

## Pyrolysis Process and Characteristics of Products from Sawdust Briquettes

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The pyrolysis of briquettes made from biomass is an available and economic technological route for the production of briquette charcoal, but by-products (tar and gas) cannot be brought into full utilization, leading to the waste of resources and the addition of environmental concerns. Temperature is the most important parameter that affects the distributions and properties of briquette charcoal. This work investigated the three kinds of products of the pyrolysis of sawdust briquette in a fixed bed across a wide temperature range (250 to 950 °C). The purpose of this experiment was to study the pyrolysis process and the properties of the resulting products (briquette charcoal, liquid, and gas) of sawdust briquettes and explore the optimum operating temperature to generate good quality briquette charcoal, liquid, and gaseous products simultaneously. According to the results, the optimum pyrolysis temperature range was 450 to 650 °C, for which the briquette charcoal produced within this range had the highest calorific value (29.14 to 30.21 MJ/kg). Meanwhile, the liquid product is considered to be useful for liquid fuels or valuable chemical materials, and the low heating value of the gaseous product was 11.79 to 14.85 MJ/Nm<sup>3</sup> in this temperature range.

*Keywords:* Sawdust briquette; Pyrolysis; Temperature; Briquette charcoal; Product characteristics

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### INTRODUCTION

It is generally accepted that fossil fuels throughout the world are both vulnerable in the short term and limited over the long term; therefore, worldwide searches for sustainable and renewable energy resources have been explored to meet a considerable part of the energy demand in the future. Increasing attention has been focused on biomass resources because they can be converted to multifarious fuels and chemicals. Environmental problems, such as air pollution and greenhouse gas emissions, also play a vital role in the utilization of renewable biomass resources, as biomass is considered to be environmentally friendly and CO<sub>2</sub>-neutral (Chen *et al.* 2015). The utilization of biomass has great potential for reducing the dependence on fossil fuels and alleviating the burden of environmental degradation (Abnisa and Wan Daud 2014).

Biomass resources are abundant and widely dispersed in China. They are primarily present in five forms: wood and forestry residues, agricultural residues, animal manure, municipal waste, and wastewater resources. And the total quantity of each are 2175, 728, 3926, 155, and 48240 Mt (million tons), respectively (Shen *et al.* 2010b). In the past few years, a variety of biomass feedstocks, including forest and agricultural residues, have been selected as subjects of research; however, a majority of them have been used without

pretreatment and are unsuitable for the large-scale industrialization use in the energy conversion process because they have lower energy density and higher transportation and storage costs than fossil fuels. Additionally, large reaction equipment is needed when original biomass materials are utilized directly. These characteristics of biomass materials are the bottlenecks for its industrial utilization, and it is crucial to convert loose agricultural and forestry residues into high-density and high-value solid materials of uniform size before utilization (Khardiwar *et al.* 2013). The biomass briquette technique provides a promising solution to the effective utilization of biomass resources. This technique can be defined as a compression molding process for converting low-bulk density biomass into solid fuels with high energy density.

Presently, interest in smokeless briquettes as fuel has been growing because of their high density, high calorific value, and small amount of environmental pollution. Briquette charcoal has been given attention as a potential substitute for charcoal and coal in developing countries. The pyrolysis of briquette is an available technological route for the production of briquette charcoals. No binders are added in this technology, which reduces processing costs; however, by-products such as tar and gas cannot be brought into full utilization, leading to the waste of resources and environmental concerns. It is very crucial to investigate the manufacturing process to ensure that the three products (briquette charcoal, tar, and gas) can be used simultaneously.

Pyrolysis has been considered one of the most promising techniques for utilizing biomass (Maschio *et al.* 1992) and is the initial step for other thermochemical conversion processes, such as combustion and gasification (Elmay *et al.* 2015). Biomass pyrolysis is defined as the technique of converting lignocellulosic materials into liquid products, along with non-condensable gases and solid chars, by heating in the absence of oxygen or in reduced air. Pyrolysis can convert biomass feedstock to high-energy density bio-oil, solid char, and gas with high conversion ratio (Demirbas 2007), allowing the products' distributions and qualities to be regulated depending on operating parameters (such as temperature, heating rate, or catalyst).

The solid products (briquette charcoal) can be used as a substitute for coals and traditional charcoals for some applications in chemistry, metallurgy, environmental protection, barbecuing, and living fuel (Mwampamba *et al.* 2013). The liquid product is not only an important chemical material but also a potential fuel oil. The gaseous product is a kind of biogas applied in heating and electricity generation.

The pyrolysis temperature is the most important parameter affecting the pyrolysis behaviors and product distribution of solid, liquid, and gas (Guizani *et al.* 2014). In this work, briquettes made of Chinese fir sawdust were chosen as the pyrolysis object, and pyrolysis tests were performed in a fixed bed across a wide range of temperatures (250 to 950 °C). The yields and characteristics of the three products were analyzed in detail. The aim of this study was to evaluate the pyrolysis process and the physical and chemical properties of the pyrolysis products and explore the optimum operating temperature for generating briquette charcoal, liquid, and gaseous products simultaneously. These investigations provide a comprehensive understanding of the pyrolysis characteristics of biomass briquettes and benefit both the design and optimization of the thermochemical conversion process. In addition, this technology expands the utilization of biomass briquettes and accelerates the industrial process of the large-scale utilization of biomass resources.

## EXPERIMENTAL

### Materials

Sawdust briquettes were collected from a briquette manufacturer in the Fujian province of China. The sawdust (15% of moisture content) was pressed in the screw extrusion molding machine at 175 °C. The prepared products are bar briquettes of 30 mm diameter and 100 mm length. The physical properties such as unit density, shatter resistance, and resistance to water penetration were tested with different methods.

