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Research Article

Enhancing the Phenolic Content of Bio-Oil by Acid Pre-Treatment of Biomass

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ABSTRACT. Pyrolysis of lignocellulosic biomass with acidic pre-treatment to produce valuable bio-chemicals has been carried out in an integrated pyrolysis-gas chromatograph/mass spectrometry system. Three different waste biomasses (fir wood sawdust, pine wood sawdust and nutshell) were subjected to acidic solution to specify the acid pre-treatment effect on biomass chemical structure, thermal degradation profile and pyrolysis products. Post acid pre-treatments, the changes in the biomasses and thermal degradation profile were studied through proximate, structure and ultimate analysis and thermogravimetric. The pre-treatment significantly reduced the inorganic, cellulose and hemicellulose content in biomass samples. According to the pyrolysis experiment results, acid pre-treatment provided the increasing of the amount of phenolic in the degradation products at 10 min pyrolysis time. All the results would assist further understanding of thermal decomposition and thermo-chemical application for bio-fuels and bio-chemicals of fir wood sawdust, pine wood sawdust and nutshell.

Keywords: Pyrolysis, lignocellulosic biomass, acid pre-treatment, renewable chemicals, *fir wood sawdust, pine wood sawdust, nutshell*

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1. Introduction

Pyrolysis is a promising thermochemical conversion process which can be used to produce valuable gaseous, liquid and solid products from biomass (Gvero *et al.* 2016). Biomass is a sustainable and renewable energy and bio-chemical source if evaluate in sustainable way. In 2006, 5% of the world's primary energy depletion provided from renewable energy source and it is estimated that this ratio will increase to 10% in 2030s (Gu *et al.* 2013). In addition to that, renewable energy production from biomass can provide substantial towards the aims of the Kyoto Agreement in extinguish to the complications of climate change (Bridgewater *et al.* 2004).

Agricultural biomass includes crop residues like as leaf, stalk, shell, stem and stone. Typically, lignocellulosic biomass consists of cellulose, hemicelluloses and lignin. It also contains some proportions of inorganic species. The amount of the ash originated from the inorganic quantity varies from less than 1% to 15% in biomass and agricultural residues (Đurić, *et al.* 2014; Yaman 2004). Some recent studies show that additives act as catalyst to produce higher yields of sugars (Zhuang *et al.* 2001; Lian *et al.* 2010; Lian *et al.* 2013; Layton *et al.* 2011; Chi *et al.* 2013). However, presence of inorganics in biomass can generally inhibit the production of levoglucosan and phenolic compounds (Mourant *et al.* 2011; Patwardhan *et al.* 2010; David *et al.* 2017). Inorganics content in biomass structure can be reduced via acidic pre-treatment of biomass. In literature, different types of biomasses (pinewood, straw, hay and bagasse) were exposed to acidic pre-treatment. This process provides the reducing inorganic content from 600 mg kg^{-1} to 90 mg kg^{-1}. In addition to that, significant increase of the organic oil yield is obtained compared to the untreated biomasses (Oudenhoven *et al.* 2016; Pecha *et al.* 2015; Oudenhoven *et al.* 2015).

Pyrolysis experiments based on determination of gaseous and liquid product can be done by using a simultaneous technique, pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS). Py-GC/MS has been successfully carried out to estimate the thermal decomposition behaviour and pyrolysis products of biomass. The technique is highly sensitive, rapid and it can separate and detect the complex mixture compounds (Gu *et al.* 2013). Qiang et al. (2009), examined the sawdust pyrolysis with Al/SBA-15 catalysts by using Py-GC/MS. Jeon et al. (2013), utilized SBA-15 for catalytic pyrolysis of cellulose, hemicelluloses and lignin with Py-GC/MS.

In literature, the studies about pyrolysis of untreated and acid pre-treated fir wood sawdust, pine wood sawdust and nutshell are uncommon. The objective of this study is to specify the acid pre-treatment effect on biomass chemical structure, and degradation behaviour of all

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samples during pyrolysis process. For this purpose, pyrolysis of untreated and acid pre-treated fir wood sawdust, pine wood sawdust and nutshell have been carried out by using pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS). The feature that distinguishes this study from other similar Py-GC/MS studies is that the pyrolysis reaction time is 10 min. Another aim of the present study is to increase the formation of phenolic content by extending the pyrolysis time.

