Improvement of Solid-State Biogas Production from Wood by Concentrated Phosphoric Acid Pretreatment

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Cellulose solvent- and organic solvent-based lignocellulose fractionation (COSLIF) has been repeatedly shown to be a cost-effective and promising process to modify the structure of different lignocelluloses. It has been repeatedly reported to improve enzymatic hydrolysis and ethanol production from different lignocelluloses. In this study, COSLIF was used to improve biomethane production from pine (softwood), poplar (soft hardwood), and berry (hard hardwood) *via* solid state anaerobic digestion (SSAD). Feed to inoculum (F/I) ratio, which plays a major role in SSAD, was set to 3, 4, and 5. After the pretreatment, 39, 33, and 24% higher methane yield from pine was achieved for F/I ratios of 3, 4, and 5, respectively. However, the methane yield from the hardwoods was not improved by the pretreatment, which was related to overloading of the digester. Compositional analysis showed considerable reduction in hemicellulose and lignin content by the pretreatment. Structural changes in the woods, before and after the pretreatment, were examined by X-ray diffractometer and scanning electron microscopy. The results showed that the crystallinity of cellulose was decreased and accessible surface area was drastically increased by the pretreatment.

Keywords: Biogas; Concentrated phosphoric acid pretreatment; Hardwood; Softwood; Solid-state anaerobic digestion

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INTRODUCTION

Anaerobic digestion (AD), one of the oldest biological processes, can contribute to the reduction of greenhouse gas emissions by substituting fossil energy sources (Mata-Alvarez *et al.* 2000; Wulf *et al.* 2006). In an AD process, a microbial consortium synergistically decomposes organic materials in the absence of oxygen to produce methane and carbon dioxide, which are the main components of biogas. Biogas production ranks as one of the most efficient ways to obtain biofuel (Tsavkelova and Netrusov 2012).

Biogas processes are classified to liquid (wet) and solid state (dry) processes depending on the solids content. The solids content in the solid state anaerobic digestion (SSAD) is typically greater than 15%, while it is lower than 15% for liquid anaerobic digestion (LAD). SSAD has been claimed to be advantageous over LAD for a number of reasons, including smaller specific reactor volume, fewer moving parts, lower energy input for heating, easier handling of the end-product, and lower parasitic energy loss (Guendouz *et al.* 2008; Cheng *et al.* 2010). However, unlike LAD, feed to inoculum ratio is a very important factor in SSAD, affecting the results of biogas production, and it should be optimized for an efficient biomethane production (Kabir *et al.* 2015a,b).

Among numerous organic materials, lignocelluloses have recently been considered as appropriate feedstocks for SSAD because of their abundant availability and low moisture content (Taherzadeh and Karimi 2008; Singhania *et al.* 2009). However, the recalcitrant structure of lignocelluloses is the most important obstacle in their utilization *via* AD (Shafiei *et al.* 2011; Bateni *et al.* 2014). Hence, a pretreatment process is needed aiming to reduce the recalcitrance of these materials, *i.e.*, by reducing cellulose crystallinity, increasing accessible surface area, and removing lignin and hemicelluloses (Alvira *et al.* 2010; Amiri and Karimi 2013; Karimi and Chisti 2015).

Chemical pretreatment methods, including alkali (Salehian and Karimi 2013), dilute acid (Hsu *et al.* 2010), and steam explosion (Shafiei *et al.* 2013) treatments, are among the techniques usually applied. However, the majority of these processes suffer from severe reaction conditions (high temperature and/or high pressure) and high energy consumption (Poornejad *et al.* 2014).

To overcome these drawbacks, a new lignocellulose pretreatment, known as cellulose solvent- and organic solvent-based lignocellulose fractionation (COSLIF), was recently developed by Zhang *et al.* (2007). In addition to reducing utility consumption and initial capital investment, this method results in lower sugar degradation and inhibitor formation, compared to the other pretreatments. COSLIF is performed at modest processing conditions of 60 °C and atmospheric pressure using a non-volatile cellulose solvent (concentrated phosphoric acid) and a volatile organic solvent (ethanol) (Sathitsuksanoh *et al.* 2011).