#### *Unit density*

The unit density of bar briquette can be obtained by weighting its quality and calculating its volume based on its diameter and length (measured by Vernier caliper) (Lajili *et al.* 2014). The following equation was used to calculate the bulk density of bar briquette,

$$\rho = \frac{m}{\frac{\pi}{4} d^2 l} \quad (1)$$

where  $\rho$  ( $g/cm^3$ ),  $m$  (g),  $d$  (cm) and  $l$  (cm) represent the bulk density, quality, diameter, and length respectively.

#### *Shatter resistance*

The shatter test was aimed to obtain the percentage of weight loss of briquettes after falling action. A certain quality (about 500 g) of briquettes were placed in a suitable plastic bag. The plastic bag would be dropped freely upon the cement ground at a height of 2 m. Repeat this operation 2 times and then weigh the briquette. The weight loss was calculated by the following equation,

$$\text{Percent weight loss (\%)} = (m_1 - m_2) / m_1 \quad (2)$$

$$\text{Shatter resistance (\%)} = 100 - \text{percent weight loss} \quad (3)$$

where  $m_1$  (g) and  $m_2$  (g) represent the weight of briquette before and after being dropped, respectively.

#### *Resistance to water penetration*

The percentage of water absorbed by an individual briquette was tested when the briquette was immersed into water. Each briquette was weighted and then immersed in distilled water at 25 °C for 5 s. It was taken out and the water was wiped off the surface. Finally, the briquette was weighted. The resistance to water penetration was determined by the following formula,

$$\text{Water gain by briquette} = (m_2 - m_1) / m_1 \quad (4)$$

$$\text{Resistance to water penetration (\%)} = 100 - \text{water gain by briquette (\%)} \quad (5)$$

where  $m_1$  (g) and  $m_2$  (g) represent the weight of dry briquette and weight of wet briquette, respectively.

Each test described above was repeated several times, and an average value was obtained to represent the physical characteristic. The unit density, shatter resistance, and

resistance to water penetration of sawdust bar briquette were 1.20 g/cm<sup>3</sup>, 99.02%, and 94.05%, respectively.

The briquettes were cut into uniform size cubes of 20 mm for use in a pyrolysis reactor. Proximate and ultimate analyses of the samples were performed to understand the compositions and estimate the potential of the materials for producing bioenergy. The materials were dried at 105 °C for the determination of moisture according to ASTM E871-82. The dried materials were stored in a desiccator for further studies. The evaluations of ash and volatile matter content on a dry basis were conducted according to the standard methods ASTM D1102-84 (2007) and ASTM E872-82 (2013), respectively. The fixed carbon was calculated as the difference. The chemical compositions of the samples were determined for the C, H, N, and S contents using a PE-2400 elemental analyzer (PerkinElmer Corporation, USA). The oxygen content was calculated as the difference. The higher heating values (HHV) of the samples were measured using an oxygen bomb type-calorimeter Parr 6300 (Parr Instrument Company, USA). The basic characteristics of the sawdust briquettes are given in Table 1, similar to reports for Chinese fir sawdust presented by other researchers (Wu and Qiu 2015).

**Table 1.** Proximate and Ultimate Analysis of Sawdust Briquettes

Proximate analysis (wt.%)				HHV (MJ/kg)	Ultimate analysis (wt.%, dry)				
W	V	A	FC		C	H	N	S	O*
5.00	79.04	2.18	13.78	19.71	49.86	6.00	0.86	0.15	43.07

\*By difference

## Methods

The pyrolysis experiments with the sawdust briquettes were carried out in a fixed-bed reactor made of quartz with a length of 500 mm and an internal diameter of 30 mm. The quartz reactor was equipped with an inert gas (N<sub>2</sub>) supplied from above and a volatile outlet from below to connect the condensing system. The reactor was externally heated by an electric furnace, and a Pt-Rh-Pt thermocouple was placed inside the bed to control the temperature. A movable feeding tank made of stainless steel mesh was used to rapidly move the samples into the heated center of the reactor at the start of pyrolysis. The volatiles produced during pyrolysis were cooled through a condensing system consisting of two U-tubes located in a cold trap maintained at below 0 °C.

The pyrolysis experiments were conducted at eight different temperatures, ranging from 250 to 950 °C, to study the effect of temperature on the pyrolysis process and product characteristics of the sawdust briquettes. Purified nitrogen at a flow rate of 100 mL/min was continuously flushed into the reactor to provide an inert atmosphere and purge volatiles produced during pyrolysis from the reactor. Once the reactor was preheated to the target temperature, the feeding tank that the 5-g samples had been placed in was moved rapidly into the heated center of the reactor. It took about 1 to 2 s to introduce the feeding tank into the bed. The sample was maintained there for 30 min to remove all volatiles. The device was then allowed to cool naturally, and the N<sub>2</sub> flow remained to prevent solid char from being oxidized. When room temperature was reached in the reactor, the yield of the solid product, namely sawdust briquette charcoal, was calculated according to the overall weight loss of the feeding tank and materials after reaction. The yield of liquid product was determined by weighing the two U-tubes before and after the experiments. The gaseous yield was determined by the difference from a mass balance. All experiments were carried

out at atmospheric pressure. Each pyrolysis experiment was repeated three times, and the reported results are the averages of three experiments to eradicate discrepancies.

### Analysis of Properties of Pyrolysis Products

The proximate and ultimate analyses of the briquette charcoal obtained at various pyrolysis temperatures were conducted following the same procedures used for material characterizations. The FTIR spectra of the briquette charcoals were recorded in transmission mode between 4000 and 400  $\text{cm}^{-1}$  using a Magna-IR550 Fourier transform infrared spectrometer (Nicolet, USA) with a KBr compression method. The surface morphologies of the briquette charcoal were observed by scanning electron microscopy (SEM-S-3400, Hitachi, Japan).