2. Materials and Methods

The biomass and acid pre-treated method that were used in this study are described in this section. The experimental apparatus for the biomass preparation, determination of their properties and Py-GC/MS apparatus are also specified.

2.1 Materials

Fir wood sawdust (FS), pine wood sawdust (PS) and nutshell (NS) were chosen as biomass feedstock from Trabzon, located in North of Turkey. All biomass samples were air-dried at room temperature and then ground in a high speed rotary cutting mill (8000 rpm) and sieved. 425-600 µm sized samples were used for all experiments in the study. Prior to the characterization studies, acid pre-treatment experiments and Py-GC/MS experiments, biomasses were dried at 105 °C for 24 h and kept in a desiccator.

2.2 Acid pre-treatment of biomass

1 M sulphuric acid (H_2SO_4) solution was added to 1 g of each FS, PS and NS individually. Agitation of acid and biomass sample proceeded for 1 hour at the room temperature using a magnetic stirrer. After pre-treatment, the samples were washed with ultra-pure water until pH of the supernatant was equal to pH of ultra pure water. Before the Py-GC/MS experiments, the samples were filtrated, dried for 24 h at 105 °C and kept in a desiccators. Acid pre-treated FS, PS and NS were labelled A-FS, A-PS and A-NS, respectively.

2.3 Characterization of biomass and acid-treated biomass samples

True density and bulk density of FS, PS, NS, A-FS, A-PS and A-NS samples were determined by using gas pycnometer (Micromeritics-AccuPyc II 1340) and American Standard Test Method (ASTM E 873-82) Proximate and structural analyses of samples were applied to specify weight fractions of moisture, ash, volatile matter, fixed carbon, extractives, hemicelluloses, lignin and cellulose content. Ultimate analysis was performed on samples to determine the elemental composition. The weight fractions of carbon, hydrogen and nitrogen were obtained by using Elemental Analyser (Leco CHN628 Series). According to the ultimate analysis results, H/C, O/C, and higher heating value (HHV) were also determined.

The identity of functional groups involved in the binding of biomass were specified using Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer, Spectrum100) with built-in diamond-germanium ATR single reflection crystal. Baseline correction was applied before each measurement. FTIR spectrums of FS, PS, NS, A-FS, A-PS and A-NS samples were obtained using an average of 128 scans over the range between 380 cm^{-1} and 4000 cm^{-1} with a spectral resolution of 4 cm^{-1}.

Thermal decomposition behaviours of the samples were specified using Thermogravimetric Analysis (TGA, SETARAM, Labsysevo). Mass changes of FS, PS, NS, A-FS, A-PS and A-NS to the temperature were quantified and recorded. A sample mass of 10±3 mg in the Al_2O_3 100µL crucible was used for each run. Nitrogen was flowed 20 mL min^{-1} as carrier gas. The samples were heated from ambient temperature to 1000 °C at heating rate 10°Cmin^{-1}.

2.4 Py-GC/MS experiments

Pyrolysis experiments were performed by using Py-GC/MS System (Frontier Py-2020is pyrolyzer, Shimadzu QP2010 GC/MS) to separate and detect degradation products. Pyrolysis temperature was 550 °C and reaction time was 10 min. Frontier Ultra Alloy column (30 m×0.25 mm×0.25 µm film thickness) was used to chromatic separation of volatile products. Temperature of the column and injection part was 40 °C and 320 °C, respectively. Carrier gas was Helium which flowed 1.0 mL min^{-1}. NIST mass spectral library was used to identification of peaks from pyrolysis products.

3. Results and Discussion

In this section, results from the characterization of the biomass feedstocks and acid pre-treated biomass feedstocks, and detailed pyrolysis product characterization are presented and discussed.

3.1 Characterization of biomass and acid pre-treated biomass samples

The results of true and bulk densities of biomass samples were given in Table 1. True densities of FS, PS and NS were not significantly change but bulk densities of FS, PS and NS were drastically decreased by applying acid pre-treatment. This behaviour showed that, the porosity of the samples was increased by hydrolyzing the carbohydrates present in the material structure, especially the hemicelluloses (Li *et al.* 2004).

The results of proximate and structural analyses of biomass samples were given at Table 2. The moisture content of all untreated biomass samples were decreased by applying acid pre-treatment.