Concentrated phosphoric acid disrupts the linkages between cellulose, hemicellulose, and lignin through biomass dissolution and thereby greatly increases cellulose accessibility (Rollin *et al.* 2011). This method is widely used for improvement of ethanol production from lignocelluloses (Wirawan *et al.* 2012; Moradi *et al.* 2013); however, to our knowledge, no previous work has been carried out to investigate the effect of this promising pretreatment technology on biogas production from lignocelluloses.

In this study, the effects of COSLIF pretreatment on SSAD of three different woods were investigated. The biogas production from untreated and pretreated pine, poplar, and berry was studied by solid state anaerobic batch digestion assays. Moreover, structural analyses using X-ray diffractometer (XRD) and scanning electron microscopy (SEM), as well as analyses of structural carbohydrates and lignin, were performed to investigate the changes caused by the pretreatment.

EXPERIMENTAL

Materials

Three different kinds of woods, pine (*Pinus sibirica*) as a softwood, poplar (*Populus alba*) as a soft hardwood, and berry (*Morus alba*) as a hard hardwood, were used as representatives of different types of wood. They were obtained from the park waste transport platform of Isfahan municipality (Isfahan, Iran), debarked, ground, and screened to obtain powders with size of between 20 and 80 mesh (295 to 833 μm). The wood powders were then stored in sealed plastic bags at room temperature until use.

Pretreatment

COSLIF pretreatment was performed on each wood powder according to the method described by Rollin *et al.* (2011). One gram of wood powder was mixed with 8 mL of 85% phosphoric acid at 60 °C for 45 min in 50 mL plastic centrifuge tube. The dissolution of biomass was stopped by the addition of 20 mL ethanol (95% v/v) as an organic solvent. Solid/liquid separation was then conducted by centrifugation at 4,500 rpm for 15 min, and the supernatant was then discharged. Next, 40 mL of ethanol was added to the solid fraction and thoroughly mixed. The solids were then separated by centrifugation (4,500 rpm for 15 min). Afterwards, the solids were washed twice with 40 mL of distilled water. The last slurry of solids in distilled water was neutralized using 2 M sodium carbonate solution. Finally, the pretreated wood was separated by centrifugation (4,500 rpm for 15 min) and the supernatant was decanted. This pretreated solid fraction was then freeze-dried for 48 h and stored in airtight plastic bags at room temperature until use.

Inoculum Preparation

Effluent of a 7000 m^3 mesophilic anaerobic digester (Isfahan municipal sewage treatment, Isfahan, Iran) was used as an inoculum for biogas production. To increase the total solid (TS) and volatile solid (VS) content of the inoculum, it was centrifuged at 4,500 rpm for 30 min to obtain desirable TS and VS contents of 8 and 4.5%, respectively. After decanting the supernatant, the sludge was mixed to obtain a homogenous inoculum (Mirmohamadsadeghi *et al.* 2014). Finally, the inoculum was kept at 37 °C for one week to be stabilized and then used in all SSAD assays.

Solid-state Anaerobic Digestion

A predetermined amount of the untreated or pretreated woods was added to sealable 118 mL glass reactors to obtain different feed to inoculum ratios (F/I) of 3, 4, and 5 based on VS contents. Inoculum (5 g) and the necessary amount of distilled water were added to each reactor to achieve the initial TS content of 18 ± 0.2%. Finally, the reactors were sealed with butyl rubber and aluminum caps, and the headspaces were purged with pure nitrogen gas for about 2 min to provide anaerobic conditions. The reactors were then incubated in an oven at mesophilic conditions (37 ± 1 °C) for 45 days (Hansen *et al.* 2004). A blank reactor containing inoculum without any substrate was also assessed to determine the methane production from the inoculum. All SSAD setups were run in triplicates. Gas samples were taken and analyzed for the produced gas volumes and compositions in every 2 to 5 days during 45 days of biogas production.

Analytical Methods

TS and VS contents of the untreated and pretreated woods and inoculum were measured by drying at 105 °C (Sluiter *et al.* 2008a) followed by ignition of the dried residues at 575 °C (Sluiter *et al.* 2008b) to a constant weight.

The compositions of untreated and pretreated woods were analyzed according to the standard method presented by NREL (Sluiter *et al.* 2008c). The concentration of sugars was analyzed by high-performance liquid chromatography (HPLC) equipped with RI detector (Agilent 1100, Agilent Technologies, Palo Alto, CA) and an Aminex HPX-87P column (Bio-Rad, Richmond, CA, USA). The column temperature was set at 80 °C, and the mobile phase was deionized water at a flow rate of 0.6 mL/min. The acid soluble lignin was determined by UV spectroscopy (Rayleigh UV-1601, BRAIC, Beijing, China) at wavelength of 320 nm. All compositional analyses were performed in duplicates, and the average values are presented.

