>p</i> -Cresol	0.54	0.19	
5	Guaiacol	0.51	0.33	
6	Creosol	0.53	0.25	
7	2-Methoxy-4-vinylphenol	0.40	0.12	
8	Syringol-	1.01	0.61	
9	3,5-Dimethoxy-4-hydroxytoluene	1.05	0.33	
10	Isoeugenol	0.30	0.10	
11	2,6-Dimethyl-3-(methoxymethyl)-benzoquinone	0.55	0.12	
12	(E)-4-Propenylsyringol	0.68	0.19	
13	n-Hexadecanoic acid	1.07	0.36	
14	Octadecanoic acid	0.33	0.15	
		12.50	4.72	

4. Conclusions

Two-step pretreatment, ACSE followed by ACO of EFB, was performed under a temperature range of 180–220 °C and residence time of 5–20 min after impregnation with 0.5%–2.0% dilute sulfuric acid. The mass balance and the chemical composition of pretreated EFB fractions were noticeably affected by the reaction temperature, residence time, and acid concentration during the steam explosion process. Moreover, glucose and xylose contents decreased under the acid-catalyzed pretreatment conditions. All the analyses together with the XRD peaks showed that the crystallinity of cellulose increased by increasing severity factor. In this experiment, the effect of two-step pretreatment was in no way remarkable but showed potential to advance it. Further study is needed to sort out the optimal conditions for this two-step EFB pretreatment to conclusively suggest its potential for EFB fractionation.

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References

- United States Department of Agriculture Economics, Statistics and Market Information System. Oilseeds: World Markets and Trade. Available online: https://downloads.usda.library.cornell.edu/usda-esmis/files/ tx31qh68h/sq87bv06k/9z903025j/oilseed-trade-09-12-2018.pdf (accessed on 21 December 2018).
- 2. Pleanjai, S.; Gheewala, S.H.; Garivait, S. Environmental evaluation of biodiesel production from palm oil in a life cycle perspective. *Asian J. Energy Environ.* **2007**, *8*, 15–32.
- 3. Shrotri, A.; Kobayashi, H.; Fukuoka, A. Catalytic conversion of structural carbohydrates and lignin to chemicals. *Adv. Catal.* **2017**, *60*, 59–123.
- 4. Brownell, H.; Yu, E.; Saddler, J. Steam-explosion pretreatment of wood: Effect of chip size, acid, moisture content and pressure drop. *Biotechnol. Bioeng.* **1986**, *28*, 792–801. [CrossRef] [PubMed]
- Choi, W.-I.; Park, J.-Y.; Lee, J.-P.; Oh, Y.-K.; Park, Y.C.; Kim, J.S.; Park, J.M.; Kim, C.H.; Lee, J.-S. Optimization of NaOH-catalyzed steam pretreatment of empty fruit bunch. *Biotechnol. Biofuels* 2013, *6*, 170. [CrossRef] [PubMed]
- 6. Emmel, A.; Mathias, A.L.; Wypych, F.; Ramos, L.P. Fractionation of eucalyptus grandis chips by dilute acid-catalysed steam explosion. *Bioresour. Technol.* **2003**, *86*, 105–115. [CrossRef]
- Alvira, P.; Tomas-Pejo, E.; Ballesteros, M.; Negro, M.J. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresour. Technol.* 2010, 101, 4851–4861. [CrossRef] [PubMed]
- 8. Zhao, X.; Cheng, K.; Liu, D. Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. *Appl. Microbiol. Biotechnol.* **2009**, *82*, 815. [CrossRef] [PubMed]
- 9. Gonzalez, M.; Canton, L.; Rodriguez, A.; Labidi, J. Effect of organosolv and soda pulping processes on the metals content of non-woody pulps. *Bioresour. Technol.* **2008**, *99*, 6621–6625. [CrossRef] [PubMed]
- 10. Lee, J.H.; Moon, J.G.; Choi, I.-G.; Choi, J.W. Study on the thermochemical degradation features of empty fruit bunch on the function of pyrolysis temperature. *J. Korean Wood Sci. Technol.* **2016**, *44*, 350–359. [CrossRef]
- Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D. Determination of Ash in Biomass; Laboratory Analytical Procedure (LAP) Technical Report NREL/TP-510-42622; National Renewable Energy Laboratory: Golden, CO, USA, 2005.
- Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. Determination of Structural Carbohydrates and Lignin in Biomass; Laboratory Analytical Procedure (LAP) Technical Report NREL/TP-510-42618; National Renewable Energy Laboratory: Golden, CO, USA, 2008.
- Sluiter, A.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D. Determination of Extractives in Biomass; Laboratory Analytical Procedure (LAP) Technical Report NREL/TP-510-42619; National Renewable Energy Laboratory: Golden, CO, USA, 2005.

- Lee, J.H.; Hwang, H.; Moon, J.; Choi, J.W. Characterization of hydrothermal liquefaction products from coconut shell in the presence of selected transition metal chlorides. *J. Anal. Appl. Pyrol.* 2016, 122, 415–421. [CrossRef]
- 15. Moon, J.; Lee, J.H.; Hwang, H.; Choi, I.-G.; Choi, J.W. Effect of inorganic constituents existing in empty fruit bunch (EFB) on features of pyrolysis products. *J. Korean Wood Sci. Technol.* **2016**, *44*, 629–638. [CrossRef]
- Kim, J.-Y.; Lee, J.H.; Park, J.; Kim, J.K.; An, D.; Song, I.K.; Choi, J.W. Catalytic pyrolysis of lignin over HZSM-5 catalysts: Effect of various parameters on the production of aromatic hydrocarbon. *J. Anal. Appl. Pyrolysis* 2015, 114, 273–280. [CrossRef]
- 17. Overend, R.P.; Chornet, E. Fractionation of lignocellulosics by steam-aqueous pretreatment. *Philos Trans R Soc Lond A* **1987**, *321*, 523–536. [CrossRef]
- Haghighi Mood, S.; Hossein Golfeshan, A.; Tabatabaei, M.; Salehi Jouzani, G.; Najafi, G.H.; Gholami, M.; Ardjmand, M. Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment. *Renew. Sust. Energ. Rev.* 2013, 27, 77–93. [CrossRef]
- Kapoor, M.; Raj, T.; Vijayaraj, M.; Chopra, A.; Gupta, R.P.; Tuli, D.K.; Kumar, R. Structural features of dilute acid, steam exploded, and alkali pretreated mustard stalk and their impact on enzymatic hydrolysis. *Carbohydr. Polym.* 2015, 124, 265–273. [CrossRef] [PubMed]
- Chen, W.H.; Pen, B.L.; Yu, C.T.; Hwang, W.S. Pretreatment efficiency and structural characterization of rice straw by an integrated process of dilute-acid and steam explosion for bioethanol production. *Bioresour. Technol.* 2011, 102, 2916–2924. [CrossRef] [PubMed]
- 21. Zimbardi, F.; Viola, E.; Nanna, F.; Larocca, E.; Cardinale, M.; Barisano, D. Acid impregnation and steam explosion of corn stover in batch processes. *Ind. Crops Prod.* **2007**, *26*, 195–206. [CrossRef]
- Fockink, D.H.; Sánchez, J.H.; Ramos, L.P. Comprehensive analysis of sugarcane bagasse steam explosion using autocatalysis and dilute acid hydrolysis (H₃PO₄ and H₂SO₄) at equivalent combined severity factors. *Ind. Crops Prod.* 2018, 123, 563–572. [CrossRef]
- 23. 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] [PubMed]



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