Higher volatile matter content is desirable for pyrolysis process. In addition, acid pre-treatment ensured in the removal of minerals, as indicated by the lower ash content of A-FS, A-PS and A-NS. Acid pre-treatment provided increasing of volatile matter content from 80.74% to 87.15%; 81.96% to 85.21% and 72.78% to 79.17% for FS, PS and NS, respectively. Acid pre-treatment was also decreased hemicellulose and cellulose content, while increased lignin content.

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Table 1
True and bulk densities of biomass samples

	FS	A-FS	PS	A-PS	NS	A-NS
True density [g/cm^3]	1.39	1.39	1.39	1.35	1.36	1.40
Bulk density [g/cm^3]	0.38	0.23	0.40	0.21	0.98	0.74

According to ultimate analysis (Table 3), carbon content of FS and PS increased, while oxygen content decreased after application of the acidic pre-treatment. Carbon content of NS did not change significantly, even oxygen content increased slightly. Higher heating value of FS and PS, calculated using Dulong's formula on ultimate analysis data, increased from 14.76 MJ/kg to 18.59 MJ/kg and 16.93 MJ/kg to 18.43 MJ/kg after acid pre-treatment. Higher heating value of NS decreased from 18.21 MJ/kg to 16.47 MJ/kg because of the higher oxygen content of A-NS.

Lignocellulosic biomass usually has several absorption bonds at 3300 cm^{-1}, 2923 cm^{-1}, 1466 cm^{-1}, 1370 cm^{-1} and 1329 cm^{-1} in FTIR spectrum. Located absorption bands are relevant with the lignocellulosic components such as cellulose, hemicelluloses and lignin (Sim *et al.* 2012). Cellulose includes glyosidic linkages, hydroxyl groups and carboxyl. Hemicelluloses and lignin are mainly formed ether bonds. In addition to this, hemicelluloses can be characterized by high amount of carboxyl groups (Taherzadeh and Karimi 2008).

Table 2
Proximate and structural analyses of biomass samples

Proximate Analysis (wt.%)	**FS**	**A-FS**	**PS**	**A-PS**	**NS**	**A-NS**
Moisture*	7.01	3.02	6.32	3.07	6.41	4.52
Ash **	0.21	0.07	0.72	0.08	1.46	0.03
Volatile matter**	80.74	87.15	81.96	85.21	72.78	79.17
Fixed carbon**	12.04	9.76	11.00	11.64	19.35	16.28
Extractive	12.51	18.89	11.30	19.37	14.56	11.44
Hemicellulose	24.90	13.21	23.42	14.17	23.82	18.21
Lignin	42.30	53.71	39.30	44.21	45.42	57.12
Cellulose	20.08	14.12	25.26	22.17	14.74	13.20

*as received.
**dry basis.
***Fixed carbon= 100-(Moisture+Ash+Volatile matter)
****Cellulose=100–(Extractives + Hemicellulose +Lignin+ Ash)

FTIR spectrums of FS, PS, NS, A-FS, A-PS and A-NS were given in Fig. 1, Fig. 2 and Fig. 3, respectively. The absorption bands at 1157 cm^{-1}, characteristic of glycosidic linkages, were relatively more abundant in untreated biomass samples. When compared the A-FS to the FS, the bands based on aromatic skeletal of lignin at 1510 cm^{-1} and syringyl and guaiacyl condensed lignin at 1327 cm^{-1} increased slightly where the lignin content of A-FS increased. When compared the PS to the A-PS, the peak intensity at 1035 cm^{-1} referring to the removal of crystalline cellulose were decreased sharply. The peak intensity at around 900 cm^{-1} referring to the removal of amorphous cellulose was decreased in acid pre-treated biomass sample (Li *et al.* 2010). The peak intensity at about 1700 cm^{-1}, corresponding to the carbonyl functional groups in hemicellulose, became less intense due to efficient removal of hemicelluloses (Chen *et al.* 2017).