XRD patterns of the treated and untreated woods were obtained by X-ray diffractometer (Philips, X'pert, Netherlands). XRD analyses were carried out at 40 kV and 30 mA, and the spectra were collected in the range of 2θ = 5 to 80° with step size of 0.05°.

The microstructures of the untreated and treated woods were examined by scanning electron microscopy (SEM, Zeiss, Germany). Freeze-dried samples were coated with gold (BAL-TEC SCD 005) and analyzed at 7.5 kV.

The composition and volume of biogas produced were determined by a gas chromatograph (Sp-3420A, TCD detector, Beijing Beifen Ruili Analytical Instrument Co., China) equipped with a packed column (3 m length and 3 mm internal diameter, stainless steel, Porapak Q column, Chrompack, Germany). Nitrogen was used as a carrier gas at a flow rate of 45 mL/min. The column, injector, and detector temperatures were 40, 100, and 150 °C, respectively. A gas-tight syringe (0.25 mL, SGE analytical science, Australia) was used for gas sampling and injection. The excess gas was discharged after each gas sampling to avoid high pressure built-up in the reactors and a new gas analysis was performed to determine the gas composition in the headspace after the release. The method presented by Hansen *et al.* (2004) was used for calculating methane production volume, which is based on measuring the methane content by GC at the real reactor pressure and then converting to the standard conditions.

The alkalinity, pH, and volatile fatty acid (VFA) contents of the digested substrates were determined after suspending 4 g of the samples into 40 mL of distilled water and then centrifuging (at 4500 rpm, for 20 min). Total VFAs and alkalinity were measured by a two-step titration method (Lossie and Pütz 2008) using 0.1 N H_2SO_4 solution. The volume of H_2SO_4 consumed from start to reach pH 5.0 and then from pH 5.0 to 4.4 were used to calculate the alkalinity and total VFAs, respectively (Lossie and Pütz 2008).

RESULTS AND DISCUSSION

Effect of the Pretreatment on the Composition of Woods

The compositions of untreated and pretreated woods are presented in Table 1. The VS contents of the pretreated woods were lower than those of the untreated ones, which demonstrates that a part of volatile solids was removed by the pretreatments. Among the untreated woods, berry had the highest (60.1%) and poplar had the lowest (40.9%) content of glucan. No major change in the lignin content was observed as a result of COSLIF pretreatment, except for poplar. Hemicellulosic carbohydrates, *i.e.*, xylan, galactan, arabinan, and mannan, were the most diminishing part released by the pretreatment. Hence, the removal of hemicellulosic carbohydrates was the most important change caused by the pretreatment, accounting for up to 37, 62, and 71% removal for pine, poplar, and berry, respectively. Decrease in the hemicellulosic carbohydrates, due to concentrated phosphoric acid pretreatment, was also reported for sweet sorghum bagasse (Goshadrou *et al.* 2011), corn stover (Zhu *et al.* 2009), Napier grass (Takata *et al.* 2013), and rice straw (Moradi *et al.* 2013). In comparison to hardwoods, hemicellulose removal was lower for the softwood, most probably due to the softwoods higher recalcitrant structure (Taherzadeh and Karimi 2008). It has been frequently shown that the pretreatment of softwoods are more difficult than hardwoods (Overend *et al.* 1987; Janga *et al.* 2012). Furthermore, there was a remarkable increase in glucan content after the pretreatment. The glucan contents were increased by 10.6, 25.8, and 53.1% by the pretreatment for pine, berry, and poplar, respectively. Similar increases in glucan content, caused by concentrated phosphoric acid pretreatment were also reported for sweet sorghum bagasse (26.4%) (Goshadrou *et al.* 2011) and rice straw (25.2) (Moradi *et al.* 2013). The increase in glucan content can be explicated by material loss due to the dissolution of other carbohydrates during the pretreatment.

