

## Article

# Mechanical and Alkaline Hydrothermal Treated Corn Residue Conversion in to Bioenergy and Biofertilizer: A Resource Recovery Concept

Subhash Paul, Animesh Dutta \* and Fantahun Defersha 

School of Engineering, University of Guelph, Guelph, ON N1G2W1, Canada; paulchsubhash@yahoo.ca (S.P.); fdefersh@uoguelph.ca (F.D.)

\* Correspondence: adutta@uoguelph.ca

Received: 18 January 2018; Accepted: 23 February 2018; Published: 28 February 2018

**Abstract:** In this research fall time harvested corn residue (CR) was first mechanically pretreated to produce 5 mm chopped and  $<500\ \mu\text{m}$  ground particles, which underwent an anaerobic digestion (AD) process to produce biomethane and biofertilizer. Another sample of CR was pretreated by an alkaline hydrothermal (HT) process using 1%, 2% and 3% NaOH to produce solid biocarbon and the resulting alkaline hydrothermal process water (AHTPW), a co-product of biocarbon, underwent fast digestion under AD conditions to produce biomethane and biofertilizer. A predetermined HT process of  $240\ ^\circ\text{C}$  for 30 min was considered and the effect of alkali content on the HT process for biocarbon and biomethane product a rate of  $8.21\ \text{MJ kg}^{-1}$  and  $9.23\ \text{MJ kg}^{-1}$  of raw CR, respectively. Among the three selected alkaline HT processes, the 1% NaOH HT process produced the highest hybrid bioenergy of  $11.39\ \text{MJ kg}^{-1}$  of raw CR with an overall energy recovery of 62.82% of raw CR. The AHTPW of 2% and 3% NaOH HT-treated CR did not produce considerable amount of biomethane and their biocarbons contained  $3.44\ \text{MJ kg}^{-1}$  and  $3.27\ \text{MJ kg}^{-1}$  of raw CR of bioenergy, respectively. The biomethane produced from 5 mm chopped CR,  $<500\ \mu\text{m}$  ground CR and 1% alkaline AHTPW for 30 days retention time were of  $275.38\ \text{L kg}^{-1}$  volatile solid (VS),  $309.59\ \text{L kg}^{-1}$  VS and  $278.70\ \text{L kg}^{-1}$  VS, respectively, compared to non-treated CR of  $144\text{--}187\ \text{L kg}^{-1}$  VS. Nutrient enriched AD digestate is useable as liquid fertilizer. Biocarbon, biomethane and biofertilizer produced from the 1% alkaline HT process at  $240\ ^\circ\text{C}$  for 30 min can reduce the greenhouse gas (GHG) emissions of Ontario.

**Keywords:** biomethane; bioenergy; biofertilizer; alkaline hydrothermal; anaerobic digestion

## 1. Introduction

Lignocellulosic biomass (LB) such as wood, agricultural residues, energy crops, grass, forest residues, etc. is an alternative source to fossil fuel energy in North America [1]. Corn (*Zea mays* L.) residue (CR) is a potential bioenergy producing LB, which could reduce foreign oil dependency. Global CR production is  $885.3\ \text{Mt year}^{-1}$  (grain/residue ratio of 1:1 basis) of which 35.5% is in the USA and 1.21% ( $10.70\ \text{Mt year}^{-1}$ ) is in Canada [2–4]. CR alone accounts for about 58% of the total agricultural crop residues of Canada [5]. About 62% ( $6.6\ \text{Mt year}^{-1}$ ) of Canadian CR is produced in Ontario [4]. All available agricultural residues have the potential to be converted into bioenergy production [6,7] but CR is currently decomposed as unharvested in the farm due to the unavailability of suitable technology at the farm level, therefore this unharvested CR produces greenhouse gases (GHGs). Although anaerobic digestion (AD) of agricultural feedstock has a high GHG-saving potential to produce renewable energy, but AD of the secondary feedstocks such as crop residue and agricultural waste is recognized as a viable solution for GHG emission reduction [8]. Aboveground CR can provide  $2.66\text{ to }2.93\ \text{t ha}^{-1}\ \text{year}^{-1}$  of soil organic carbon (SOC) into soil [3], which needs  $5.91\text{ to }6.51\ \text{ha}^{-1}\ \text{year}^{-1}$  of CR. For the water and wind erosion protection, along with the retention of soil organic matter (SOM),

5.25–12.50 t ha<sup>−1</sup> year<sup>−1</sup> of CR needs to remain unharvested [9], but 3 t ha<sup>−1</sup> year<sup>−1</sup> (12% of CR) of unharvested CR can protect water and soil erosion [10]. Laird and Chang [11] studied the impact of aboveground CR removal from 0 to 90% on SOM for 19 years and found that within 15 cm depths from soil surface, farms with removed residue contained 12% less SOC, 12.6% less total N, 7.3% less cation exchange capacity and 12.3% less total respiration, respectively, compared to non-removed residue farms in silt loam soil. Removal of CR reduces GHG emissions, especially CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O and NO<sub>3</sub><sup>−</sup> leaching [12,13].

Most LBs are composed of hemicellulose (23–32% of total solid (TS)), cellulose (38–50% of TS), and lignin (10–25% of TS) [14]. Cellulose is a crystalline and hemicellulose is a complex structure with various carbohydrate polymers (polysaccharides) [15,16]. Lignin creates a physical barrier during enzymatic action on the carbohydrate fraction of LB. Lignin is also a phenolic group polymer. The structural strength of a plant and protection against microbial attack are provided by lignin [1].

Among all types of bioenergy conversion technologies such as gasification, pyrolysis, syngas fermentation, cellulosic ethanol production and biogas production in AD, AD consumes the least energy with the benefit of GHG emission reduction [17]. Although LB has high methane potential for anaerobic digestion, its high value of C/N ratio and its structural complexity inhibit AD processes [14]. Therefore, pretreatment is essential for the production of biomethane from LB [18,19]. Degradation of variable cell walls, cellulose and lignin compound of LB is very slow in normal AD processes [20], but LB can be a potential AD substrate after appropriate pretreatment in such a way that its inhibitory substances can stay below the inhibition limit [14]. Commonly used pretreatment methods of LB are mechanical, thermal, chemical and thermochemical. Chopping, blending, milling and grinding are mechanical pretreatment techniques to reduce biomass size and breaking the hard cell walls so that microbial activity can more easily be possible during the AD process. Microbial pretreatments such as fungal treatment of agricultural biomass do not improve methane production in AD [21]. Thermal hydrolysis, wet oxidation (heating with air/O<sub>2</sub>), and steam explosion are considered in the thermal pretreatment category. Wet oxidation ruptures the crystalline structure of LB [22], but a huge mass loss occurs due to CO<sub>2</sub> production. In the case of thermal hydrolysis, the temperature is normally kept below 180 °C (150–180 °C) whereas steam explosion is carried out at higher temperatures (up to 240 °C) and up to 3.35 MPa pressure [23] where inhibitory substances (furfural and hydroxyl-methyl furfural (HMF)) are produced [24,25]. Mass losses would also happen in steam explosion treatment due to the presence of water vapor. A recent study by Minaret and Dutta [7] noticed higher mass losses during vapor state HT biochar production than that of liquid state HT biochar. Chemical pretreatment is carried out by using acid, alkali or oxidizing agents (H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, FeCl<sub>3</sub>, etc.) to degrade the lignin content. Degradation of lignin produces phenolic compounds during the oxidation process [26], which are AD inhibitors. During acidic treatment LB produces inhibitory substances such as furfural and HMF. Various bases such as NH<sub>4</sub>OH, NaOH, KOH, Ca(OH)<sub>2</sub>, and aqueous ammonia are used in alkali hydrolysis [27–33] to avoid inhibition. The lignocellulosic structure of biomass can be decomposed partially by NaOH pretreatment which helps to recover bioenergy from LB [34]. In addition of these pretreatment methods, a new method is being used for wet biomass, which is called the hydrothermal process, where submerged biomass is heated at 180 °C to 260 °C temperature for 5 min to 240 min to degrade its cellulose and hemicellulose portion, which is suitable for AD. Biomass is kept under water in a HT cylinder, its air is removed by flushing nitrogen and the minimum pressure of the HT cylinder is maintained to keep water in a liquid state, but in this process the pH of hydrothermal process water (HTPW) goes down to 2.3 to 3.5 [35], and needs to be increased to 6.5 to 7.5 range before it is used for AD. The LB degradation rate in HT processes can be increased if acid or alkali hydrolyzed biomass is used. HTPW of LB alone decreases the pH during HT process and if acid hydrolyzed LB is used in this process, then the pH of HTPW will further reduce and it will not be suitable for AD. On the other hand, if alkali-treated LB is used in this hydrothermal process, then the pH of HTPW will increase, which will be favorable to AD. Therefore, alkali-treated HTPW can produce biomethane in AD processes

with acceptable pH values. This alkali-added hydrothermal treated combined process is referred here as the alkaline hydrothermal process.

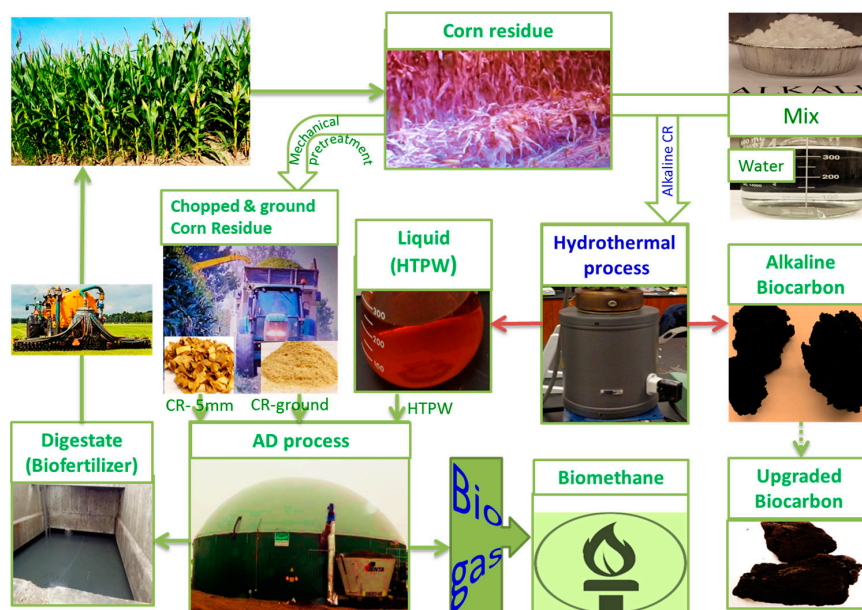
Among the various LB pretreatment methods, hydrothermal pretreatment of LB produces more biogas than any other method using treated and untreated LB. Biogas production can be increased by 132% and 226% for alkali (NaOH) and hydrothermal pretreatment of LB, respectively, compared to its untreated condition [36]. The HT process produces solid, liquid (aqueous soluble) and gaseous ( $\text{CO}_2$ ) products. HT of 260 °C temperature contains about 40% of organic carbon in its HTPW, which has potential to be used in anaerobic digestion [37] to produce biomethane. After (mandatory) addition of alkali (NaOH or KOH) to change the pH [38] of HTPW from 2.3 to 3.5 [35] to neutral, it can produce biogas in an AD process. Phenolic compounds cause strong AD inhibition both in autooxidation and gas production in wet conditions [39]. Raw, 3% NaOH pretreated (not heated) and HT pretreated at 250 °C for 10 min of rice straw could produce 140.0 L  $\text{kg}^{-1}$ , 184.8 L  $\text{kg}^{-1}$  and 315.9 L  $\text{kg}^{-1}$  VS, respectively, in a mesophilic AD study using 60 days retention time [38]. Among all chemically pretreated CRs, the CR treated with  $\text{H}_2\text{O}_2$  and NaOH for 1 h, followed by a mesophilic batch AD process, produced 66.27% and 57.18% more biomethane, respectively, than untreated CR of 187 L  $\text{kg}^{-1}$  VS biomethane. All other chemically treated CRs produced lower biomethane than these two, but 23–43% hemicellulose and 24–45% lignin were removed in these chemical pretreatments [40], which is a significant mass loss of the AD substrate. Steam explosion at 250 °C and 1.2 MPa for 10 min produced 55% more methane than untreated CR of 144 L  $\text{kg}^{-1}$  VS as the maximum whereas 1.5% KOH treated CR produced 45% more methane. On the other hand, 1.5% KOH mixed CR at 250 °C and 1.2 MPa for 10 min produced 80% more methane than untreated CR of 143.8 L  $\text{kg}^{-1}$  VS [41].