Table 3
Ultimate analysis of FS, PS, NS and acid pre-treated samples

Ultimate Analysis [wt.%]	**FS**	**A-FS**	**PS**	**A-PS**	**NS**	**A-NS**
C	41.34	46.34	46.60	48.22	49.81	49.11
H	6.86	7.71	6.38	7.04	6.24	5.54
N	0.24	0.18	0.34	0.25	0.62	0.23
O*	50.55	45.67	44.58	44.50	42.33	45.12
H/C	1.99	1.99	1.64	1.75	1.50	1.35
O/C	0.91	0.74	0.72	0.69	0.64	0.69
HHV [Mj/kg]**	14.76	18.59	16.93	18.43	18.21	16.47

*By difference.
**Calculated by using the Dulong formula (Harker and Backhurst, 1981).

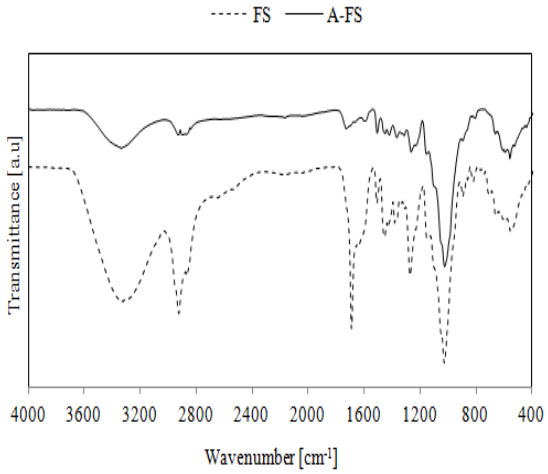

Fig. 1 FTIR spectrum of FS and A-FS

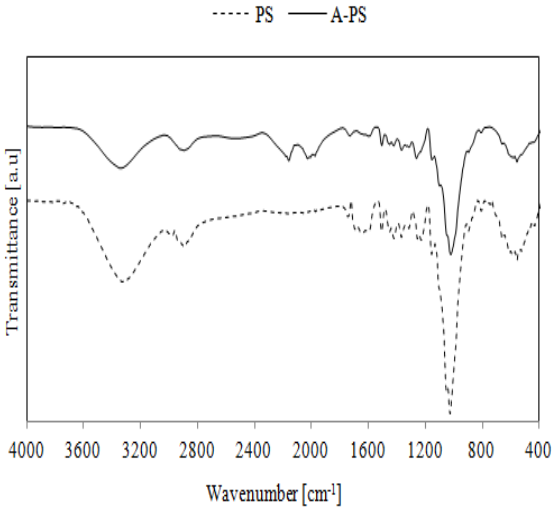

Fig. 2 FTIR Spectrum of PS and A-PS

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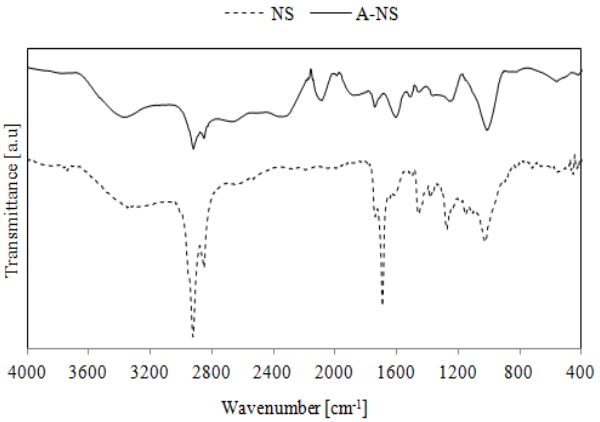

Fig. 3 FTIR Spectrum of NS and A-NS

3.2. Thermogravimetric analysis of biomass and acid pre-treated biomass samples

Devolatilization step has a significant role for pyrolysis process. Particularly, attention should be paid to the light hydrocarbons which are produced at the end of thermal degradation (Aboulkas *et al.* 2009). TGA studies have been carried out to determine thermal characteristics of materials such as thermal stability, degradation temperatures, etc. The results of TG and dTG curves of the FS, PS, NS, A-FS, A-PS and A-NS were given in Fig. 4, Fig. 5 and Fig. 6, respectively. According to the TG thermograms of biomass samples, the mass lose range can be divided into three steps due to variable-slope curves. The first step starts at about 50 °C and finishes at about 150 °C for all biomass samples. This could have been owing to the vaporization of the moisture in consequence of removal of physically adsorbed water of the sample.