Table 1. Composition of Untreated and COSLIF Pretreated Woods as well as Overall Solid Recovery after the Pretreatment

Substrate	TS (%)	VS (%)	Total Lignin* (%)	Glucan (%)	Other poly-carbohydrates** (%)	Solid recovery (%)
Pine	96.0 ± 0.1	95.3 ± 0.2	28.7 ± 0.7	55.1 ± 0.0	18.6 ± 1.2	-
Pretreated pine	95.7 ± 0.1	89.4 ± 0.6	29.7 ± 0.1	61.0 ± 6.4	11.7 ± 0.9	72.4
Poplar	96.6 ± 0.3	94.4 ± 0.5	27.5 ± 0.9	40.9 ± 4.3	18.1 ± 1.7	-
Pretreated poplar	95.8 ± 0.1	81.8 ± 0.2	20.2 ± 1.7	62.7 ± 8.5	6.9 ± 0.3	57.7
Berry	95.4 ± 0.1	95.2 ± 0.1	18.2 ± 2.3	60.1 ± 0.0	13.2 ± 0.5	-
Pretreated berry	95.6 ± 0.1	89.0 ± 0.5	18.0 ± 0.3	75.6 ± 1.9	3.8 ± 0.4	64.5

* Sum of acid soluble lignin (ASL) and acid insoluble lignin (AIL) contents
** Sum of xylan, galactan, arabinan, and mannan contents

Solid-state Anaerobic Digestion

The effects of COSLIF pretreatment on biogas production from the woods by SSAD were evaluated by comparing the methane yields from pretreated *vs.* untreated materials. The accumulated methane productions obtained after 45 days of SSAD are shown in Fig. 1. According to the literature, F/I ratio is a highly important factor in anaerobic digestion (Cui *et al.* 2011; Brown and Li 2013), as a decrease in methane production by 35% was reported (Liu *et al.* 2009) for green wastes by increasing F/I ratio from 1.6 to 5. Thus, to evaluate the F/I ratio together with determining the effectiveness of the pretreatment, the experiments were performed at three different F/I ratios of 3, 4, and 5 in this study.

An improvement in the methane yield was achieved by the pretreatment only for pine, in which the pretreatment increased the methane production by 39, 33, and 24% for F/I ratio of 3, 4, and 5, respectively (Fig. 1). On the other hand, pretreatment of poplar and berry (hardwoods) was accompanied with no increase in the methane production. At F/I ratio of 3, the methane yield from pretreated poplar and berry showed a decrease of 28 and 45%, respectively, in comparison to those of the untreated woods (Fig. 1). Moreover, in the cases of poplar and berry, increasing F/I ratios resulted in decreasing methane yields obtained from both untreated and pretreated woods (Fig. 1).

The highest decrease in the methane production was obtained when berry was pretreated. This can be related to the availability of more digestible materials, leading to overloading, due to the lesser lignin content and more glucan content in berry (which resulted in less recalcitrant structure), in comparison to that of pine and poplar woods. Untreated berry showed therefore the highest methane potential in SSAD when the lowest F/I ratio was applied (Fig. 1). Considering the results obtained from the treated berry, the effects of F/I ratio on the methane yield were not as considerable as that from the untreated wood. The reason might be the presence of higher amounts of easily digestible materials (higher glucan content) after the pretreatment (Table 2), while the system was strongly overloaded already at the lowest F/I ratio (Fig. 1).