From the above information, it can be noted that mechanically pretreated LB in water will be of neutral pH; alkali treated LB will be of higher pH value (>7.0) than that of HT-treated strong acidic slurry. Mechanically pretreated LB still will have a constructional barrier to AD microbes. Alkaline HTPW, referred to as AHTPW below the microbial inhibition limit, will have possibility to overcome the above problems to maximize biomethane production. Limited addition of alkali in a predetermined HT process with controllable inhibitory parameters can maximize biomethane and biocarbon production. Therefore for this fixed hydrothermal process condition, addition of three individual levels of alkali such as 1%, 2% and 3% of NaOH were considered. Here it can be noticed that 8000 mg  $\text{L}^{-1}$  Na in AD substrate is strongly inhibited and 3500–5500 mg  $\text{L}^{-1}$  Na in AD substrate is moderately inhibited [42]. That means 1% NaOH can provide 5750 mg  $\text{L}^{-1}$  Na in water. But in a hydrothermal process some Na will be in the solid biocarbon as ash. Therefore, 1%, 2% and 3% NaOH were considered to be added to find out the suitable AHTPW to produce a maximum amount of biomethane in AD and biocarbon as the co-product. Biocarbon will be available for upgrading in a suitable acidic wash. Mechanical treatment needs only chopping or blending or grinding technology. Raw and mechanically-treated CR can produce biomethane only in AD whereas alkaline hydrothermally-treated CR can produce two types of bioenergy: biomethane and biocarbon. Both can produce liquid biofertilizer as the AD digestate. Therefore both types of treatment were selected for maximizing bioenergy and biofertilizer production (Figure 1).

Bio-waste to resource recovery and management systems produces sustainable green energy, which reduces climate change [43]. Biomass is a source of energy and nutrients and the recovery of these two resources at useable form is challenging. The recent waste management strategy launched in 2016 by the Government of Ontario in Canada is the circular economy which aims to eliminate waste, keep resources in use to extract the maximum value, minimize waste generated at the end-of-life, deliver a more competitive economy and help to reduce environmental impacts. The Circular Economy is beyond recycling compared to the traditional linear economy of make-use-dispose (landfill) strategy [44–46]. Bio-carbon production from biomass is an established technology where organics in hydrothermal process water are unused. Various researchers have mostly used hydrothermal processes in 250 °C to 270 °C for 10 min to 60 min for good quality biochar production where the 35% to 45% soluble biomass in the process water was unused. In this research we considered complete available

biomass both in the soluble and insoluble fractions in hydrothermal process water for bioenergy production and nutrient recovery.

To the best of our knowledge, the enhancement of methane production in AD with coproduction of biocarbon using liquid stage alkaline HT pretreated fall harvested CR has not been studied. The aim of the present study was to produce biocarbon and biomethane from CR and AD digestate used in corn/crop farms as biofertilizer. Production of biocarbon and biomethane in an alkaline HT process is a new concept. The AD digestate will be available to be used as biofertilizer. This concept will enrich the resource recovery strategy of a corn growing country with zero waste production as shown in Figure 1 and will reduce GHG emissions.



**Figure 1.** Conceptual framework of the corn residue and its alkaline hydrothermal hybrid bioenergy conversion processes in the resource recovery concept.

## 2. Methodology

### 2.1. Sample Collection and Feedstock Preparation

Fall harvested above ground standing plant CR was used as the substrate of this study. Complete corn plant samples were manually harvested (above 6 to 10 cm from the ground) from a southern Ontario farm in the fall of 2015 (5 November 2015). Ontario farmers traditionally harvest a small portion of CR in the spring when 7% to 10% silica is mixed with CR during harvesting and the spring harvested CR ash content is about 10% to 15% [12] where its combustion quality is decreased, therefore, fall-time harvested CR was considered for this research. Harvested plants were brought to the Biorenewable and Innovation Laboratory of the University of Guelph, Ontario and ears were immediately separated from plants, then leaves and tassels were cut off from the stalk and weighed. Then all of these components were dried at up to  $103\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$  for 24 h and an additional 48 h (for a total of 72 h) to follow ASABE standards, S358.2 (ASABE standard, 2008) [47] to determine the moisture content and dry matter. The dried sample was stored in Ziploc<sup>®</sup> plastic bags for laboratory experiments. For the sustainable CR harvesting, leaves, stalk and tassels were considered as CR for further laboratory experiments. During grain harvesting in the fall by a combine, cobs and husks are spread into the land where they are degraded before the next spring. Roots with 6–10 cm stem, cobs and husks are kept in the soil [48], which can be the source of SOM. The rest of the CR can be divided into two major parts, namely leaves (including the sheath) and stems (including shanks, tassels and lower ears). According to research results from Iowa State University, after separating



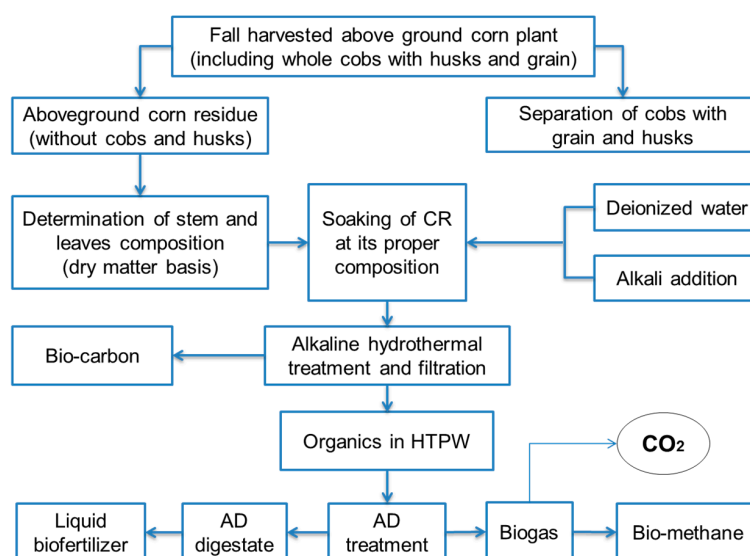
cobs and husks the fall harvesting above ground CR dry matter is composed of about 60% stem and 40% leaves [49]. The CR collected for this research was of the same composition. Therefore, for the consistency of laboratory experiments, the fall harvesting CR composition of 40% leaves dry matter and 60% stem dry matter was maintained for all experiments of this research.

## 2.2. Mechanical Pretreatment

Collected dry CR was chopped by a sheet metal cutter into  $\leq 5$  mm size at predetermined composition on a dry basis of leaves and stem that were mixed up for individual batches. A sample of same composition was ground at 420 rpm in a ball mill (model: RETSCH PM 100, RETSCH Mill, CL, USA) for 4 min and sieved to  $<500$   $\mu\text{m}$  size. For each batch, 5% feedstock total solid (TS) was maintained by taking 18.5 g dried CR and 350 mL deionized water.

## 2.3. Alkaline Hydrothermal Pretreatment

The cellulose degradation starting temperature is normally 220–240 °C and the hemicellulose degradation starting temperature is normally 180–200 °C, respectively, in non-catalytic HT processes [50,51]. In the HT process, cellulose is converted into glucose but hemicellulose is converted into xylose within 230 °C for  $\leq 30$  min, which are suitable to AD but at  $\geq 250$  °C temperature these two products are converted into furan compounds [52]. Therefore, the degraded organics of HTPW of the 240 °C for 30 min hydrothermal process were suitable for an AD process to produce biomethane. CR was chopped to  $\leq 5$  mm and soaked in 1%, 2%, and 3% NaOH water for 3 h as recommended by Teater et al. [53] so that CR stayed as 5% of the mixture and it was maintained by taking 18.5 g dry CR and 350 mL deionized water. Excess soaked water was decanted and this sample was transferred into a Parr 600 mL series 4560 mini reactor (Parr Instrument Company, Moline, IL, USA), deionized water (same as was decanted) was added into the reactor and liquid stage HT was carried out at 240 °C for 30 min following the method of Minaret and Dutta [7]. The liquid and solid hydrochar (i.e., biocarbon) mixture of the reactor was separated using a 20  $\mu\text{m}$  filter paper. The solid sample was placed in an aluminum container and it was kept in the muffle furnace to dry up according to the ASTM E1756 (at 103 °C  $\pm$  3 °C for 24 h). The filtered liquid, which is AHTPW, was transferred into a glass container, sealed and kept it at 4 °C in a refrigerator to use in AD for biogas production. A schematic diagram of CR harvesting, collection and the sample preparation for alkaline hydrothermal pretreatment of CR, its product separation and resource recovery is shown in Figure 2.



**Figure 2.** Flow diagram of alkaline hydrothermal pretreatment process, its products separation and resources recovery.