The collected liquid product was extracted with dichloromethane, and the dichloromethane-soluble fraction, which contained the most compounds in the liquid product, was used for gas chromatography-mass spectroscopy (GC-MS) analysis. The main organic components in the pyrolysis oil were qualitatively analyzed by GC-MS, performed on an Agilent 7890A/5975C (USA) instrument equipped with a HP-5 quartz capillary column (length, 30 m; film thickness, 0.25  $\mu\text{m}$ ; internal diameter, 0.25 mm). The column temperature was retained at 50  $^{\circ}\text{C}$  for 2 min, then was increased to 280  $^{\circ}\text{C}$  at a rate of 5  $^{\circ}\text{C}/\text{min}$ , and then was kept constant for 20 min. The carrier gas was helium, and the sweep rate was maintained at 1.6 mL/min. The temperature of the injector was 250  $^{\circ}\text{C}$ , and the injector split ratio was 10:1. The NIST mass spectra library provided the foundation for the identification of each peak in the chromatograms.

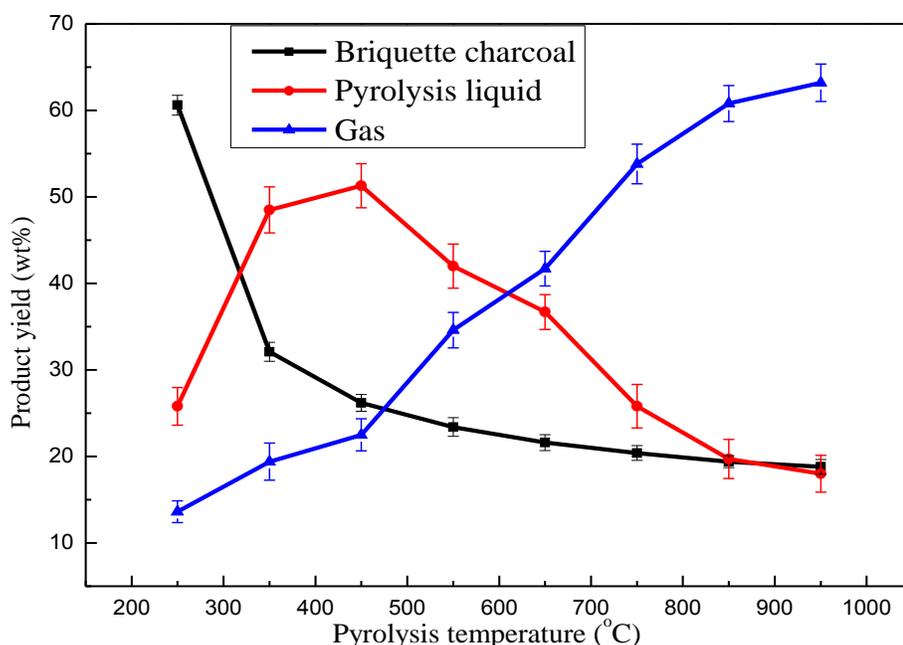
The gaseous compounds from the pyrolysis of the sawdust briquette were analyzed using a gas chromatograph GC-2014 (Shimadzu Company, Japan) equipped with a Shin Carbon ST100/120 micro-packed column and a capillary column. A TCD (thermal conductivity detector) was applied to detect inorganic compounds ( $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ ), and a FID (flame ionization detector) was used for determination of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_2$ . The gaseous components were qualitatively determined by a contrast with standard gas, and quantitatively determined using the single point external standard. The heat values of the gases were calculated according to the volume fraction of the combustible compounds.

## RESULTS AND DISCUSSION

### Products Distribution

The yield distribution of pyrolysis products (solid, liquid, and gas) has a close association with pyrolysis temperature (Shadangi and Mohanty 2014). The weight percentages of the products obtained at different temperatures (250 to 950  $^{\circ}\text{C}$ ) from the pyrolysis of the sawdust briquette are given in Fig. 1. The figure shows the connection between the yield distribution of the products and pyrolysis temperature. The yield of the briquette charcoal decreased from 63.40 to 20.90 wt.% as the temperature was increased from 250 to 650  $^{\circ}\text{C}$ . After that, the decrease in solid yield with increase in temperature was not distinct. In other words, the depolymerization of the raw material or the release of volatile matters is primarily focused on the lower temperatures in the range of 250 to 650  $^{\circ}\text{C}$  (Burhenne *et al.* 2013). The yield of the liquid product increased gradually in the temperature range of 250 to 450  $^{\circ}\text{C}$  and reached a maximum of 52.28% at 450  $^{\circ}\text{C}$ , and then decreased from 52.28% to 16.95% when the temperature increased sequentially from

450 to 950 °C. The trend of variation in weight percentage of gaseous yield with increasing pyrolysis temperature was incremental under the scope of the temperature investigated. A more substantial growth in gaseous yield was observed when the temperature was above 450 °C. This phenomenon results from secondary reactions such as cracking and rearrangement of the unstable volatile matters and the solid residue at higher temperatures (> 450 °C), leading to the formation of incondensable gas (Morf *et al.* 2002; Şensöz and Angın 2008). The temperature range of 450 to 650 °C thus should be the better choice for pyrolysis temperature, taking the yields of the three types of products into consideration.



**Fig. 1.** The yield distribution of sawdust briquette pyrolysis as a function of temperature

In the temperature range of 450 to 650 °C, the yield of the briquette charcoal was above 20%, ensuring the production of the major product (Bhattacharya *et al.* 1990). The temperature of 450 °C maximized the production of the pyrolysis liquid, and temperature of above 450 °C favored the yield of the gaseous product. According to the practical situation in the selection of obtaining high yield of liquid or gaseous products, an appropriate operating temperature can be determined.