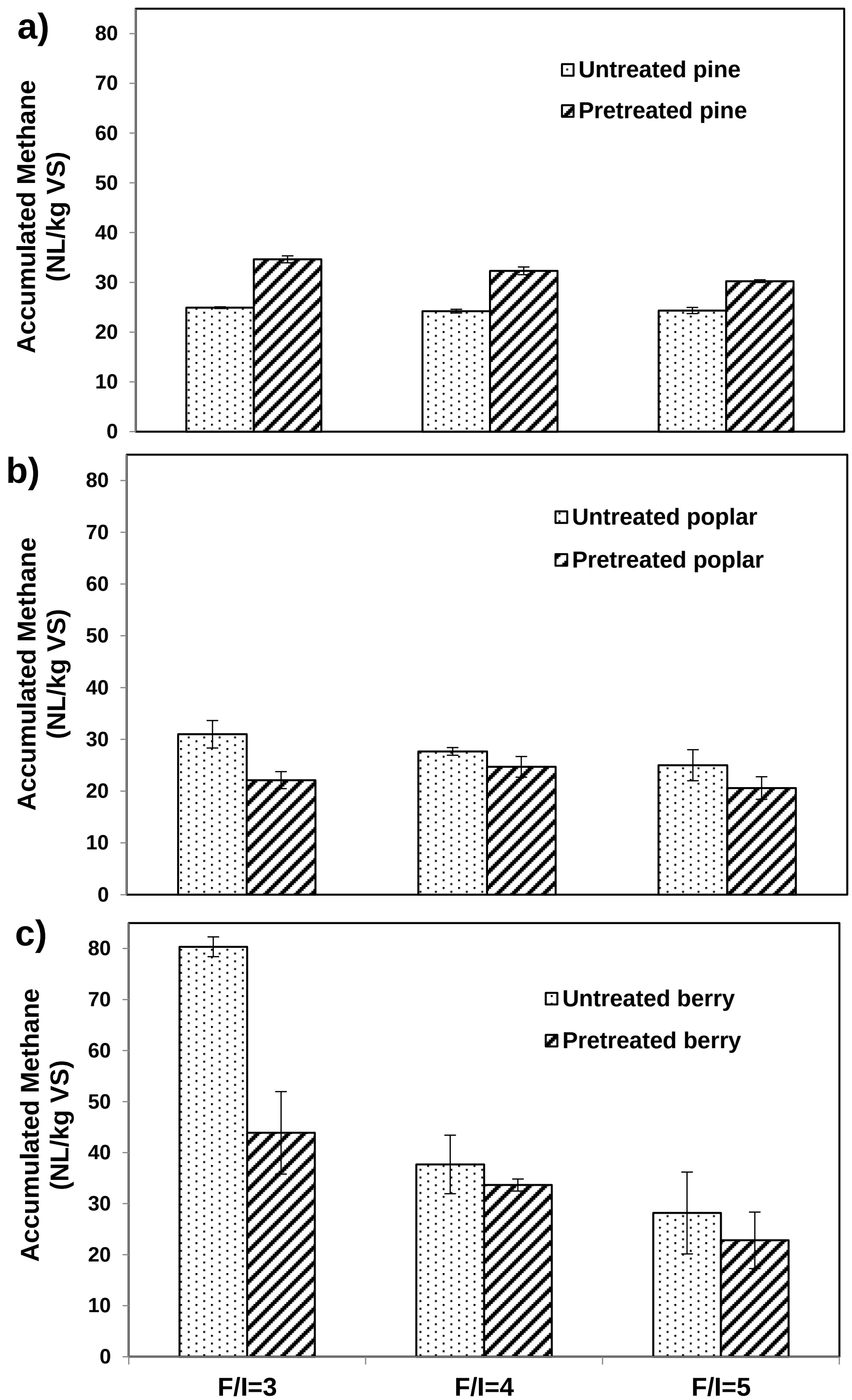

Fig. 1. Effects of F/I ratio on accumulated methane yield during 45 day SSAD of untreated and pretreated a) pine wood, b) poplar wood, and c) berry wood

Reactor Characteristics

Generally, overloading the anaerobic digestion system would lead to reactor failure and low methane yields. This is caused by the accumulation of VFAs, which in turn can cause imbalances within the microbial consortium responsible for the degradation of organic matters and methane production. A high concentration of VFAs will result in a dramatic drop in pH, especially when there is not enough buffering capacity. Low pH values can be expected to cause inhibitions in methanogenic activity and consequently disruption in the anaerobic digester performance. Therefore, the pH and the VFA/alkalinity ratio are determining factors for assessing the performance of degradation processes (Lossie and Pütz 2008).

Table 2. VFA/alkalinity Ratio and pH Obtained after 45 Days of SSAD using Untreated and Pretreated Woods

Sample		F/I Ratio	VFA/Alkalinity Ratio	Final pH
Blank		0	0.8	8.0
Pine	Untreated	3	0.6	8.5
		4	0.5	8.1
		5	0.7	7.2
	Pretreated	3	1.0	7.5
		4	0.5	7.8
		5	0.4	7.7
Poplar	Untreated	3	0.5	8.4
		4	0.1	8.5
		5	0.3	8.3
	Pretreated	3	1.0	6.5
		4	0.8	6.6
		5	0.9	6.6
Berry	Untreated	3	0.4	8.3
		4	0.6	8.3
		5	1.0	7.1
	Pretreated	3	0.3	7.8
		4	4.2	5.7
		5	3.5	5.7