#### 2.4. Ultimate Analysis, Proximate Analysis and Higher Heating Value

Ultimate analysis, proximate analysis and higher heating value (HHV) of the raw CR (ash included) and biocarbons produced from different alkaline hydrothermal conditions were determined. The TS was determined according to the ASTM E1756 method by drying at  $103\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$  for 24 h in a muffle furnace. To account for the presence of volatile fatty acids (VFAs) and organics of low boiling point in HTPW and food waste AD inoculum, the same muffle furnace was set at  $60\text{ }^{\circ}\text{C}$  for 96 h to dry them without loss. Then the dried samples were ground at 420 rpm for 4 min in a ball mill (model: RETSCH PM 100) and stored it in a desiccator. According to the ASTM E1755 method, the ash content of TS was determined. TS was combusted at  $575\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$  for 3–5 h in a muffle furnace to determine ash content. ASTM E872 method was followed to determine volatile matter. The muffle furnace was set at  $950\text{ }^{\circ}\text{C} \pm 20\text{ }^{\circ}\text{C}$  for 7 min to determine ash content. CHNSO analyzer (Model: FLASH 2000, Thermo Scientific, Waltham, MA, USA) was used to determine elemental composition of dry TS and bio-carbon. This is known as ultimate analysis (determination of carbon, hydrogen, nitrogen, sulfur and oxygen). The HHV of all samples were determined in dry with ash basis using a bomb calorimeter (model: IKA C200, IKA, Wilmington, NC, USA) after calibration for uniform measurement. Alkali content of AHTPW was determined and it was deducted from alkaline total solid (ATS) of AHTPW and found the organic TS portion of AHTPW. It was used to compare with mechanical pretreated CR for biomethane production:

$$\text{Alkali in biocarbon} = \text{Weight of dry biocarbon} \times (\text{ash content of alkaline biocarbon} - \text{ash content of non-alkaline biocarbon}) \quad (1)$$

$$\text{Alkali in AHTPW} = \text{Added alkali} - \text{Alkali in biocarbon} \quad (2)$$

$$\text{Alkali content in AHTPW} = (\text{Weight of alkali in AHTPW}) / (\text{Weight of AHTPW}) \times 100\% \quad (3)$$

$$\text{Organic TS content} = \text{ATS} - \text{Alkali content} \quad (4)$$

#### 2.5. Elemental Analysis

Dried ground sample of  $<50\text{ }\mu\text{m}$  was mixed in deionized water to make a 5% TS-containing mixture for AD and it was further diluted 100 times for laboratory experiments and elemental analysis. The 100 times dilution was carried out for maintaining the limit of the used kits and laboratory equipment. The K content of AHTPW and raw CR solution was determined in Agricultural and Food Laboratory of the University of Guelph where an Inductively Coupled Plasma (ICP) analyzer was used. Nitrogen (N) was determined by using HACH TNT 880 kits, phosphorus (P) was determined by using HACH TNT 843 kits and sulfur (S) was determined by using HACH TNT 864 kits. The used block digester model was a HACH DRB 200 (HACH, Loveland, CO, USA) and the spectrophotometer model was HACH DR 5000 (HACH, Loveland, CO, USA). Total organic carbon (TOC) was determined by a TOC meter (Model: TOC-VCPN, Shimadzu Corporation, Kyoto, Japan). Total VFA of liquid samples was determined by HACH TNT 872 kits and COD (chemical oxygen demand) of liquid samples was determined by HACH 21259 kits (COD vial), respectively.

#### 2.6. Anaerobic Digestion

Two mechanically treated (chopped and ground) CR samples (Section 2.2) and AHTPW of three fixed diluted alkaline CRs such as 1%, 2% and 3% NaOH (Section 2.3) were taken in 160 mL biochemical methane potential (BMP) bottles and set them in an incubator with shaker facility (New Brunswick Scientific; capacity: 88 BMP bottles to produce biogas in AD. A BMP bottle of 63 mm diameter was filled with 25 mL CR or AHTPW substrate with 25 mL seed inoculum. Inoculum was collected from the municipal food waste AD plant of Toronto and kept it in a refrigerator at  $4\text{ }^{\circ}\text{C}$ . Inoculum was used within 3 days of collection. AD batch experiments were set up in such a condition that the substrate and inoculum volume ratio was 1:1 [41,54]. The pH of the mixture was recorded by a digital

pH meter. The mixture pH range was set at 6.5 to 7.5 by using trace amount of acetic acid (for a few BMP bottles). Then the BMP bottles' inside air were removed by flushing with nitrogen gas for about two minutes. Then each bottle was closed and sealed immediately after flushing. Each type of substrate was triplicated in BMP bottle to carry out AD. As reference, three BMP bottles were filled with 50 mL inoculum only to carry out AD in this way. The AD temperature was set at  $36\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  in the shaker incubator and all sealed BMP AD bottles were set in the hole of the incubator tray and started running. Biogas volume of each BMP AD was measured by a 50 cc glass gas syringe once in a day (at a fixed time). This helped to maintain the biogas production pattern consistency. The volume of biogas produced in each BMP AD was recorded every day for 30 days and the total biogas production was determined by their summation. Most of the farm AD processes are carried out for 20 to 30 days retention time, which is a common practice. In case of cellulose AD treatment, the daily biogas production rate from cellulose is dropped to 0 around the day 30 [55]. In this research the methane potential for a long period of time was not determined, because AD digestate was considered to use as liquid bio-fertilizer where a portion of organic carbon was available for SOC source along with SOM which is important for sustainable crop production. An amount of 5 to 20 cm<sup>3</sup> biogas was collected in a glass gas syringe from each individual BMP AD every day and immediately it was injected onto a Gas Chromatography (GC), GC-Thermal Conductivity Detector (GC-TCD) 6890N from Agilent Technologies (Mississauga, ON, Canada) to determine its composition (CH<sub>4</sub> and CO<sub>2</sub>). The used GC column was pre-calibrated by standard gas. Then AD digestate nutrients were determined. The method is explained in Section 2.5.

### 2.7. Energy Recovery

The energy recovery ratio (ERR) of resultant products compared to raw CR was calculated according to the used method of two previous researches [56,57]. The ERR of bio-carbon and bio-methane produced in this research was calculated according to the following equations [56]:

$$\text{ERR}_{\text{bio-carbon}} (\%) = 100 \times (\text{Yield}_{\text{bio-carbon}} \times \text{HHV}_{\text{bio-carbon}}) / \text{HHV}_{\text{CR}} \quad (5)$$

$$\text{ERR}_{\text{bio-methane}} (\%) = 100 \times (\text{Yield}_{\text{bio-methane}} \times \text{HHV}_{\text{bio-methane}}) / \text{HHV}_{\text{CR}} \quad (6)$$

$$\text{ERR} (\%) = \text{ERR}_{\text{bio-carbon}} (\%) + \text{ERR}_{\text{bio-methane}} (\%) \quad (7)$$

Here,  $\text{ERR}_{\text{bio-carbon}}$  and  $\text{ERR}_{\text{bio-methane}}$  are energy recovery ratio for bio-carbon and energy recovery ratio for bio-methane, respectively compared to raw dry CR.

## 3. Results and Discussion

### 3.1. Proximate and Ultimate Analysis of Corn Residue and AD Inoculum

The collected feed stock (mentioned in the Section 2.1) was characterized (mentioned in the Section 2.4). The feedstock characterization results are given in Table 1.

**Table 1.** Proximate and ultimate analysis of standing plant corn residue and inoculum for AD.

Parameter	Unit	Value	
		Corn Residue	Inoculum (AD Digestate)
TS	% (wet basis, wb)	53.28 ± 0.11	3.54 ± 0.47
Volatile solid (VS)	% (dry basis, db)	84.79 ± 2.23	40.89 ± 0.42
Ash content	% (db)	2.34 ± 0.06	38.56 ± 0.16
Fixed carbon (FC)	% (db)	12.86 ± 2.18	20.15 ± 0.27
Higher heating value (HHV)	MJ kg <sup>-1</sup> (db)	18.13 ± 0.06	14.698 ± 0.12
C	% (db)	45.29 ± 0.12	26.98 ± 0.40
H	% (db)	5.77 ± 0.13	3.56 ± 0.07
N	% (db)	0.88 ± 0.97	3.26 ± 0.13
S	% (db)	Not detected	0.21 ± 0.18
O	% (db)	48.08 ± 0.30	65.99 ± 0.33

### 3.2. Composition of Corn Residue and Its Alkaline Hydrothermal Process Water

According to Section 2.5, laboratory analytical experiments were carried out which are shown in Table 2. The total solid content in AHTPW was increased for increase of its alkali concentration. Therefore the VS content of AHTPW was decreased for increase of its alkali concentration. For presence of alkali (e.g., NaOH), some lignin is degraded and it stays in the liquid AHTPW. The C/N ratio for 1% NaOH treated AHTPW was the lowest (37.27) among three AHTPW samples. C/N ratio of 2% and 3% NaOH treated AHTPW were close to raw CR because higher delignification occurred [33], which stayed in AHTPW. Therefore its TS say ATS, TOC and nitrogen content were higher but COD content was lower than 1% NaOH treated AHTPW (Table 2). It can be noticed that non-alkaline HTPW had pH of 3.83 whereas 1%, 2% and 3% AHTPW had pH of 6.10, 9.00 and 9.80, respectively. After 240 °C, NO<sub>3</sub><sup>−</sup> started to convert into N<sub>2</sub> gas [58] but for the fixed temperature and time, here only alkali had an effect on the C/N ratio. Therefore based on these three alkaline hydrothermal processes, the 1% AHTPW was suitable for further AD treatment because of its 6.10 pH and C/N ratio of 37. In next section we will compare the biomethane production of mechanically-treated and alkali-treated CR.

**Table 2.** Major compounds of CR, non-alkaline and alkaline HTPW organics and inoculum.

Name of AD Substrate	pH of AD Substrate	TS in AD Substrate (%) wb	VS in AD Substrate (%TS)	Total VFA in AD Substrate (%TS)	COD in TS (g kg <sup>−1</sup> )	TOC in TS (g kg <sup>−1</sup> )	TKN in TS (g kg <sup>−1</sup> )	C/N Ratio
CR	6.50	5.00	84.79 ± 2.23	17.65 ± 0.45	2087 ± 8	450.00	9.75 ± 0.15	46.15
Non-alkaline HTPW	3.83	1.48	73.02 ± 0.96	23.78	1776 ± 3	367.57	8.67	42.40
1% NaOH AHTPW	6.10	3.55 ± 0.03	62.73 ± 0.87	34.46 ± 0.28	1764 ± 12	175.93	4.72 ± 0.09	37.27
2% NaOH AHTPW	9.00	4.79 ± 0.10	58.85 ± 0.07	36.50 ± 0.24	1226 ± 26	312.04	6.99 ± 0.15	44.64
3% NaOH AHTPW	9.80	5.27 ± 0.09	54.33 ± 1.09	36.50 ± 0.02	1171 ± 16	286.22	6.28 ± 0.12	45.58
Inoculum (food waste AD digestate)	8.22	3.54	40.89 ± 0.42	4.27 ± 0.34	975 ± 2.82	266.95 (TC = 629)	59.32	11