## Properties of the Briquette Charcoal

### *Basic analysis of the briquette charcoal*

The basic properties of the briquette charcoal created at different pyrolysis temperatures are shown in Table 2. Particularly, the proximate analysis and higher heating value (HHV) are important indexes for measuring the quality of the solid biomass fuel. With the pyrolysis temperature increasing from 250 to 650 °C, the volatile content in the briquette charcoal decreased from 62.80% to 15.92% and the fixed carbon content increased from 33.40% to 75.43%; however, the change was not obvious at temperatures higher than 650 °C. The ash content was the non-volatile substance and non-combustible material in the charcoal (Angın and Şensöz 2014) and its content showed an increasing tendency due to the release of the volatile matters with increase in pyrolysis temperature. The HHVs of the briquette charcoals prepared at different pyrolysis temperatures are also

shown in Table 2. The HHVs of the charcoal obtained between 250 and 950 °C were 22.98 to 30.21 MJ/kg, much higher than that of sawdust briquette. The HHVs first increased and then decreased with the increase in temperature, and the turning point, representing a maximum value, was between 550 and 650 °C. The HHVs produced at 550 °C and 650 °C were 30.21 MJ/kg and 29.30 MJ/kg, respectively; these values are approaching the HHV of soft coal (29 MJ/kg) (Amutio *et al.* 2012). From the ultimate analyses, with the increasing of pyrolysis temperature, the carbon content increased from 63.89% at 250 °C to 88.05% at 950 °C. Inversely, the hydrogen and oxygen contents of the solid charcoal reduced gradually with increasing temperature. These findings suggest that dehydrogenation reactions occurred during the charring process and the degree of carbonization became stronger as the temperature increased.

**Table 2.** The Basic Properties of the Sawdust Briquette Charcoal at Different Pyrolysis Temperatures on Dry Basic

Pyrolysis Temperature (°C)	250	350	450	550	650	750	850	950
Proximate Analysis (dry, wt%)								
Volatile	62.80	37.32	27.51	17.73	15.92	15.04	14.50	12.89
Ash	3.80	5.58	6.16	7.56	8.65	8.27	8.69	8.31
Fixed Carbon	33.40	57.10	66.33	74.71	75.43	76.69	76.81	78.80
HHV (MJ/kg)	22.98	27.41	29.14	30.21	29.30	28.25	28.07	28.03
Ultimate Analysis (wt%)								
C	63.89	75.02	77.53	82.57	84.64	86.28	88.04	88.05
H	4.96	3.29	2.59	1.91	1.25	0.69	0.39	0.23
O	30.52	21.01	19.04	14.68	12.68	12.28	11.23	11.2
N	0.32	0.35	0.37	0.40	0.33	0.36	0.39	0.27
S	0.31	0.33	0.47	0.44	0.41	0.39	0.31	0.25

The basic properties of the briquette charcoals obtained in the temperature range of 450 to 650 °C were compared to the properties of the raw materials (sawdust briquette) and traditional wood charcoal, which originated from some softwood species (Demirbas *et al.* 1997; Mwampamba *et al.* 2013). These comparisons are presented in Table 3.

**Table 3.** A Comparison of Properties between the Briquette Charcoal and those of Briquette and Traditional Wood Charcoal

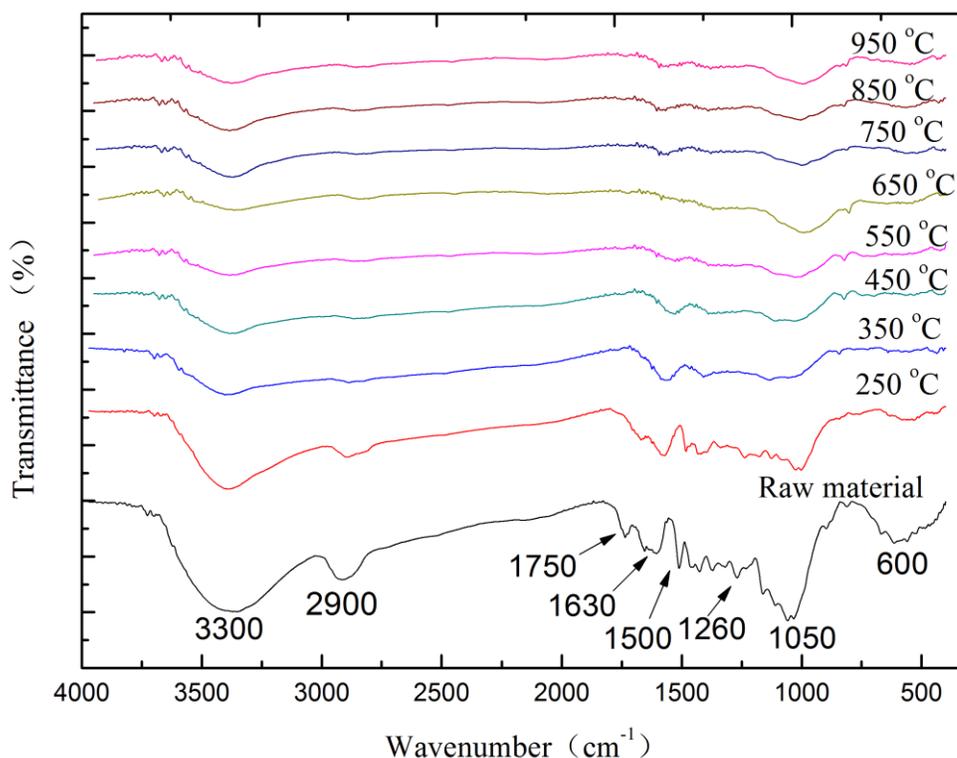
Sample	Volatile (%)	Fixed Carbon (%)	Ash (%)	HHV (MJ/kg)
Briquette	79.04	13.78	2.18	19.71
Briquette Charcoal	27.15-15.59	66.33-75.43	6.16-8.65	29.14-30.21
Traditional Wood Charcoal	25.00-15.00	70.00-86.00	<5	30-33