The final pH and VFA/alkalinity ratios for SSAD of untreated and pretreated woods are presented in Table 2. Overall, the reactors digesting the pretreated woods had lower final pH values in all cases in comparison to that of digesting the untreated samples. However, the final pH values, measured after 45 days of SSAD, were higher than 7 in most of the reactors, indicating suitable digesting conditions. Nevertheless, the obtained pH values of 6.6 for the pretreated poplar, at all three F/I ratios, and particularly pH of 5.7 for the pretreated berry at F/I ratios of 4 and 5, indicated acidification of these reactors due to VFA accumulation. The final VFA/alkalinity ratios were in the range of 0.3 to 1.0, except for the pretreated berry at F/I ratios of 4 and 5, where the highest values of 4.2 and 3.5 were detected (Table 2). These highest VFA/alkalinity ratios together with the lowest pH of 5.7 indicated souring of the reactors (Brown *et al.* 2012). Souring is an evidence of heavily loaded reactors (Lossie and Pütz 2008), demonstrating the existence of higher amounts of digestible materials due to the pretreatment of hardwoods compared to that of pretreated softwood. Similarly, Zhu *et al.* (2010) reported failure in SSAD of corn stover pretreated with 7.5% sodium hydroxide, due to accumulation of VFA. The COSLIF process may therefore be efficient for SSAD of hardwoods only when lower F/I ratios are applied.

X-Ray Diffraction Analysis

XRD patterns of untreated and pretreated pine, poplar, and berry woods are shown in Fig. 2 a, b, and c, respectively.