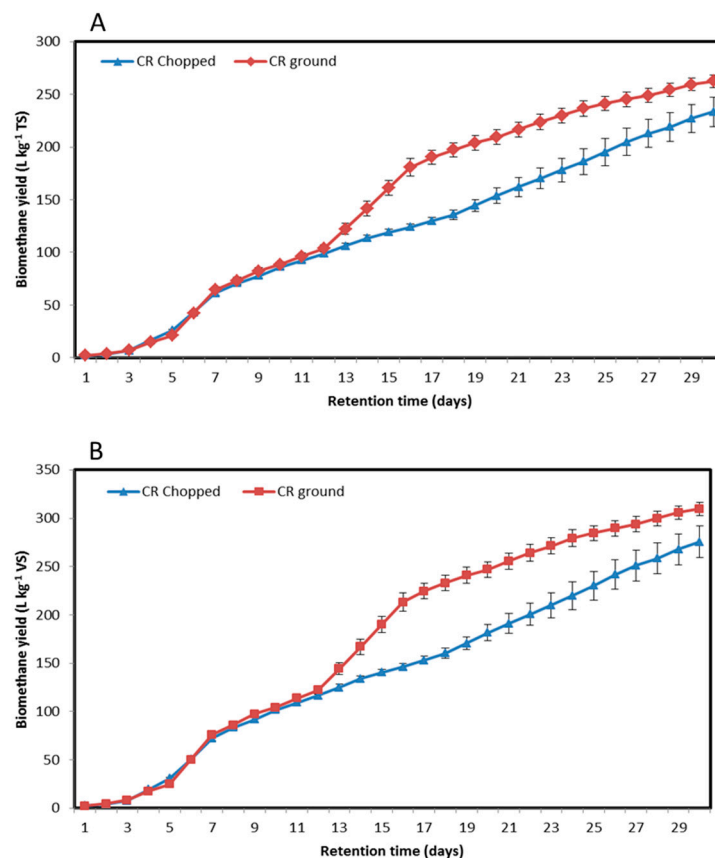
### 3.3. Anaerobic Digestion

#### 3.3.1. Biomethane Yield from Mechanically Pretreated Corn Residue

Mechanical pretreatment of CR was carried by: (i) chopping to 5 mm size and (ii) grinding and sieving to <500 µm size for anaerobic digestion, which is described in Section 2.2. The biomethane production from 5% TS containing AD of these two mechanically-treated CRs are shown in Figure 3A,B, respectively, in L kg<sup>−1</sup> TS and L kg<sup>−1</sup> VS basis. Biomethane production from 5 mm chopped and <500 µm ground AD were 233.50 ± 13.87 L kg<sup>−1</sup> TS and 262.50 ± 5.91 L kg<sup>−1</sup> TS, respectively, for 30 days retention time whereas these values were 275.38 ± 16.35 L kg<sup>−1</sup> VS and 309.59 ± 6.97 L kg<sup>−1</sup> VS, respectively in VS basis. The ground CR produced 12.42% more biomethane than chopped CR. The grinding operation could break down the hard structure of CR, which helped in hydrolysis and AD microbes faced less barriers than in chopped CR. Here it can be noticed that, after the sieving operation, the oversized CR portion (not used in this research) would possibly contain a higher amount of lignin due to its strong structure. Untreated CR can produce 143.8 L kg<sup>−1</sup> VS methane [41] to 186.74 L kg<sup>−1</sup> VS methane [40]. Here it can be noticed that CR contains high moisture (≥50%) during corn harvesting time and it needs drying before grinding, which consumes drying and grinding operational energy, but if it is possible to blend into <500 µm size material, then the same result can be attained. For blending operations, fiber can create problems. Chopping is possible during co-harvesting of CR with grain harvesting. Farm level available silage corn harvesting machinery can be applied after slight modification to chop CR at 1–2 mm size to get better results. Bio-methane production from dry chopped CR and dried ground CR had minor differences. Drying facilities are not



available at the farm level. Ontario farmers traditionally keep their CR unharvested until natural sun drying in the next spring and within this time about 66% of the dry matter is lost. When it is harvested in the spring, about 10–15% soil is mixed with it [12,59]. For this reason the wet chopped pre-treatment CR in the fall is favorable for AD compared to ground CR.



**Figure 3.** Cumulative biomethane yields from 5 mm chopped and <500 µm ground corn residue. (A) in TS basis; (B) in VS basis.

### 3.3.2. Biomethane Yield from Alkaline Hydrothermal Process Water of Corn Residue

Biomethane produced in the AD process from different AHTPW both on an ATS and organic TS basis, is shown in Figure 4A and VS basis is shown in Figure 4B. It can be noticed from these two figures that biomethane production from 2% alkali- and 3% alkali-added AHTPW stopped on day 13 and day 4, respectively, after production of trace amounts of biomethane (19.25 L kg<sup>-1</sup> VS and 7.34 L kg<sup>-1</sup> VS, respectively). Added alkali in the alkaline hydrothermal pretreatment would stay both in produced biocarbon as ash and mixed in AHTPW. Organic TS of AHTPW was determined following the method of Section 2.4. Hemicellulose and cellulose degradation starting temperature is normally 180–200 °C and 220–240 °C, respectively in non-catalytic HT processes [50,51]. In HT processes, within 230 °C for ≤30 min residence time cellulose is converted into glucose. Xylose is formed from hemicellulose with 230 °C treatment for ≤30 min. These two products are suitable for AD but at ≥250 °C temperature these two products are converted into furan compounds [52]. About 90% of the primary sugar of cellulose and hemicellulose stays in HTPW of 200 °C to 260 °C [60,61]. The sugar content of HTPW reached the maximum at 230 °C for 40 min to 60 min and after that it decreased with the increase of HT temperature and residence time [52]. At a constant residence time of 10 min, water insoluble (biocarbon) content is decreased from 80% of feedstock at 180 °C to 39.5% for feedstock at 280 °C following a constant decreasing rate but under the same conditions the organic content in HTPW remains comparatively constant from 200 °C to 240 °C, after that it decreased at a constant rate [51]. The HTPW containing

hemi-cellulosic and cellulosic organics like sugar and fatty acids (mostly acetic acid) are suitable for AD; but with the increase in process temperature  $> 240\text{ }^{\circ}\text{C}$  cellulosic sugar (hexose, i.e., glucose) is converted into HMF in the  $230\text{ }^{\circ}\text{C}$  to  $260\text{ }^{\circ}\text{C}$  range and then levulinic acid and formic acid [51,60–63], which are AD process inhibitors. Pentoses (arabinose, xylose) are a type of sugar in hemicellulose that is generally degraded into furfural and various organic acids at temperatures above  $220\text{ }^{\circ}\text{C}$  [61,64]. On the other hand, a trace amount of lignin-derived compounds also remains in the HTPW which are mainly phenolic compounds [65]. In the HT process of  $\leq 250\text{ }^{\circ}\text{C}$  cellulose derived glucose does not degrade into furan compounds such as HMF, 2-furaldehyde (2-FA), levulinic acid and lactic acid, but it is mostly degraded at  $300\text{ }^{\circ}\text{C}$  temperature [66]. Addition of NaOH or  $\text{Ca}(\text{OH})_2$  to lignocellulosic biomass in HT treatment loosens the bonds between lignin and hemicellulose, increasing the specific surface area and enzymatic digestibility to produce the highest glucose levels, whereby NaOH addition improves the efficiency of HT processes [67,68]. The hydrothermal temperature of  $250\text{ }^{\circ}\text{C}$  is the determining temperature for formation of HMF, levulinic acid, formic acid, lactic acid, glycolic acid etc. in pure water medium [51,60,69]. In acid/alkaline catalytic hydrothermal process of  $250\text{ }^{\circ}\text{C}$  is required for full conversion of glucose where 16% is HMF [69]. The yield of formic acid and acetic acid increased rapidly with the increase in temperature until  $220\text{ }^{\circ}\text{C}$ , but the yield of AD-inhibitory levulinic acid (a HMF degradation product) is increased at a very low rate until  $240\text{ }^{\circ}\text{C}$  and after that at a higher rate. The yield of glycolic acid is increased at a low constant rate until  $260\text{ }^{\circ}\text{C}$  temperature and after that the rate is increased [51]. In alkaline hydrothermal condition glucose conversion into HMF is lower than in neutral and acidic hydrothermal condition at the same temperature. The maximum HMF in HT process is produced at pH 1.5 to 2.5, whereas minimum HMF is produced at pH 2.9 to 10 with non-degradation of fructose [69]. Barkat et al., [39] studied bio-methane production from furan and lignin-derived compounds and found that 450, 430, 453, and 105 mL  $\text{CH}_4$  were produced, respectively per gram of HMF (cellulose derivative), furfural (hemicellulose derivative), syringaldehyde (lignin-derivative) and vanillin (lignin derivative) in 20–30 days retention time although these are normally called inhibitory substances in AD.

Under both basic and acidic conditions nitrate is converted into nitrogen in a reduction reaction and the destruction of  $\text{NO}_3^-$  reaction is accelerated by increasing the temperature ( $200\text{--}350\text{ }^{\circ}\text{C}$ ), pressure (4–18 MPa) and time. At a pH value of 4, 4.5% of  $\text{NO}_3^-$  is converted into  $\text{N}_2$  at  $250\text{ }^{\circ}\text{C}$  and  $<30$  min residence time, which is increased to 100% at  $350\text{ }^{\circ}\text{C}$  temperature and 2 h residence time [58] and as a result the C/N ratio is increased. Therefore, the selected hydrothermal process of  $240\text{ }^{\circ}\text{C}$  for 30 min is suitable for alkaline HT process for maximum useable bioenergy recovery both in biocarbon and biomethane compared to raw CR. In this HT process condition, production of furan compounds such as HMF, levulinic acid, lactic acid etc. may remain at a trace amount.

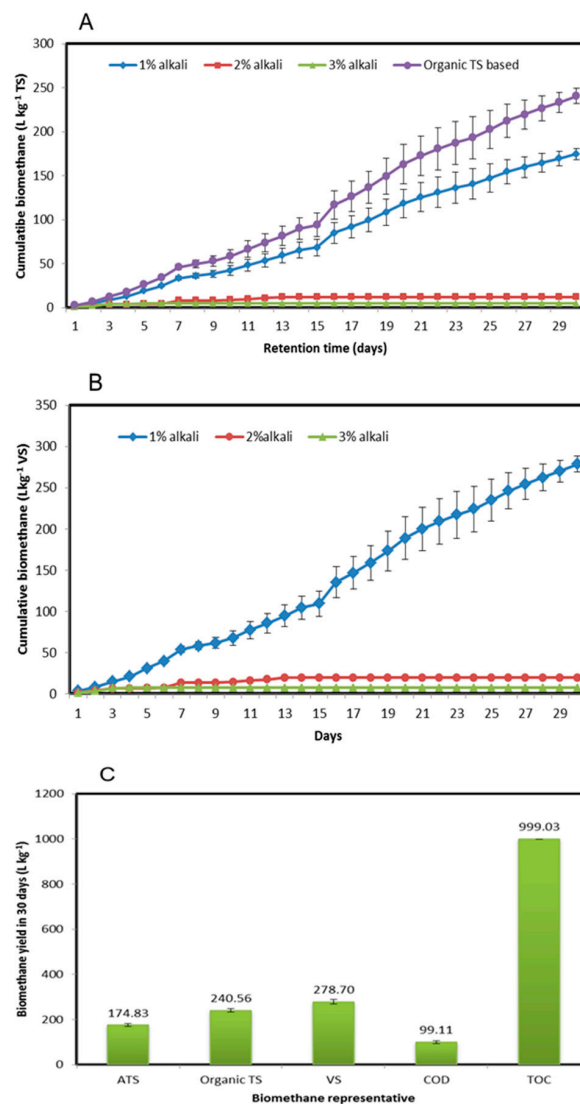
It can be noticed from Figure 4A,B that biomethane production from 2% alkali and 3% alkali added AHTPW stopped on day 13 and day 4, respectively, after production of trace amounts of biomethane ( $19.25\text{ L kg}^{-1}\text{ VS}$  and  $7.34\text{ L kg}^{-1}\text{ VS}$ , respectively). From the calculation of the alkali content of AHTPW, it can be noticed that  $8223\text{ mg L}^{-1}$  and  $7188\text{ mg L}^{-1}$  of Na, respectively were present in these two AHTPW, which strongly inhibits AD. AD microbes are strongly inhibited by  $8000\text{ mg L}^{-1}$  Na and the medium inhibited by  $3500\text{--}5500\text{ mg L}^{-1}$  Na in the AD substrate [42]. Previous researchers used higher amount of alkali for pretreatment of CR for delignification and the liquid was squeezed or filtered out before their AD set up. Separated liquid contained lignin products which were phenolic compounds and it was in high alkali metal which strongly inhibits AD [39]. Pretreatment of LB by 3% NaOH reduces 24–45% lignin from LB without heating [41] which stayed in the AD substrate. Alkali pretreatment by 10% NaOH can remove 45% lignin and 54% hemicellulose, respectively [70,71]. These two reasons can be responsible for interfering with the 2% and 3% alkaline AHTPW AD and basically they did not produce biogas. The pH values of substrates were adjusted before AD set up. The organic TS of 1% NaOH, 2% NaOH and 3% NaOH added AHTPW were calculated to be 2.58%, 3.36% and 4.03% wet basis, respectively. It can be calculated from Table 2 and Figure 4A that the 1% alkaline hydrothermal process water produced  $174.83 \pm 6.15\text{ L kg}^{-1}\text{ ATS}$ ,  $240.56 \pm 8.49\text{ L kg}^{-1}$  organic