The fixed-carbon and ash contents of the briquette charcoal were higher than those of briquette because of carbonization. The HHV of the briquette charcoal reached approximately 30 MJ/kg, which was greater than the sawdust briquette by about 52%. This indicates that pyrolysis of briquette improved its fuel quality. The briquette charcoal had a similar amount of volatile content, but slightly lower fixed carbon contents than those of traditional wood charcoal. The ash content of briquette charcoal was a little higher than that of traditional wood charcoal. This may be due to a small amount of mechanical

impurities (such as dust) having been mixed in briquette fuels when loose sawdust was converted into briquette by compressing and molding. The heating value of briquette charcoal prepared in the optimum temperature range is slightly lower when compared to traditional wood charcoal because of slightly lower fixed carbon for briquette charcoal but reached the value of commercial briquette charcoal (Hirunpraditkoon *et al.* 2014). These results make it possible to conclude that sawdust briquette charcoal has potential for being an alternative for traditional wood charcoal.

#### FTIR analysis

FTIR spectra of the raw materials and briquette charcoals obtained at various pyrolysis temperatures are shown in Fig. 2. The spectra can be applied to characterize the changes of various chemical functional groups in the solid charcoal with increasing pyrolysis temperature. The main typical functional groups in the raw materials were as follows: a wide peak at 3600 to 3200  $\text{cm}^{-1}$  for the O-H Stretching vibration, a peak at 2800 to 3000  $\text{cm}^{-1}$  caused by the stretching vibration of alkyl C-H, a peak at 1750  $\text{cm}^{-1}$  caused by C=O stretching vibration, two peaks at 1630  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$  corresponding to C=C vibration in aliphatic and aromatic structures, respectively, a peak between 1300 and 1000  $\text{cm}^{-1}$  caused by C-O-(C)/(H) stretching vibrations and O-H deformation vibration, and a peak between 750 and 500  $\text{cm}^{-1}$  caused by C-H bending vibration. These major absorption bands in the FTIR spectrum of sawdust briquette represented the typical structures of lignin, cellulose, and hemicellulose, which are the main constituents of biomass resources. These major chemical groups in the raw materials are very non-stable and can be easily ruptured.



**Fig. 2.** FTIR spectra of the raw material and charcoal produced at various temperatures

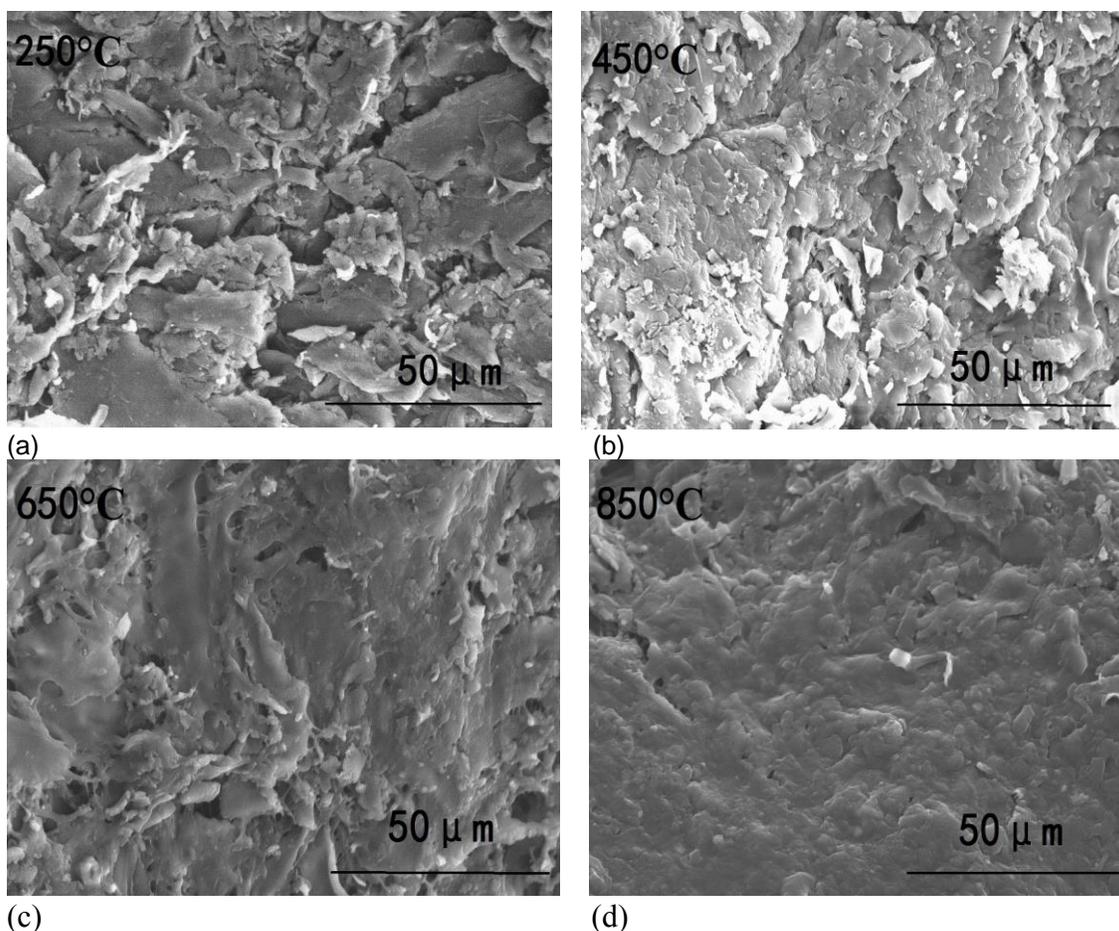
From the FTIR spectra it is apparent that the type and content of the chemical groups in the raw materials decreased gradually as the pyrolysis temperature increased. The shape of the spectra for the briquette charcoal obtained at 250 °C was similar to that of the raw material but the intensities of the peaks became weak (Chen *et al.* 2012), which indicated that some of the chemical bonds, O-H, C=O, and C-O, began to break (Gu *et al.* 2013). The peak at around 2900 cm<sup>-1</sup> was not observed at temperatures 350 °C and above, indicating the rupture of the methylene group (-CH<sub>2</sub>-) in hemicellulose at the lower temperature (Shaaban *et al.* 2013). Vibrations of peaks detected at 1750 cm<sup>-1</sup> (C=O) and 1260 cm<sup>-1</sup> (C-O-) became weak at 250 °C and disappeared at 350 °C, leading to the formation of some small molecular gases, such as CO and CO<sub>2</sub>. When the raw materials were pyrolyzed at 450 to 550 °C, the degradation of lignin was prominent. The peaks of C=C band vibration (1630 to 1500 cm<sup>-1</sup>) and aromatic C-H deformation (810 to 750 cm<sup>-1</sup>) provided evidence for the presence of an aromatic structure (Yuan *et al.* 2015). When the pyrolysis temperature was above 650 °C, most of the volatile compounds were released and the charcoal became more and more thermally stable. The spectrum of the charcoals obtained at 750 to 950 °C were more simplified and invariable, in which few peaks remained including some representative peaks of aromatic rings. These FTIR characteristics of the materials and charcoals in the experimental temperature range (250 to 950 °C) indicate that the pyrolysis reactions of sawdust briquette mainly occur at temperatures below 650 °C.