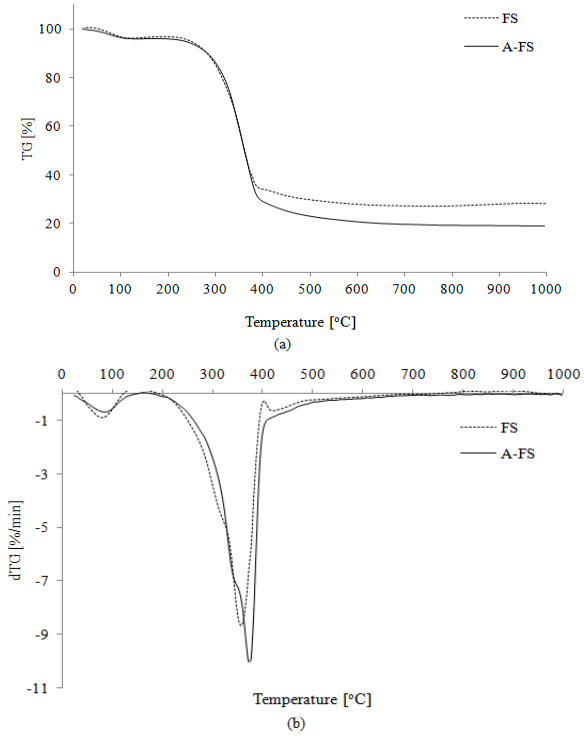

Fig. 4 TG and dTG curves of (a) FS and (b) A-FS

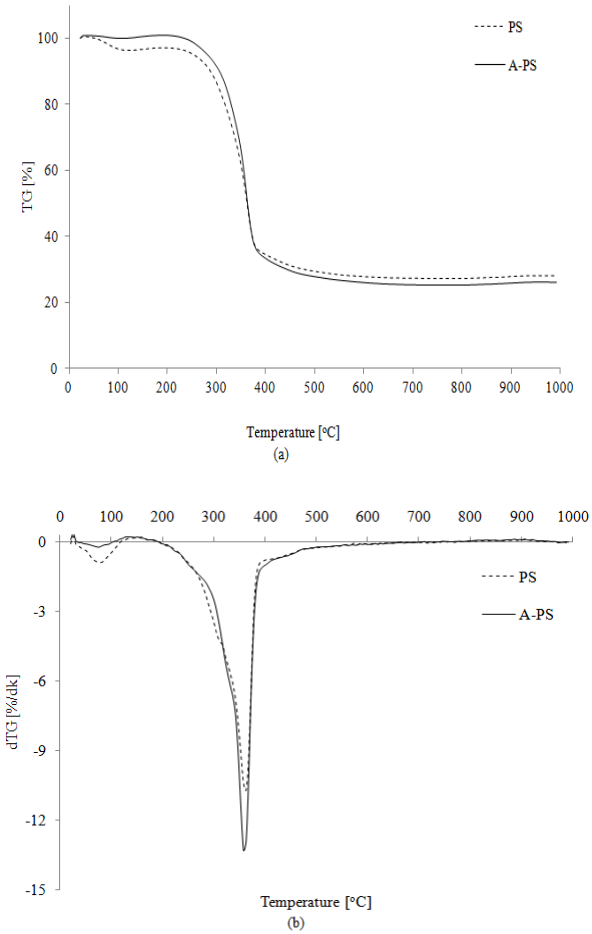

Fig 5. TG and dTG curves of (a) PS and (b) A-PS

Following the TG curve the main devolatilization step began at about 200 °C and finished at 420 °C. This step indicated decomposition of hemicellulose and cellulose referred as active pyrolysis zone, since mass loss rate is high.

After 420 °C, passive pyrolysis zone started and mass loss rate was lower. Then, no further essential weight loss was detected. These thermal behaviours were clarified by the components of FS, PS and NS. FS, PS and NS mainly consisted of hemicellulose, cellulose and lignin like all other lignocellulosic materials. The thermogravimetric behaviour of these components have been studied before and it is well known that hemicellulose, cellulose and lignin accomplish their decomposition within the temperature ranges of 210-325 °C, 310-400 °C, and 160-900 °C, respectively (Açıkalın 2011). Based on these temperature intervals, the minor and major reactions observed in active pyrolysis zone can be attributed to decomposition of hemicellulose and cellulose.