TS and  $278.70 \pm 9.84 \text{ L kg}^{-1} \text{ VS}$ , respectively. The total biomethane production can also be presented in the form of ATS, organic TS, VS, COD and TOC (Figure 4C). It can be noticed from this figure that at 1% alkaline hydrothermal treated CR can produce biomethane of  $174.83 \pm 6.17 \text{ L kg}^{-1} \text{ ATS}$ ,  $240.56 \pm 8.49 \text{ L kg}^{-1} \text{ organic TS}$ ,  $278.70 \pm 9.84 \text{ L kg}^{-1} \text{ VS}$ ,  $99.11 \pm 6.8 \text{ L kg}^{-1} \text{ COD}$  and  $999.03 \text{ L kg}^{-1} \text{ TOC}$  of AHTPW, respectively. To the best of our finding, previous researchers could enhance methane production from corn residue to maximum of  $258.8 \text{ L kg}^{-1} \text{ VS}$  from 1.5% KOH (K of  $10,446 \text{ mg L}^{-1}$ ) mixed CR at  $250^\circ\text{C}$  and 1.2 MPa for 10 min steam explosion. It produced 80% more methane than untreated CR of  $143.8 \text{ L kg}^{-1} \text{ VS}$  where alkali pretreatment duration time was 12 h at  $20^\circ\text{C}$ . Previous researchers squeezed its black liquor out from their samples before set up for AD [41]. Therefore a large portion of KOH, hemicellulose and lignin (VS) would be removed and huge waste water with diluted lignin and hemicellulose was produced as black liquor. Basically methane was produced from cellulosic VS in their research. Though their methane production is high based on unit weight of VS, it might not be high enough based on total VS of CR. A large portion of lignin and hemicellulose were separated with black liquor. A typical olive wood sample could reduce solid in steam explosion for 5 to 25 min at  $190^\circ\text{C}$  to  $240^\circ\text{C}$  followed by a peroxide and alkali pretreatment for 12 h where solid of 37.45% of CR at  $190^\circ\text{C}$  and 23.80% of CR at  $240^\circ\text{C}$ , respectively were used for AD [72]. If this black liquor was not separated, then it supposed to be within K inhibition limit and phenolic inhibition limit of AD. Methane production from 2% KOH (K of  $13,929 \text{ mg L}^{-1}$ ) treated CR was  $205.1 \text{ L kg}^{-1} \text{ VS}$  after separation of black liquor [41]. Potassium inhibition in AD is  $2500\text{--}4500 \text{ mg L}^{-1}$  for medium inhibition and  $12,000 \text{ mg L}^{-1}$  for strong inhibition [42]. The liquid hydrothermal process to maximize biomethane and biocarbon production from CR can be  $240^\circ\text{C}$  for 30 min where oxidation could control for keeping the process at liquid stage. The process of our present research is the combination of alkali treated (chemical treatment) and liquid hydrothermal of  $240^\circ\text{C}$  for 30 min. This process increased not only the biomethane production but also produced another solid biofuel referred as biocarbon to use as substitution of coal. In addition, the AD digestate was available for use as biofertilizer.

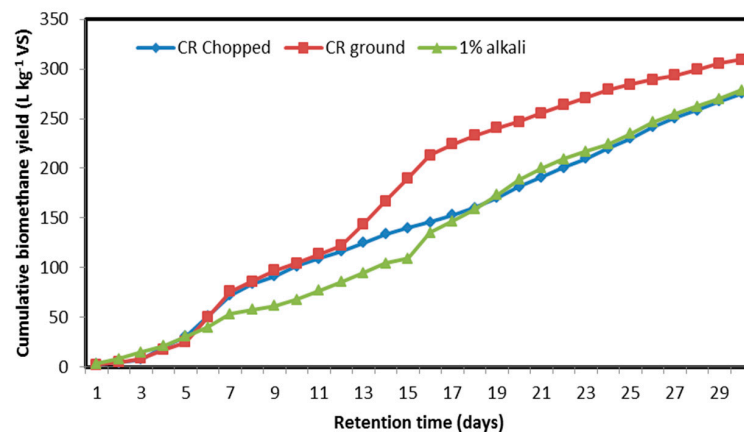
Based on above discussion, the appropriate hydrothermal process condition for maximum useable bio-carbon (biochar) and hydrothermal process water suitable for anaerobic digestion was selected as  $240^\circ\text{C}$  for 30 min for this research.

### 3.3.3. Biomethane Yield Comparison between Mechanical and Alkaline Hydrothermal Treated Corn Residue

Cumulative biomethane production for 30 days retention time from two mechanically pretreated (5 mm chopped and  $<500 \mu\text{m}$  ground) and 1% alkaline hydrothermal treated CR in VS basis is shown in Figure 5. The biomethane produced from 5 mm chopped,  $<500 \mu\text{m}$  ground and 1% alkaline hydrothermal pretreated CR was  $275.38 \pm 16.35 \text{ L kg}^{-1} \text{ VS}$ ,  $309.59 \pm 6.97 \text{ L kg}^{-1} \text{ VS}$  and  $278.70 \pm 9.84 \text{ L kg}^{-1} \text{ VS}$ , respectively. The ground mechanically treated CR produced the highest biomethane but this pretreatment needs extra arrangements for drying and grinding operations which can be replaced by blending operations for wet CR. The fiber present in CR can create operational problems. Chopping can be easily completed if CR is co-harvested with grain harvesting period. Silage harvester can perform this operation after little modification. Biomethane produced from AHTPW and 5 mm chopped CR in AD process was similar ( $278.70 \text{ L kg}^{-1} \text{ VS}$  and  $275.38 \text{ L kg}^{-1} \text{ VS}$ ). The alkaline hydrothermal pretreatment produces two types of bioenergy such as biomethane and biocarbon. Biocarbon can be used as a substitute for coal. Therefore the two types of bioenergy of 1% alkaline HT treated CR together produced higher amount of bioenergy compared to only biomethane from mechanical pretreated (chopped or ground) CR. The fuel quality of biocarbon produced from 1% alkaline hydrothermal pretreated CR will be discussed in the next section.



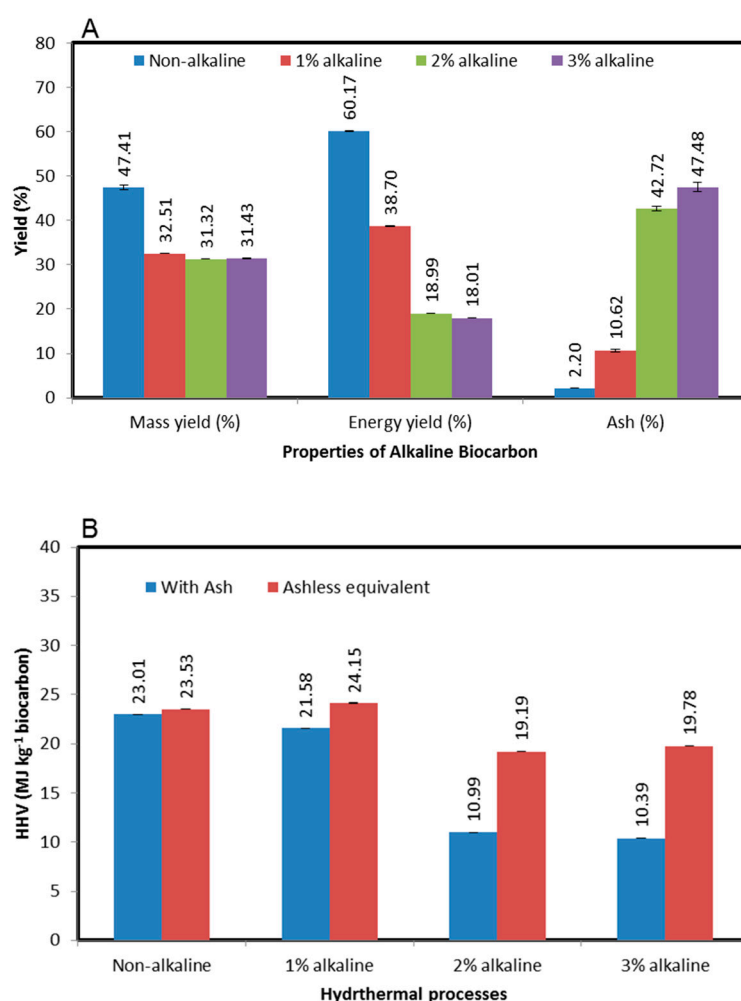
**Figure 4.** Biomethane yield in batch BMP experiment of AHTPW of alkaline hydrothermal pretreated corn residue. (A) cumulative yields in TS basis; (B) cumulative yields in VS basis; (C) 30 days' total production of 1% alkali pretreated CR represented in various forms.



**Figure 5.** Cumulative biomethane yields of mechanical treated and 1% alkaline hydrothermal treated CR.

### 3.4. Biocarbon from Alkaline Hydrothermal Treated Corn Residue

The effect of the alkali composition in the alkaline hydrothermal process condition of 240 °C for 30 min on mass yield, energy yield and ash content is shown in Figure 6A and their HHVs are shown in Figure 6B, respectively. Mass yield and energy yield were determined based on methods used by Kambo and Dutta [73]. Mass yield and energy yield of biocarbon samples were reduced with increase in alkali content for this hydrothermal process whereas their ash content were increased by the increase of alkali content (Figure 6A). Non-alkaline, 1% alkaline, 2% alkaline and 3% alkaline hydrothermal process of 240 °C for 30 min produced biocarbon contained 47.41%, 32.51%, 31.32% and 31.43% mass yield, respectively. They contained energy yields of 60.17%, 38.70%, 18.99% and 18.01%, respectively. These biocarbons contained ash of 2.20%, 10.62%, 42.72% and 47.48%, respectively. These biocarbons had HHVs of 23.01 MJ kg<sup>-1</sup>, 21.58 MJ kg<sup>-1</sup>, 10.99 MJ kg<sup>-1</sup>, and 10.39 MJ kg<sup>-1</sup>, respectively with ash. If their ash were removed (acid washing), they would have HHVs of 23.53 MJ kg<sup>-1</sup>, 24.14 MJ kg<sup>-1</sup>, 19.19 MJ kg<sup>-1</sup>, and 19.78 MJ kg<sup>-1</sup> TS, respectively.



**Figure 6.** Properties of different alkaline hydrothermal pretreated corn residue biocarbons. (A) mass yield, energy yield and ash content; (B) higher heating value (HHV).

In a recent study, hydrothermal liquefaction of macro-algae at 350 °C for 15 min produced 9.8–17.8 wt % biocrude, 10.9–18.6 wt % biochar and some aqueous organics [57] with potential energy values. Compared to this result, the 1% alkaline hydrothermal process of 240 °C for 30 min produced 51.16 wt % organics suitable for AD and 29.06 wt % organics as bio-coal on an ash-free basis. Coconut



husks can produce hydrochar of 77.1 wt % at 140 °C, which is reduced to 67.8 wt % at 200 °C in hydrothermal carbonization for 1–4 h time [74], whereas miscanthus can produce biochar of 72.5 wt % at 190 °C and 44.9 wt % at 260 °C in hydrothermal carbonization for 30 min time [73]. In both cases, organics in the liquid were not used for bioenergy production. Biomass with high moisture can be converted into relatively pure bio-oil in hydrothermal liquefaction with high yields compared to pyrolysis processes [75]. For liquefaction of high lipid and high moisture biomasses such as algae, the hydrothermal process is considered as a promising technology [76]. The bio-carbon produced in alkaline hydrothermal process is useable as a substitute for coal. The ultimate analysis (CHNSO content) and HHV of bio-carbon produced in non-alkaline and 1% alkaline hydrothermal process in ash free condition are shown in Table 3.