#### *Scanning electron microscopy (SEM) analysis*

The comparisons of some of the SEM images of the briquette charcoals obtained at typical temperatures were analyzed to illustrate the evolution of the surface morphologies with increasing pyrolysis temperature. The SEM photos of the charcoals obtained at 250, 450, 650, and 850 °C are shown in Fig. 3. The briquette was prepared from the loose sawdust by mechanical pressing at certain temperature and pressure. An irregular laminated structure of the charcoal surface can be observed in Fig. 3(a), and this feature became increasingly less clear with increasing temperature, almost vanishing by Fig. 3(d). These suggest that the release of volatile compounds may promote the shrinkage of the internal structure of charcoal as temperature is increased, leading to a compact texture. There were almost no pores on the surface of the charcoal generated at the lower temperatures (Fig. 3(a) and Fig. 3(b)) and some pores emerged at 650 °C (Fig. 3(c)). But the phenomenon that the majority of pores on surface disappeared and only a few smaller pores existed was observed at 850°C (Fig. 3(d)). This suggested charcoal may melt and deform, leading to pores shrinking or even closing at higher temperature (Wang *et al.* 2009b). Meanwhile, a smooth morphology of charcoal was obtained. These phenomena described are similar to those of sawdust char reported by another work (Zhang *et al.* 2015).

#### **Properties of the Pyrolysis Oil**

Bio-oil originates from the degradation of lignocellulosic biomass resources, and it is well known to be a complex mixture that contains various kinds of molecular compounds of different sizes (Zhang *et al.* 2007). The complexity of a pyrolysis oil composition makes it very difficult to identify all of its compounds. In the aspect of qualitative and quantitative analysis of pyrolysis oil, a “good enough” indication of the chemical composition is provided by GC-MS analysis (Jung *et al.* 2008). The results of GC-MS analyses of the pyrolysis oil from the pyrolysis of the sawdust briquette at different temperatures are shown in Table 4.



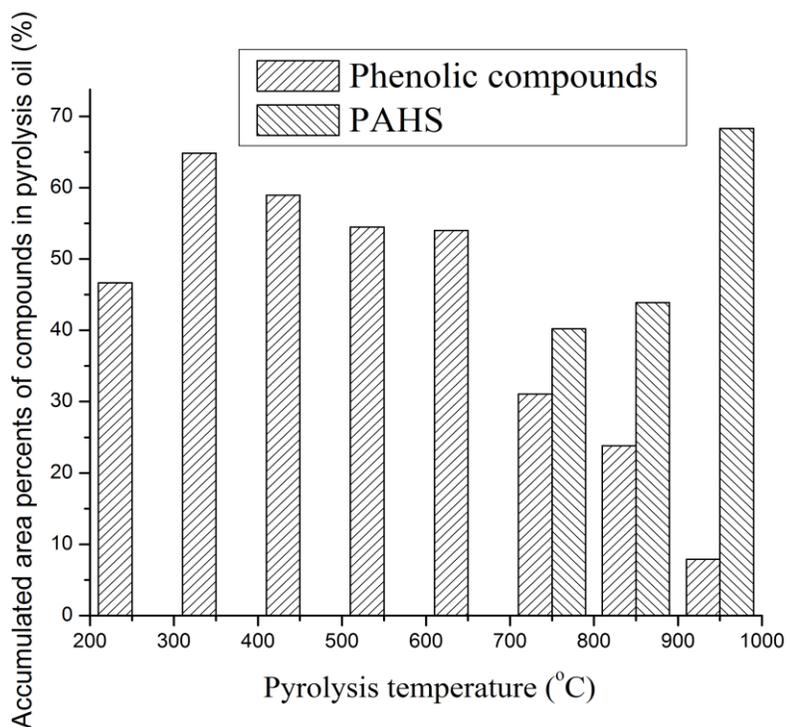
**Fig. 3.** The SEM photos of the briquette charcoal obtained at different pyrolysis temperature (1000×magnification)

The values quoted below represent the related GC-MS area percent (%). The types and contents of compounds in the pyrolysis oil varied greatly with temperature. The organic compounds identified in the pyrolysis oil obtained at low temperatures (250 to 650 °C) mainly included many oxygenated compounds such as aldehydes, ketones, furans, and phenols. Nevertheless, the major compounds in the pyrolysis oil obtained at higher temperatures (750 to 950 °C) were aromatics with a single ring (benzene and indene) and polycyclic aromatic hydrocarbons (PAHS).