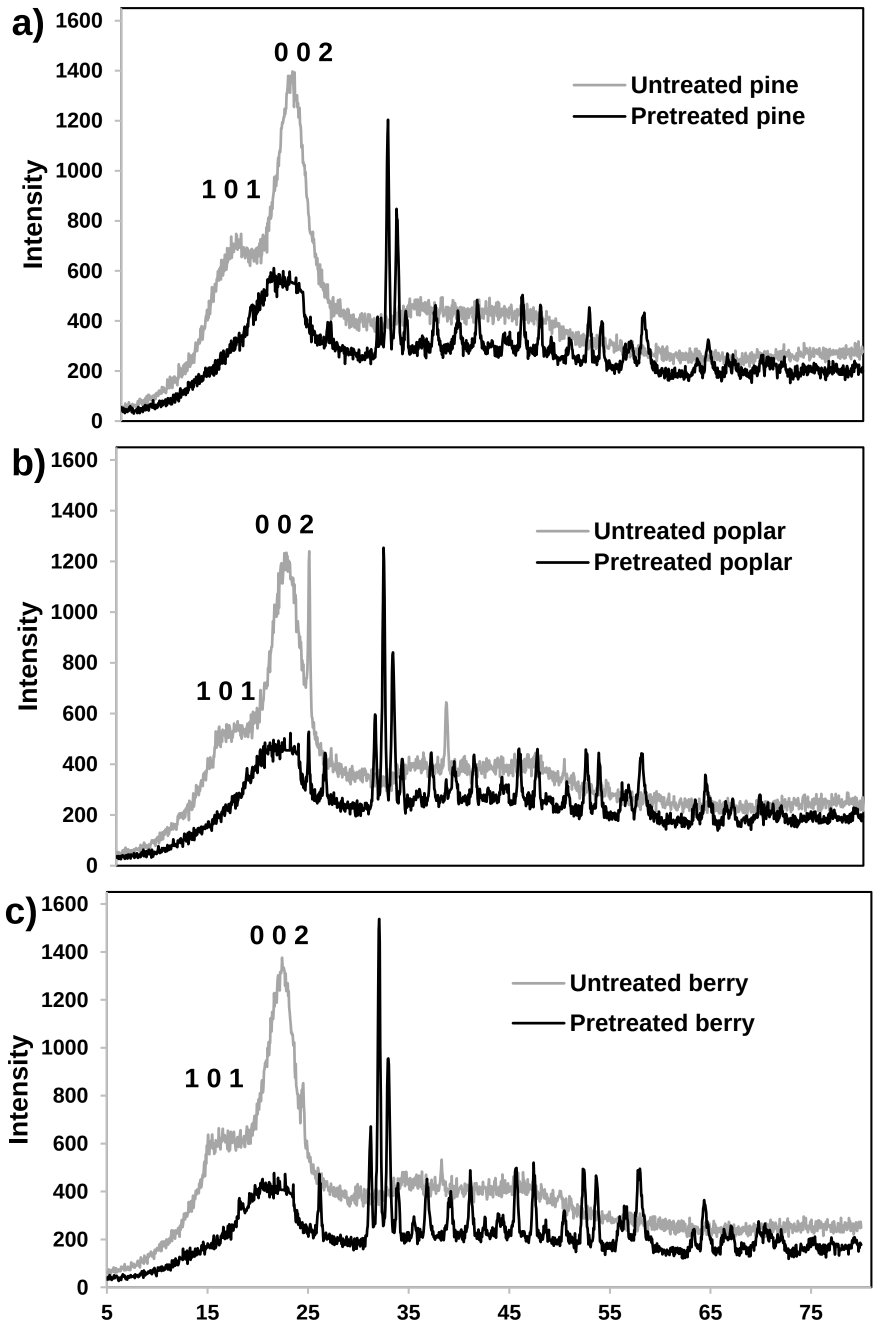

Fig. 2. XRD patterns of untreated and pretreated a) pine, b) poplar, and c) berry