**Table 3.** CHNSO content and HHV of non-alkaline and 1% alkaline hydrothermal process produced bio-carbon in ash free condition.

Bio-Carbon Name	C (% of TS)	H (% of TS)	N (% of TS)	S (% of TS)	O (% of TS)	HHV Dry Ash Free (MJ kg <sup>-1</sup> )
Non-alkaline	56.83 ± 0.31	5.87 ± 0.08	1.35 ± 0.01	0.18 ± 0.01	35.77 ± 0.32	23.53 ± 0.12
1% alkaline	57.76 ± 0.28	5.88 ± 0.01	1.21 ± 0.01	0.14 ± 0.00	35.01 ± 0.25	24.14 ± 0.15

### 3.5. Hybrid Bioenergy Production

In the alkaline hydrothermal process, two separate product streams such as the water insoluble organics and water soluble organics are produced. The produced biocarbon and water-soluble organics are alkaline, which is the ash content in the case of biocarbon. Therefore the amount of alkali addition in the alkaline hydrothermal process is the limiting factor for HHV of biocarbon and biomethane produced from AHTPW. Biocarbon is considered to be used as a substitute of coal where minimum ash content is desired. On the other hand, mechanically-treated CR produced only biomethane. HHV of methane is 55.53 MJ kg<sup>-1</sup> methane with density of 0.717 kg m<sup>-3</sup> [77] at 0 °C temperature and atmospheric pressure which is equivalent to 35.178 MJ m<sup>-3</sup> at 36 °C temperature and atmospheric pressure. The produced biomethane of these hydrothermal processes were converted into their higher heating value (methane volume in m<sup>3</sup> kg<sup>-1</sup> TS × HHV of methane in MJ m<sup>-3</sup>). Biocarbon and biomethane produced at 240 °C for 30 min residence time provided useable energy. In context of useable energy yield with reference to raw dry CR, mechanically treated and alkali-treated hybrid bioenergy production was considered. In the AD, 2% alkali and 3% alkali added hydrothermal process water did not produce considerable amount of biomethane, which is discussed in Section 3.3.2. The useable bioenergy produced using 5 mm chopped CR and <500 µm ground CR were 8.21 ± 0.049 MJ kg<sup>-1</sup> CR and 9.23 ± 0.21 MJ kg<sup>-1</sup> CR, respectively. On the other hand, hybrid bioenergy production from 1% alkaline, 2% alkaline and 3% alkaline CR were 11.39 MJ kg<sup>-1</sup> CR, 3.44 MJ kg<sup>-1</sup> CR and 3.27 MJ kg<sup>-1</sup> CR, respectively. For 2% alkaline and 3% alkaline CR, only biocarbon was produced with 42.72% and 47.48% ash, respectively (Figure 6A). Although 1% alkaline CR produced biocarbon of 10.62% ash with HHV of 21.58 MJ kg<sup>-1</sup>, it can be upgraded to ash-free biocarbon of HHV of 24.15 MJ kg<sup>-1</sup> (Figure 6B) after acidic washing or other ash removing technology, it will be ready to use as a substitute of coal. Therefore, based on this research, the most favourable alkaline hydrothermal process condition of corn residue for hybrid useable bioenergy production is the 1% alkaline treatment at 240 °C for 30 min residence time. Previous researchers found biomethane production from raw CR in AD process was 144 L kg<sup>-1</sup> VS [41] to 187 L kg<sup>-1</sup> VS [42], which is equivalent to 122 L kg<sup>-1</sup> TS to 151 L kg<sup>-1</sup> TS (energy value of 4.29 MJ kg<sup>-1</sup> raw CR to 5.31 MJ kg<sup>-1</sup> raw CR) based on this research. The overall discussion pointed that it would have possibility to produce less energy from ground CR in AD because of grinding losses. On the other hand grinding operations consume extra energy for drying. Therefore after considering technical and energy consumption aspects, mechanically-treated chopped CR might be favorable to the farmers for bioenergy production. In this research the HT process consuming energy is not considered, but considering the high specific heat capacity value of water,

increasing the amount of water in the hydrothermal reactor increases the HT process consumption of energy [57], which can be minimized by using a maximum composition of biomass in the process. Therefore, optimization of CR and water ratio for minimum HT process energy consumption value is important for a HT process. In the case of two similar studies, of 7.7% (dry) corn husk with 92.3% water and 14.3% miscanthus with 85.7% water were used in hydrothermal process to produce good quality biochar [7,73].

This hybrid energy production from hydrothermally processed biomass (both solid and liquid) has not been carried out by any other researchers until this research. Therefore this hybrid bioenergy production from hydrothermally processed corn residue represents an innovation in the bioenergy production area.

### 3.6. Energy Recovery

Based on the data of this research the ERR equaled 45.28% and 50.91% of raw CR, respectively, for mechanically treated 5 mm chopped and  $<500\ \mu\text{m}$  ground CR in the AD process. Previous researchers found that the untreated CR energy recovery (ERR) in the AD process equaled 23.66% to 29.29% of raw CR based on the HHV of raw CR of  $18.13\ \text{MJ kg}^{-1}$  [41,42]. Use of impurity-free fall harvested CR may be one reason for the higher ERR value of the mechanically-treated CR of this research. Another prominent reason might be use of smaller sized CR for mechanical treatment in this research. On the other hand, 1% alkaline hydrothermal treated ( $240\ ^\circ\text{C}$  for 30 min) CR recovered hybrid energy (ERR) of 62.82% of raw CR where  $\text{ERR}_{\text{bio-carbon}}$  and  $\text{ERR}_{\text{bio-methane}}$  were 38.76% and 24.06%, respectively. It can also be noticed that for only biocarbon production, 2% alkaline and 3% alkaline HT treated CR recovered 18.97% and 18.04% energy of raw CR with 42.72% ash and 47.48% ash, respectively. Due to their very high ash contents, these two biocarbons are not useable. ERR of ground CR in the AD process is 11.91% less compared to the ERR of the 1% alkaline-HT treated CR. Therefore 1% alkaline HT-treated CR can recover the highest amount of hybrid bioenergy of 62.82% of raw CR with two useable bioenergy sources (biocarbon and biomethane). Although the alkaline hydrothermal process for biocarbon and biomethane production was not carried out until this research, some studies on alkaline hydrothermal liquefaction were carried out. The energy recovery from alkaline liquefaction of brown macro-algae can be over 80% higher compared to its non-alkaline liquefaction [57]. The presence of lipid content in brown macro-algae may be the main reason. The alkaline liquefaction of the swine carcass recovered energy of 93.63% due to the presence of high fat [56]. Most of the lipids of brown macro-algae and fat content of swine carcass were converted into bio-oil. On the other hand, CR is mostly composed of hemicellulose, cellulose and lignin. Their HHVs are also lower than those of lipid and fat. In case of AD of AHPW, some carbon stays in unconverted form in the AD digestate, which is ultimately available as SOC source when the digestate is used as liquid fertilizer in the corn farm.

### 3.7. Nutrient Recovery

The digestate of AHTPW AD is available for use as liquid fertilizer. The nutrient contents of HTPW (non-alkaline) and AHTPW (alkaline, which would stay in AD digestate with their unchanged value [78,79], were determined according to Section 2.5 in the Environmental Engineering laboratory. The nutrient contents of AD digestate were then evaluated for TS of 1% alkaline AHTPW (Table 4). It can be calculated from Tables 2 and 4 (for TS) that, 20.16% nitrogen, 12.23% phosphorus, 18.41% potassium and 12.38% sulphur are recoverable if the AHTPW AD digestate is applied on the harvested corn field. For biogas enhancement, biomass treated by NaOH and KOH have similar effects but due to its higher price the use of KOH is discouraged [30]. Considering the difficulty of Na recycling [80], KOH may be a substitute of NaOH for its environmental benefit but for its higher cost, it may not be considered although waste streams containing KOH are considered as a fertilizer [30]. On the other hand, if biocarbon is upgraded by  $\text{H}_2\text{SO}_4$  washing, its waste water will be S rich and this liquid also will be a source of nutrients. AD digestate would be S enriched if it can be mixed with wastewater of biocarbon ash removal with  $\text{H}_2\text{SO}_4$ . This will reduce the use of chemical fertilizer on

corn farms. If all processes were available in the farm area, then biocarbon upgrading waste water and AD digestate as liquid fertilizer can be mixed to apply it on the corn farm. Thus S-containing chemical fertilizer application in the farm will be reduced which will indirectly save fertilizer cost for farmers.

**Table 4.** Nutrient contents available for biofertilizer.

Name of Nutrient	Digestate Type		
	Raw Corn Residue (g kg <sup>-1</sup> TS)	HTPW (g kg <sup>-1</sup> TS)	AHTPW (g kg <sup>-1</sup> TS)
Nitrogen (N)	16.62 ± 0.08	17.75	4.72 ± 0.09
Phosphorus (P)	1.51 ± 0.14	0.39	0.26 ± 0.14
Potassium (K)	26.00	16.22	6.74
Sulfur (S)	45.49 ± 1.85	19.07	9.46 ± 1.85

### 3.8. Further Study

Further study at bench scale for bioenergy and nutrient recovery is suggested in the laboratory. After successfully completion of this study, further pilot scale study is suggested at a corn farm area for corn residue hybrid bioenergy conversion and nutrient recovery to use back in the corn farm as a resource recovery concept. The pilot scale further study is shown in the Figure S1 of supplementary material.

## 4. Conclusions

In this research two mechanically pretreated fall harvested CRs, namely 5 mm chopped and <500 µm ground and three alkaline-treated, namely 1% NaOH, 2% NaOH and 3% NaOH HT pretreated CR were examined for maximum bioenergy production and nutrient recovery. The 1% NaOH added alkaline hydrothermal treated CR at 240 °C for 30 min HT process could produce biomethane at 278.70 ± 9.84 L kg<sup>-1</sup> VS and biocarbon of 21.58 MJ kg<sup>-1</sup> ATS with ash of 10.62% db. Mechanically treated 5 mm chopped and <500 µm ground CR produced biomethane at 275.38 ± 16.35 L kg<sup>-1</sup> VS and 309.59 ± 6.97 L kg<sup>-1</sup> VS. Alkaline HT pretreatment with 2% and 3% alkali did not produce considerable amounts of biomethane from AHTPW containing excess alkali due to its inhibition of AD and their solid biocarbons also had low HHVs (10.99 MJ kg<sup>-1</sup> ATS and 10.39 MJ kg<sup>-1</sup> ATS) with ash content of 42.72% and 47.48%, respectively. The 1% alkaline hydrothermally treated CR recovered the highest amount of hybrid bioenergy of 62.82% of raw CR with two useable bioenergy sources (biomethane and biocarbon). The nutrient-rich AHTPW AD digestate was available as liquid fertilizer to apply into the corn farm. Further suggested study for corn residue hybrid bioenergy conversion and nutrient recovery to use back in the corn farm as a resource recovery concept is suggested.