Cellulose and hemicellulose in biomass are mainly degraded in the temperature range of 250 to 450 °C (Yang *et al.* 2007). The glycosidic linkages between the monomer units of cellulose and hemicellulose and some functional groups on the branched chains become reactive and rapidly rupture, leading to the formation of different unstable intermediates and functional groups (Van de Velden *et al.* 2010). These intermediate compounds undergo different reactions, such as dehydration, decomposition, oxidation, and secondary reactions (Collard and Blin 2014), which contribute to the formation of aldehydes, ketones, furans, *etc.* As shown in Table 4, the major aldehydes and ketones obtained in this temperature range were 1,2-cyclopentanedione, 3-methyl-1,2-cyclopentanedione, and 2-methyl-2-cyclopentene-1-one. The major furans were furfural, 2(5h)-furanone, and 2-furanmethanol. These furan ring compounds can be converted from

pyran rings through contraction and cyclization reactions (Shen and Gu 2009; Branca *et al.* 2013); pyran rings form the main-chain structure of cellulose and hemicellulose.

The most abundant compounds in the pyrolysis oil of the sawdust briquette were phenolic compounds, which are most likely to have been derived from the degradation of lignin owing to its molecular structure (Wang *et al.* 2009c). Lignin is a phenol polymer composed of three phenylpropane units of guaiacyl(G), p-hydroxyphenyl(H), and syringyl(S), and the main decomposition reactions happen over a large temperature range of 200 to 450 °C (Wang *et al.* 2009a). As shown in Table 4, the major phenolic compounds in the pyrolysis oil can be classified into phenolic ethers and alkylated phenols. The phenolic ethers were guaiacol, 4-methyl guaiacol, 4-ethylguaiacol, 2-methoxy-4-vinylphenol, eugenol, 2-methoxy-4-propyl-phenol, 2-methoxy-4-(1-propenyl)-, vanillin, (e)-isoeugenol, acetovanillone, 2-propiovanillone, homovanillyl alcohol, and homovanillic acid. The alkylated phenols consisted of phenol, o-cresol, 4-methylphenol, 2,4-dimethylphenol, 3,4-dimethylphenol, 1,2-benzenediol, 4-methyl-1,2-benzenediol, and 2,4-di-tert-butylphenol. The accumulated area percentages of all phenolic compounds in the pyrolysis oil obtained from sawdust briquette at all the temperatures tested are shown in Fig. 4.



**Fig. 4.** The total amount of phenolic compounds and PAHS in the pyrolysis oil at different temperatures

The total area percentages of phenolic compounds reached a maximum between 350 and 450 °C, which was consistent with the highest degradation rate of lignin – between 350 and 400 °C (Wang *et al.* 2009a). For temperatures higher than 450 °C, the related area percent of phenolic compounds decreased with increase in temperature. This may be attributed to the second reaction and release of unstable volatile compounds during the pyrolysis process.

**Table 4.** Composition of Pyrolysis Oil Identified by GC/MS Produced at Various Temperatures

RT (min)	Molecular Formula	Compound	Related area percent (%) at Various Temperatures (°C)								
			250	350	450	550	650	750	850	950	
4.588	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	Furfural	3.2	2.75	2.51						
5.164	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	2-Furanmethanol	5.07	3.38	1.74						
6.287	C <sub>6</sub> H <sub>8</sub> O	2-Methyl-2-cyclopentene-1-one		0.36	0.23	0.54	0.43				
6.659	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	2(5H)-Furanone	1.08	0.81	0.85						
6.817	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	1,2-Cyclopentanedione	2.97	2.55	2.14	2.53	1.11				
8.636	C <sub>9</sub> H <sub>10</sub>	1-Methyl-3-vinylbenzene					0.87	0.42	0.62	0.33	
9.037	C <sub>6</sub> H <sub>6</sub> O	Phenol			0.68	0.37	3.18	4.06	6.42	4.22	
9.792	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	3-Methyl-1,2-cyclopentanedione	1.4	1.11	1.43	1.32	1.05				
10.107	C <sub>9</sub> H <sub>8</sub>	Indene					1.74	6.67	7.42	11.71	
10.999	C <sub>7</sub> H <sub>8</sub> O	<i>o</i> -Cresol			0.25	1.5	4.24	4.51	4.28	0.8	
11.612	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	Guaiacol	4.44	7.62	8.05	2.88					
11.955	C <sub>7</sub> H <sub>8</sub> O	4-Methylphenol				5.9	6.61	5.73	6.82	2.7	
13.282	C <sub>10</sub> H <sub>10</sub>	2-Methylindene					1.37	2.73	3.49	0.99	
13.774	C <sub>8</sub> H <sub>10</sub> O	2,4-Dimethylphenol		0.39	0.97	2.8	5.19	3.8	3.28		
14.358	C <sub>10</sub> H <sub>8</sub>	Naphthalene						14.79	15.43	26.52	
14.613	C <sub>8</sub> H <sub>10</sub> O	3,4-Dimethylphenol					2.86	2.65			
14.725	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	4-Methyl guaiacol	5.45	14.05	10.52	7.42	2.31				
16.441	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1,2-Benzenediol			2	4.89	10.25	4.08	2.41		
17.293	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	4-Ethylguaiacol	3.65	6.91	5.79	5.32	2.44				
17.642	C <sub>11</sub> H <sub>10</sub>	Naphthalene, 1-methyl-						6.36	7.56	7.01	
18.346	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	2-Methoxy-4-vinylphenol	7.56	8.43	8.17	6.31					
18.425	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	4-Methyl-1,2-benzenediol			0.59	9.65	15.13	5.56	0.21		
19.553	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	Eugenol	2.86	3.31	3.46						
19.714	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	2-methoxy-4-propyl-Phenol	1	2.12	1.9						
20.011	C <sub>12</sub> H <sub>10</sub>	Biphenyl						2.12	1.83	1.78	
20.881	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	Phenol, 2-methoxy-4-(1-propenyl)-	5.06	3.82	4.3						