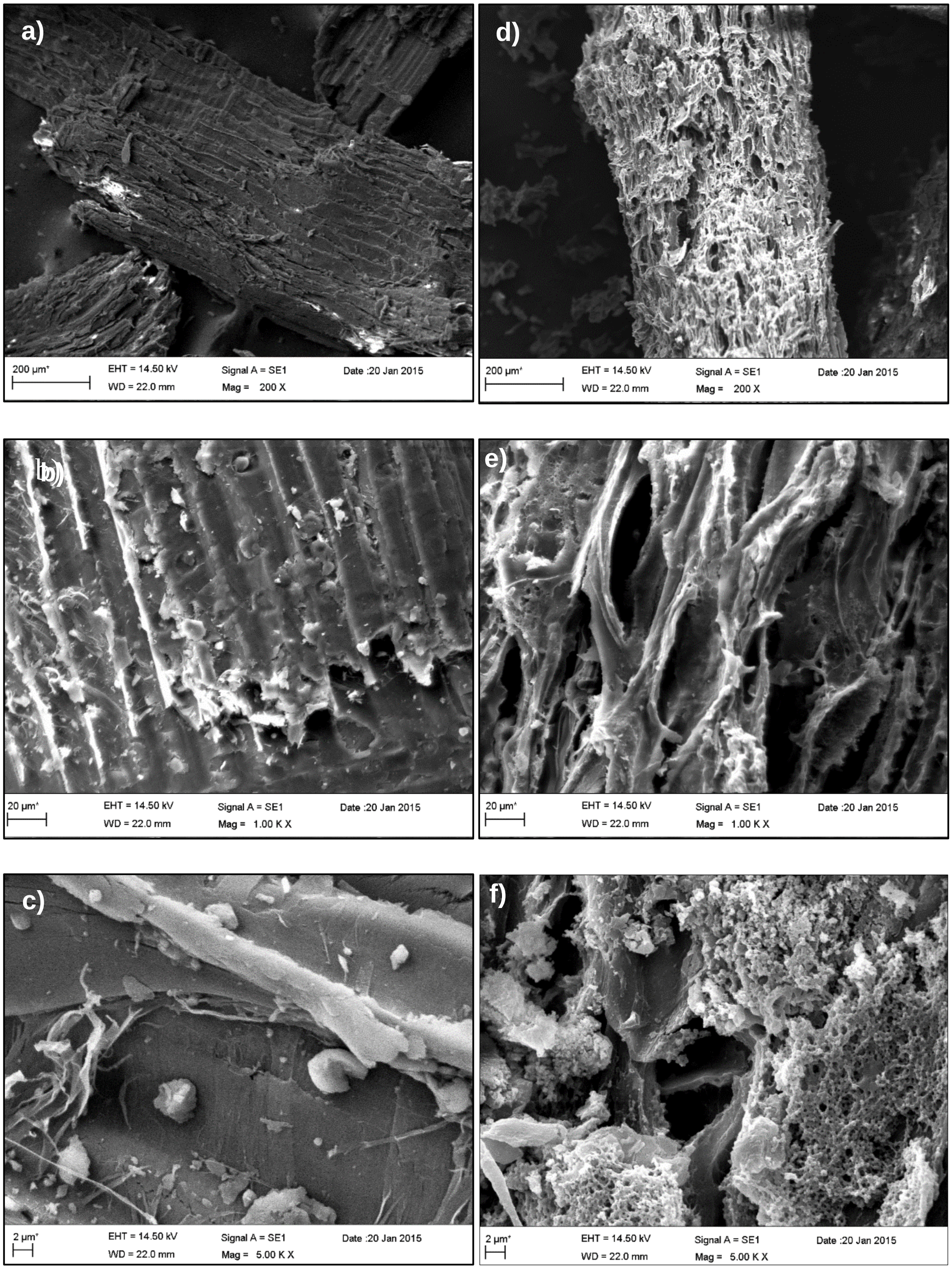

Fig. 3. SEM micrographs of untreated (a, b, and c) and COSLIF treated (d, e, and f) pine. The magnifications were 200× (a and b), 1000× (c and d), and 5000× (e and f).

Two main peaks were observed in diffraction patterns of untreated woods corresponding to (1 0 1) and (0 0 2) lattice planes, while the peak at (1 0 1) was effectively eliminated and broadened, and the peak at (0 0 2) was greatly reduced in the case of the COSLIF pretreated woods.

The peak at (0 0 2) corresponds to the distance between the hydrogen-bonded sheets in cellulose I (Cheng *et al.* 2011), which is the natural form of cellulose and has a high degree of crystallinity. This peak position varied with species and treatments, *i.e.*, 22.3, 21.9, and 22.4 for pine, poplar, and berry woods and 21.4, 20.8, and 21.6 for the corresponding pretreated ones. The transfer of the peak to lower 2θ after the treatments is evidence for structural broadening of cellulose I. The reduction of the peak at (0 0 2) of treated samples, compared to untreated ones, indicated a clear and drastic decrease in the crystalline fraction of the woods due to the COSLIF pretreatment. Similar results were previously reported for COSLIF-pretreated switchgrass (Sathitsuksanoh *et al.* 2011; Rollin *et al.* 2011).

Supramolecular Structure

In light of the improvements in biogas yields from pretreated pine, structural changes were qualitatively evaluated by SEM at different magnifications (Fig. 3). The untreated pine had a highly dense and impenetrable structure (Fig. 3a). Moreover, the fiber cells and vascular bundles in the untreated pine, observable at higher magnifications in Fig. 3b and 3c, showed a complex ordered structure. On the other hand, SEM images of the pretreated pine revealed the formation of a highly porous and accessible structure (Fig. 3d and 3e), probably due to the removal of hemicelluloses and lignin by the pretreatment. These dramatic changes in the supramolecular structures of pine caused by the pretreatment are clearly shown at the highest magnification in Fig. 3f. The original compact structure had completely disappeared after the COSLIF pretreatment. This might be the result of disruption of linkage between cellulose, hemicellulose, and lignin as well as breaking the orderly hydrogen bonds between the glucan chains caused by the pretreatment (Zhang *et al.* 2007).

The main degrading bacteria are *Clostridium*, *Ruminococcus*, and *Bacteroide*, whereas *Acetobacter* and *Eubakterium* are the main species involved in all four phases of biogas production, and *Methanococcus*, *Methanobacterium*, *Methanobrevibacter*, *Methanospirillum*, *Methanosarcina*, and *Methanothrix* are the methanogens. The sizes of theses microorganisms range from 0.2 to 20 μm despite different shapes occurring in bacteria. A high number of pores larger than the involved microorganisms' sizes could be observed in the pretreated wood.

CONCLUSIONS

1. Untreated berrywood showed higher biogas production potential in solid-state anaerobic digestion in comparison with untreated pinewood and poplarwood.
2. COSLIF process was shown to be an efficient pretreatment for the enhancement of biogas production of softwood pine during the subsequent solid-state anaerobic digestion. The improvement in the biomethane yield from pinewood was related to decrease in the cellulose crystallinity, hemicellulose and lignin removal, and increase in the accessible surface area.

3. The pretreatment was not able to improve the methane production from hardwood berry and poplar when feed to inoculum ratios of 3 to 5 were applied. The determined VFA/alkalinity ratios and pH values demonstrated souring in those reactors, which were fed with the pretreated hardwoods. This was an evidence for highly organic loading.

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