However, for hybrid bioenergy (biomethane and biocarbon) production from 1% alkaline HT process of CR at 240 °C for 30 min residence time with higher energy production of 11.39 MJ kg<sup>-1</sup> CR was observed compared to mechanically pretreated CR. Although energy production in the hybrid system was better than only biocarbon or biomethane production in recent studies, there is a possibility to further increase biomethane production from AHTPW after reducing their high C/N ratio (37–46) to a normal range (20–25). Co-digestion with high nitrogen-containing biomass such as municipal food waste can be an option. In this case the hybrid bioenergy yield will be increased if these two undervalued biomasses are used in bioenergy production. AD digestate would be S enriched if it can be mixed with the wastewater from the biocarbon ash removal by H<sub>2</sub>SO<sub>4</sub>. This will reduce the use of chemical fertilizer on corn farms. This concept will reduce GHG emissions. However, for commercial application, proper safety precaution training is required for operators of liquid alkaline hydrothermal processes at the farm level.

**Supplementary Materials:** The following are available online at [www.mdpi.com/1996-1073/11/3/516/S1](http://www.mdpi.com/1996-1073/11/3/516/S1), Figure S1: Further study for hybrid bioenergy conversion from corn residue in the resource recovery concept.

**Acknowledgments:** This research was a part of a PhD research of the School of Engineering, the University of Guelph, Canada. We are grateful to OMAFRA (the Ontario Ministry of Agriculture, Food and Rural Affairs) for arranging communication with various Ontario corn growers. We are grateful to the city of Toronto and CCI bioenergy for providing required AD inoculum. We are grateful to the CBA (Canadian Biogas Association) for arranging several visits to various Ontario AD plants to communicate with AD owners and operators. We are thanking Sheng Chang of Environmental Engineering program of the University of Guelph for arranging to use the Environmental Engineering laboratory facility.

**Author Contributions:** S.P. conceived, designed experiments and analyzed data. S.P. wrote the text. A.D. and F.D. verified data and edited the manuscript.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- Hu, F.; Ragauskas, A. Pretreatment and lignocellulosic chemistry. *BioEnergy Res.* **2012**, *5*, 1043–1066. [CrossRef]
- Graham, R.L.; Nelson, R.; Sheehan, J.; Perlack, R.D.; Wright, L.L. Current and potential US corn stover supplies. *Agron. J.* **2007**, *99*, 1–11. [CrossRef]
- Wilhelm, W.W.; Johnson, J.M.; Hatfield, J.L.; Voorhees, W.B.; Linden, D.R. Crop and soil productivity response to corn residue removal. *Agron. J.* **2004**, *96*, 1–17. [CrossRef]
- Statistics Canada. Corn: Canada's Third Most Valuable Crop. 2017. Available online: <http://www.statcan.gc.ca/pub/96-325-x/2014001/article/11913-eng.htm> (accessed on 6 February 2017).
- Khan, A.A. Potential to use biomass for bio-energy in Ontario. *Guelph Eng. J.* **2009**, *2*, 39–44.
- Hewson, D.; Aung, O.; Albion, K.J. *Assessment of Agricultural Residuals as a Biomass Fuel for Ontario Power Generation*; The University of Western Ontario: London, ON, Canada, 2010.
- Minaret, J.; Dutta, A. Comparison of liquid and vapor hydrothermal carbonization of corn husk for the use as a solid fuel. *Bioresour. Technol.* **2016**, *200*, 804–811. [CrossRef] [PubMed]
- Bacenetti, J.; Sala, C.; Fusi, A.; Fiala, M. Agricultural anaerobic digestion plants: What LCA studies pointed out and what can be done to make them more environmentally sustainable. *Appl. Energy* **2016**, *179*, 669–686. [CrossRef]
- Wilhelm, W.W.; Johnson, J.M.; Karlen, D.L.; Lightle, D.T. Corn stover to sustain soil organic carbon further constrains biomass supply. *Agron. J.* **2007**, *99*, 1665–1667. [CrossRef]
- Swan, J.B.; Higgs, R.L.; Baile, T.B.; Wollenhaupt, N.; Paulson, W.H.; Peterson, A.E. Surface residue and in-row treatment effects on long-term no-tillage continuous corn. *Agron. J.* **1994**, *86*, 711–718. [CrossRef]
- Laird, D.A.; Chang, C.W. Long-term impacts of residue harvesting on soil quality. *Soil Tillage Res.* **2013**, *134*, 33–40. [CrossRef]
- OFA. Ontario Federation of Agriculture, Consideration for Grading Agricultural Residue. 24 July 2013. Available online: <http://www.ofa.on.ca/uploads/userfiles/files/gradingagriculturalresidues-final.pdf> (accessed on 3 October 2016).
- Jin, V.L.; Baker, J.M.; Johnson, J.M.; Karlen, D.L.; Lehman, R.M.; Osborne, S.L.; Sauer, T.J.; Stott, D.E.; Varvel, G.E.; Venterea, R.T.; et al. Soil greenhouse gas emissions in response to corn stover removal and tillage management across the US corn belt. *BioEnergy Res.* **2014**, *7*, 517–527. [CrossRef]
- Sawatdeenarunat, C.; Surendra, K.C.; Takara, D.; Oechsner, H.; Khanal, S.K. Anaerobic digestion of lignocellulosic biomass: Challenges and opportunities. *Bioresour. Technol.* **2015**, *178*, 178–186. [CrossRef] [PubMed]
- Saha, B.C. Hemicellulose bioconversion. *J. Ind. Microbiol. Biotechnol.* **2003**, *30*, 279–291. [CrossRef] [PubMed]
- Pu, Y.; Zhang, D.; Singh, P.M.; Ragauskas, A.J. The new forestry biofuels sector. *Biofuels Bioprod. Biorefin.* **2008**, *2*, 58–73. [CrossRef]
- Hamawand, I. Anaerobic digestion process and bio-energy in meat industry: A review and a potential. *Renew. Sustain. Energy Rev.* **2015**, *44*, 37–51. [CrossRef]
- Zheng, M.; Li, X.; Li, L.; Yang, X.; He, Y. Enhancing anaerobic biogasification of corn stover through wet state NaOH pretreatment. *Bioresour. Technol.* **2009**, *100*, 5140–5145. [CrossRef] [PubMed]
- Mosier, N.; Wyman, C.; Dale, B.; Elander, R.; Lee, Y.Y.; Holtzapple, M.; Ladisch, M. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* **2005**, *96*, 673–686. [CrossRef] [PubMed]

20. Amani, T.; Nosrati, M.; Sreekrishnan, T.R. Anaerobic digestion from the viewpoint of microbiological, chemical, and operational aspects—A review. *Environ. Rev.* **2010**, *18*, 255–278. [[CrossRef](#)]
21. Liu, X.; Hilgsmann, S.; Gourdon, R.; Bayard, R. Anaerobic digestion of lignocellulosic biomasses pretreated with *Ceriporiopsis subvermisporea*. *J. Environ. Manag.* **2017**, *193*, 154–162. [[CrossRef](#)] [[PubMed](#)]
22. Panagiotou, G.; Olsson, L. Effect of compounds released during pretreatment of wheat straw on microbial growth and enzymatic hydrolysis rates. *Biotechnol. Bioeng.* **2007**, *96*, 250–258. [[CrossRef](#)] [[PubMed](#)]
23. Garrote, G.; Dominguez, H.; Parajo, J.C. Hydrothermal processing of lignocellulosic materials. *Eur. J. Wood Wood Prod.* **1999**, *57*, 191–202. [[CrossRef](#)]
24. Negro, M.J.; Manzanares, P.; Oliva, J.M.; Ballesteros, I.; Ballesteros, M. Changes in various physical/chemical parameters of *Pinus pinaster* wood after steam explosion pretreatment. *Biomass Bioenergy* **2003**, *25*, 301–308. [[CrossRef](#)]
25. Ramos, L.P. The chemistry involved in the steam treatment of lignocellulosic materials. *Quím. Nova* **2003**, *26*, 863–871. [[CrossRef](#)]
26. Hon, D.N.; Shiraishi, N. *Wood and Cellulosic Chemistry, Revised, and Expanded*; CRC Press: Boca Raton, FL, USA, 2000.
27. Digman, M.F.; Shinnars, K.J.; Casler, M.D.; Dien, B.S.; Hatfield, R.D.; Jung, H.J.; Muck, R.E.; Weimer, P.J. Optimizing on-farm pretreatment of perennial grasses for fuel ethanol production. *Environ. Sci. Technol.* **2010**, *101*, 5305–5314. [[CrossRef](#)] [[PubMed](#)]
28. Li, C.; Knierim, B.; Manisseri, C.; Arora, R.; Scheller, H.V.; Auer, M.; Vogel, K.P.; Simmons, B.A.; Singh, S. Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification. *Bioresour. Technol.* **2010**, *101*, 4900–4906. [[CrossRef](#)] [[PubMed](#)]
29. Brown, R.C.; Brown, T.R. *Biorenewable Resources: Engineering New Products from Agriculture*; John Wiley and Sons: Hoboken, NJ, USA, 2013.
30. Zheng, Y.; Zhao, J.; Xu, F.; Li, Y. Pretreatment of lignocellulosic biomass for enhanced biogas production. *Prog. Energy Combust.* **2014**, *42*, 35–53. [[CrossRef](#)]
31. Abdi, N.; Hamdache, F.; Belhocine, D.; Grib, H.; Lounici, H.; Piron, D.L.; Mameri, N. Enzymatic saccharification of solid residue of olive mill in a batch reactor. *Biochem. Eng. J.* **2000**, *6*, 177–183. [[CrossRef](#)]
32. Carrillo, F.; Lis, M.J.; Colom, X.; López-Mesas, M.; Valdeperas, J. Effect of alkali pretreatment on cellulase hydrolysis of wheat straw: Kinetic study. *Process Biochem.* **2005**, *40*, 3360–3364. [[CrossRef](#)]
33. Silverstein, R.A.; Chen, Y.; Sharma-Shivappa, R.R.; Boyette, M.D.; Osborne, J. A comparison of chemical pretreatment methods for improving saccharification of cotton stalks. *Bioresour. Technol.* **2007**, *98*, 3000–3011. [[CrossRef](#)] [[PubMed](#)]
34. Yao, Y.; Chen, S.; Kafle, G.K. Importance of “weak-base” poplar wastes to process performance and methane yield in solid-state anaerobic digestion. *J. Environ. Manag.* **2017**, *193*, 423–429. [[CrossRef](#)] [[PubMed](#)]
35. Kambo, H.S. Energy Densification of Lignocellulosic Biomass via Hydrothermal Carbonization and Torrefaction. Master’s Thesis, University of Guelph, Guelph, ON, Canada, 2014.
36. Chandra, R.; Takeuchi, H.; Hasegawa, T. Methane production from lignocellulosic agricultural crop wastes: A review in context to second generation of biofuel production. *Renew. Sustain. Energy Rev.* **2012**, *16*, 1462–1476. [[CrossRef](#)]
37. Wirth, B.; Mumme, J. Anaerobic digestion of waste water from hydrothermal carbonization of corn silage. *Appl. Bioenergy* **2014**, *1*, 1–10. [[CrossRef](#)]
38. Libra, J.A.; Ro, K.S.; Kammann, C.; Funke, A.; Berge, N.D.; Neubauer, Y.; Titirici, M.M.; Fühner, C.; Bens, O.; Kern, J.; et al. Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* **2011**, *2*, 71–106. [[CrossRef](#)]
39. Barakat, A.; Monlau, F.; Steyer, J.P.; Carrere, H. Effect of lignin-derived and furan compounds found in lignocellulosic hydrolysates on biomethane production. *Bioresour. Technol.* **2012**, *104*, 90–99. [[CrossRef](#)] [[PubMed](#)]
40. Hassan, M.; Ding, W.; Bi, J.; Mehryar, E.; Talha, Z.A.; Huang, H. Methane enhancement through oxidative cleavage and alkali solubilization pre-treatments for corn stover with anaerobic activated sludge. *Bioresour. Technol.* **2016**, *200*, 405–412. [[CrossRef](#)] [[PubMed](#)]
41. Li, J.; Zhang, R.; Siddhu, M.A.; He, Y.; Wang, W.; Li, Y.; Chen, C.; Liu, G. Enhancing methane production of corn stover through a novel way: Sequent pretreatment of potassium hydroxide and steam explosion. *Bioresour. Technol.* **2015**, *181*, 345–350. [[CrossRef](#)] [[PubMed](#)]