TG curves of A-PS and A-NS showed that the thermal stability of biomass was increased by applying acid pre-treatment. These results indicated that the catalytic effect of inorganics on reactivity for pyrolysis of raw material (Person *et al.* 2017; Raveendran *et al.* 1995; Asadieraghi *et al.* 2014; Williams and Horne, 1994).

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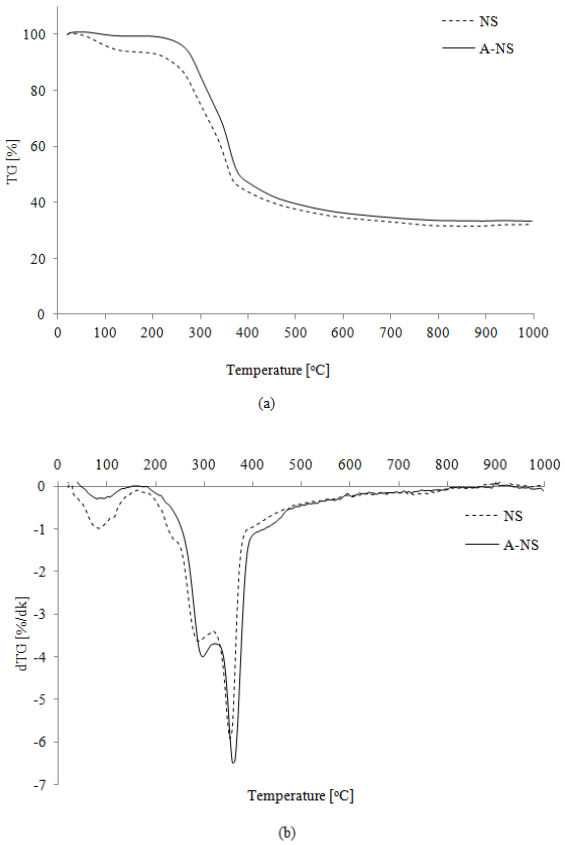

Fig. 6 TG and dTG curves of (a) NS and (b) A-NS

3.3. Py-GC/MS analysis of biomass and acid pre-treated biomass samples

In order to get some insights on the formation of pyrolysis products and further understand the effect of acid pre-treatment on the biomass pyrolysis process, experiments were performed by using Py-GC/MS equipment. The defined compounds were classified into 11 groups; aldehydes, alcohols, acids, phenols, aromatic hydrocarbons, aliphatic hydrocarbons, ketones, furans, polycyclic aromatic hydrocarbons (PAH) and oxygenates. Compounds that could not be identified by the GC-MS system were classified as unidentified. The results of products derived from pyrolysis of FS and A-FS were given in Fig. 7. It was shown that the Py–GC/MS results of FS presented the formation of a large amount of furans and oxygenates. When FS pre-treated with acid, phenolic compound content rose up to 25.10%, oxygenates were also decreased to 21.86%.

The amounts of aldehydes, alcohols, acids, phenols, aromatic hydrocarbons, aliphatic hydrocarbons, ketones, furans, PAH and oxygenates in the pyrolysis product of untreated and pre-treated PS and NS were given in Fig. 8 and Fig. 9, respectively. It can be said that, in general, the content of phenols, PAHs and oxygenates have higher values in acid pre-treated samples. A significant reduction in the amount of aromatic hydrocarbons and aliphatic hydrocarbons were observed when the PS and NS were pre-treated with acid. This result is clearly indicated that acid pre-treatment had affected the thermal degradation behaviour of the lignin.