42. Tchobanoglous, G.; Stensel, H.D.; Tsuchihashi, R.; Burton, F. *Wastewater Engineering: Treatment and Resource Recovery*, 4th ed.; McGraw Hill Education: New York, NY, USA, 2014.
43. Thomsen, M.; Seghetta, M.; Mikkelsen, M.H.; Gyldenkerne, S.; Becker, T.; Caro, D.; Frederiksen, P. Comparative life cycle assessment of biowaste to resource management systems—A Danish case study. *J. Clean. Prod.* **2017**, *142*, 4050–4058. [CrossRef]
44. Ontario, 2016. Resource Recovery and Circular Economy Act, 2016. The Ontario Government, Canada. Available online: [http://www.downloads.ene.gov.on.ca/envision/env\\_reg/er/documents/2016/012-9356.pdf](http://www.downloads.ene.gov.on.ca/envision/env_reg/er/documents/2016/012-9356.pdf) (accessed on 2 May 2017).
45. WRAP. WRAP and the Circular Economy. Waste and Resources Action Programme, Oxon, UK. 2017. Available online: <http://www.wrap.org.uk/about-us/about/wrap-and-circular-economy> (accessed on 2 May 2017).
46. Geissdoerfer, M.; Savaget, P.; Bocken, N.M.; Hultink, E.J. The Circular Economy—A new sustainability paradigm? *J. Clean. Prod.* **2017**, *143*, 757–768. [CrossRef]
47. Lizotte, P.L.; Savoie, P. Spring harvest of corn stover for animal bedding with a self-loading wagon. *Appl. Eng. Agric.* **2013**, *29*, 25–31. [CrossRef]
48. Hoskinson, R.L.; Karlen, D.L.; Birrell, S.J.; Radtke, C.W.; Wilhelm, W.W. Engineering, nutrient removal, and feedstock conversion evaluations of four corn stover harvest scenarios. *Biomass Bioenergy* **2007**, *31*, 126–136. [CrossRef]
49. Sawyer, J.E.; Mallarino, A.P. Nutrient removal when harvesting corn stover. In *Integrated Crop Management News*; Iowa State University: Ames, IA, USA, 2008.
50. Kumagai, S.; Ota, M.; Nakano, S.; Hayashi, N.; Sakaki, T. Solubilization and saccharification of barley straw by hot-compressed water treatment. *Jpn. J. Food Eng.* **2008**, *9*, 115–119.
51. Kumagai, S.; Hirajima, T. Effective Utilization of Moso-Bamboo (*Phyllostachys heterocycla*) with Hot-Compressed Water. In *Application of Hydrothermal Reactions to Biomass Conversion*; Springer: Berlin/Heidelberg, Germany, 2014; pp. 155–170.
52. Reza, M.T.; Wirth, B.; Lüder, U.; Werner, M. Behavior of selected hydrolyzed and dehydrated products during hydrothermal carbonization of biomass. *Bioresour. Technol.* **2014**, *169*, 352–361. [CrossRef] [PubMed]
53. Teater, C.; Yue, Z.; MacLellan, J.; Liu, Y.; Liao, W. Assessing solid digestate from anaerobic digestion as feedstock for ethanol production. *Bioresour. Technol.* **2011**, *102*, 1856–1862. [CrossRef] [PubMed]
54. Chen, X.; Yan, W.; Sheng, K.; Sanati, M. Comparison of high-solids to liquid anaerobic co-digestion of food waste and green waste. *Bioresour. Technol.* **2014**, *154*, 215–221. [CrossRef] [PubMed]
55. Golkowska, K.; Greger, M. Thermophilic digestion of cellulose at high-organic loading rates. *Eng. Life Sci.* **2010**, *10*, 600–606. [CrossRef]
56. Zheng, J.L.; Zhu, M.Q.; Wu, H.T. Alkaline hydrothermal liquefaction of swine carcasses to bio-oil. *Waste Manag.* **2015**, *43*, 230–238. [CrossRef] [PubMed]
57. Anastasakis, K.; Ross, A.B. Hydrothermal liquefaction of four brown macro-algae commonly found on the UK coasts: An energetic analysis of the process and comparison with bio-chemical conversion methods. *Fuel* **2015**, *139*, 546–553. [CrossRef]
58. Cox, J.L.; Hallen, R.T.; Lilga, M.A. Thermochemical nitrate destruction. *Environ. Sci. Technol.* **1994**, *28*, 423–428. [CrossRef] [PubMed]
59. Marchand, L. Cost Assessment for Cornstalk Supply Chain for Bioprocessing Purposes. 2015. Prepared for: Ontario Federation of Agriculture (OFA). Available online: <https://www.google.ca> (accessed on 2 October 2016).
60. Hoekman, S.K.; Broch, A.; Robbins, C.; Zielinska, B.; Felix, L. Hydrothermal carbonization (HTC) of selected woody and herbaceous biomass feedstocks. *Biomass Convers. Biorefin.* **2013**, *3*, 113–126. [CrossRef]
61. Reza, M.T.; Uddin, M.H.; Lynam, J.G.; Hoekman, S.K.; Coronella, C.J. Hydrothermal carbonization of loblolly pine: Reaction chemistry and water balance. *Biomass Convers. Biorefin.* **2014**, *4*, 311–321. [CrossRef]
62. Weingarten, R.; Conner, W.C.; Huber, G.W. Production of levulinic acid from cellulose by hydrothermal decomposition combined with aqueous phase dehydration with a solid acid catalyst. *Energy Environ. Sci.* **2012**, *5*, 7559–7574. [CrossRef]
63. Becker, R.; Dorgerloh, U.; Paulke, E.; Mumme, J.; Nehls, I. Hydrothermal carbonization of biomass: Major organic components of the aqueous phase. *Chem. Eng. Technol.* **2014**, *37*, 511–518. [CrossRef]

64. Antal, M.J.; Leesomboon, T.; Mok, W.S.; Richards, G.N. Mechanism of formation of 2-furaldehyde from D-xylose. *Carbohydr. Res.* **1991**, *217*, 71–85. [[CrossRef](#)]
65. Xiao, L.P.; Shi, Z.J.; Xu, F.; Sun, R.C. Hydrothermal carbonization of lignocellulosic biomass. *Bioresour. Technol.* **2012**, *118*, 619–623. [[CrossRef](#)] [[PubMed](#)]
66. Jin, F.; Zhou, Z.; Moriya, T.; Kishida, H.; Higashijima, H.; Enomoto, H. Controlling hydrothermal reaction pathways to improve acetic acid production from carbohydrate biomass. *Environ. Sci. Technol.* **2005**, *39*, 1893–1902. [[CrossRef](#)] [[PubMed](#)]
67. Ishiguro, M.; Endo, T. Addition of alkali to the hydrothermal–mechanochemical treatment of Eucalyptus enhances its enzymatic saccharification. *Bioresour. Technol.* **2014**, *153*, 322–326. [[CrossRef](#)] [[PubMed](#)]
68. Ishiguro, M.; Endo, T. Effect of the addition of calcium hydroxide on the hydrothermal–mechanochemical treatment of Eucalyptus. *Bioresour. Technol.* **2015**, *177*, 298–301. [[CrossRef](#)] [[PubMed](#)]
69. De Souza, R.L.; Yu, H.; Rataboul, F.; Essayem, N. 5-Hydroxymethylfurfural (5-HMF) production from hexoses: Limits of heterogeneous catalysis in hydrothermal conditions and potential of concentrated aqueous organic acids as reactive solvent system. *Challenges* **2012**, *3*, 212–232. [[CrossRef](#)]
70. He, Y.; Pang, Y.; Liu, Y.; Li, X.; Wang, K. Physicochemical characterization of rice straw pretreated with sodium hydroxide in the solid state for enhancing biogas production. *Energy Fuels* **2008**, *22*, 2775–2781. [[CrossRef](#)]
71. He, Y.; Pang, Y.; Li, X.; Liu, Y.; Li, R.; Zheng, M. Investigation on the changes of main compositions and extractives of rice straw pretreated with sodium hydroxide for biogas production. *Energy Fuels* **2009**, *23*, 2220–2224. [[CrossRef](#)]
72. Cara, C.; Ruiz, E.; Ballesteros, I.; Negro, M.J.; Castro, E. Enhanced enzymatic hydrolysis of olive tree wood by steam explosion and alkaline peroxide delignification. *Process Biochem.* **2006**, *41*, 423–429. [[CrossRef](#)]
73. Kambo, H.S.; Dutta, A. Comparative evaluation of torrefaction and hydrothermal carbonization of lignocellulosic biomass for the production of solid biofuel. *Energy Convers. Manag.* **2015**, *105*, 746–755. [[CrossRef](#)]
74. Nakason, K.; Panyapinyopol, B.; Kanokkantarapong, V.; Viriya-empikul, N.; Kraithong, W.; Pavasant, P. Hydrothermal carbonization of unwanted biomass materials: Effect of process temperature and retention time on hydrochar and liquid fraction. *J. Energy Inst.* **2017**, *11*, 1–11. [[CrossRef](#)]
75. Akhtar, J.; Amin, N.A. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renew Sustain. Energy Rev.* **2011**, *15*, 1615–1624. [[CrossRef](#)]
76. Tian, C.; Li, B.; Liu, Z.; Zhang, Y.; Lu, H. Hydrothermal liquefaction for algal biorefinery: A critical review. *Renew Sustain. Energy Rev.* **2014**, *38*, 933–950. [[CrossRef](#)]
77. Engineering ToolBox, Fuels-Higher Calorific Values. Available online: [http://www.engineeringtoolbox.com/fuels-higher-calorific-values-d\\_169.html](http://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html) (accessed on 19 January 2017).
78. Zhang, R.; El-Mashad, H.M.; Hartman, K.; Wang, F.; Liu, G.; Choate, C.; Gamble, P. Characterization of food waste as feedstock for anaerobic digestion. *Bioresour. Technol.* **2007**, *98*, 929–935. [[CrossRef](#)] [[PubMed](#)]
79. Lusk, P. *Methane Recovery from Animal Manures the Current Opportunities Casebook*; National Renewable Energy Lab.: Golden, CO, USA, 1998.
80. Pang, Y.Z.; Liu, Y.P.; Li, X.J.; Wang, K.S.; Yuan, H.R. Improving biodegradability and biogas production of corn stover through sodium hydroxide solid state pretreatment. *Energy Fuels* **2008**, *22*, 2761–2766. [[CrossRef](#)]