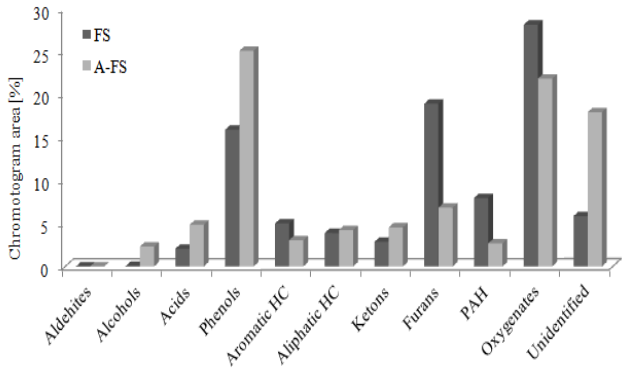

Fig. 7 Py–GC/MS detection of products evolved from pyrolysis of FS and A-FS

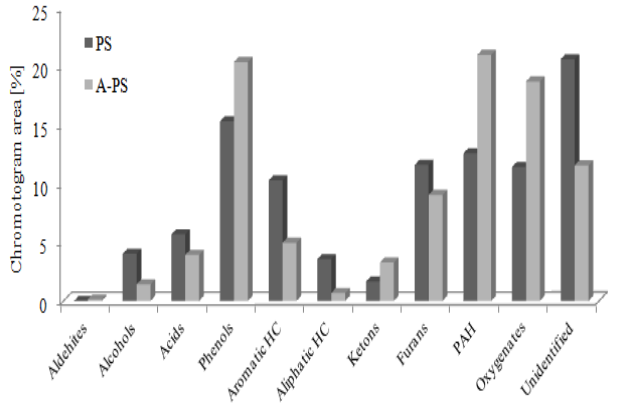

Fig. 8 Py–GC/MS detection of products evolved from pyrolysis of PS and A-PS

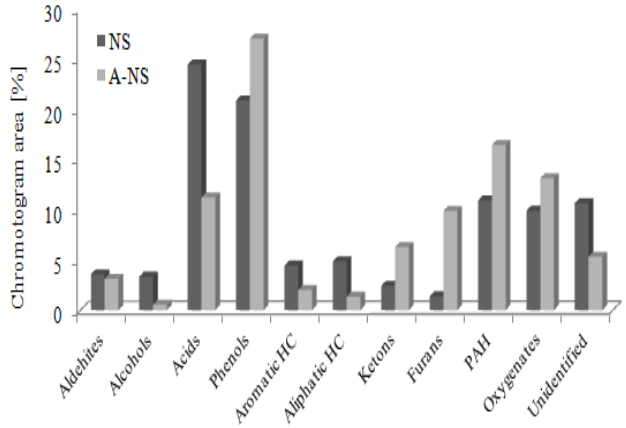

Fig. 9 Py–GC/MS detection of products evolved from pyrolysis of NS and A-NS

Das and Sarmah (2005) and Person et al. (2017) specified that phenolic compounds as lignin derivatives were decreased when biomass exposed to acid pre-treatment. But in their study, reaction time was 1 min and 2 s, respectively. Person et al. (2017), also indicated that the pyrolysis time was an important parameter for obtaining lignin derivatives. As seen from the Fig. 5 and

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Fig. 6, thermal stability of PS and NS were increased by acid pre-treatment. In this study, reaction time was 10 min. According to the Py-GC/MS results, the reaction time was suitable to overcome thermal stability of lignin.

4. Conclusion

Pyrolysis is an efficient way to produce sustainable value-added chemicals to utilize biomass in energy and bio-chemical area. In this study, effect of acid pre-treatment on the biomass physicochemical properties and biomass pyrolysis process based on thermogravimetric and Py-GC/MS analysis were investigated. Ash content of biomass has decreased by applying acid pre-treatment. Furthermore, thermal stability of acid pre-treated biomass was higher than raw biomass in conjunction with the catalytic effect of inorganics on reactivity for pyrolysis of raw material.

The volatile product determination analysis of the biomass and acid pre-treated biomass showed the relative content variations of the final products, in particular, in the decrease of aromatic hydrocarbons, and the increase of phenols. According to the above-mentioned results, acidic pre-treatment of lignocellulosic biomass with H_2SO_4 might be suitable for production phenolic rich bio-chemicals.

Nomenclature

A-FS	: Acid pre-treated fir wood sawdust
A-NS	: Acid pre-treated nutshell
A-PS	: Acid pre-treated pine wood sawdust
ATR-FTIR	: Attenuated total reflection-Fourier transform infrared spectroscopy
dTG	: Derivative thermogravimetry
FS	: Fir wood sawdust
FTIR	: Fourier transform infrared spectroscopy
HC	: Hydrocarbon
HHV	: Higher heating value
NS	: Nutshell
PAH	: Polycyclic aromatic hydrocarbon
PS	: Pine wood sawdust
Py–GC/MS	: Pyrolysis–gas chromatography/mass spectrometry
TG	: Thermogravimetry
TGA	: Thermogravimetric Analysis

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