21.113	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	Vanillin	0.87	0.6	1.17	2.35				
21.384	C <sub>12</sub> H <sub>10</sub>	2-Vinylnaphthalene							1.31	1.85
21.871	C <sub>12</sub> H <sub>8</sub>	Acenaphthylene						6.49	5.71	9.81
21.974	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	(e)-Isoeugenol	16.62	18.2	12.28	7.42	2.73			
23.13	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	Acetovanillone	2.19	1.81	1.66					
23.542	C <sub>14</sub> H <sub>22</sub> O	2,4-Di- <i>tert</i> -butylphenol						0.66	0.39	0.17
23.673	C <sub>12</sub> H <sub>8</sub> O	Dibenzofuran							0.74	1.37
24.172	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	Homovanillyl alcohol	3.95	2.72	2.43					
25.315	C <sub>13</sub> H <sub>10</sub>	Fluorene						3.55	3.28	6.94
25.3	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	2-Propiovanillone	1.3	1.26	0.93					
25.789	C <sub>15</sub> H <sub>26</sub> O	Cedrol		0.71	0.81	1.65	0.93			
27.061	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	Homovanillic acid	6.84	4.93	4.35					
29.979	C <sub>14</sub> H <sub>10</sub>	Anthracene						5.72	4.88	10.49
32.611	C <sub>15</sub> H <sub>12</sub>	2-Methylphenanthrene						0.66	1.38	1.34
32.908	C <sub>15</sub> H <sub>10</sub>	4H-Cyclopenta[def]phenanthrene						0.54	2.48	2.57

One main characteristic of the phenolic compounds in the pyrolysis oil obtained at various temperatures was that the phenolic ethers were formed at low temperatures (250 to 650 °C) while the alkylated phenol compounds formed at high temperatures (450 to 950 °C). This may be attributed to the instability of phenolic ether compounds, leading to the methoxy groups in the ortho position of hydroxyl groups being substituted by -OH, -CH<sup>3</sup>, or -H groups (Shen *et al.* 2010a). The pyrolysis oil obtained in the temperature range of 350 to 650 °C is considered to be valuable as it has important chemicals owing to its high content of phenolic compounds. For example, Guaiacol can be used for the synthesis of vanillin, and Phenol for the synthesis of phenol-formaldehyde resin adhesives (Effendi *et al.* 2008).

One obvious phenomenon of pyrolysis oil was the important concentration of polycyclic aromatic hydrocarbons (PAHS) at higher temperature (750 to 950 °C). The major PAHS presented in pyrolysis oil were naphthalene, biphenyl, acenaphthylene, anthracene, fluorene, and their derivatives. The changes of total area percent of PAHS with temperature increasing are also presented in Fig. 4. The related percentages of PAHs in pyrolysis oil increased from 40.63% at 750 °C to approximately 68.31% at 950 °C because of the deoxygenation and aromatization reactions of primary and secondary volatile components (Yu *et al.* 2014).

### Properties of the Gas Product

The main components of non-condensable gas from the pyrolysis process of the sawdust briquette were CO<sub>2</sub>, CO, H<sub>2</sub>, and CH<sub>4</sub>, and other minor compounds of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> were also detected. The variations in volume fraction of each pyrolysis gas component at different temperatures are given in Fig. 5. The fraction of each non-methane

hydrocarbon compound was less than 1% of the total volume of the gaseous product, so C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> were categorized as C<sub>2</sub> hydrocarbon compounds in this research. The lower heating value (LHV) of the gas product was calculated according to the following formula (Gil-Lalaguna *et al.* 2014),

$$LHV_{(\text{gas})} (\text{MJ}/\text{Nm}^3) = \sum(x_i * LHV_i) \quad (6)$$

where  $LHV_i$  (MJ/Nm<sup>3</sup>) and  $x_i$  represent the lower heating value and the volume fraction of each component, respectively. The smallest heating value of C<sub>2</sub>H<sub>2</sub> among non-methane hydrocarbon compounds was regarded as that of C<sub>2</sub>.

As shown in Fig. 5, the volume fractions of the gas components was highly correlated with the pyrolysis temperature. At low temperatures of 250 to 350 °C, CO<sub>2</sub> and CO were the main components, which may be attributed to the fragmentation of the unstable structural chains or linkage with intermediate functional groups like carbonyl and carboxyl (Park *et al.* 2012). The volume fraction of CO<sub>2</sub> was reduced dramatically from 47.10 to 14.20% when the temperature increased from 350 to 750 °C, which resulted from the dilution effect of H<sub>2</sub> and CH<sub>4</sub> rapidly being released at this temperature range. Meanwhile, a relatively small change was presented for the fraction of CO (around 41%). For high temperatures (T > 750 °C), a continuous increase in H<sub>2</sub> volume fraction and slower increase in other gases (CH<sub>4</sub> and C<sub>2</sub>) were observed. The production of CO at a higher temperature is derived from some of the oxygenated function groups being converted and remaining in the solid residue, such as ether linkages and hydroxyls (Liu *et al.* 2008). The production of CH<sub>4</sub> was brought by the cracking of methyl or methoxyl groups in the residues and volatile compounds (Collard and Blin 2014). The volume fraction of H<sub>2</sub> increased rapidly from 4.47% to 23.68% when the temperature increased from 450 to 950 °C. The formation of H<sub>2</sub> was mostly attributed to the dehydrogenation reaction during the charring process (Collard and Blin 2014).

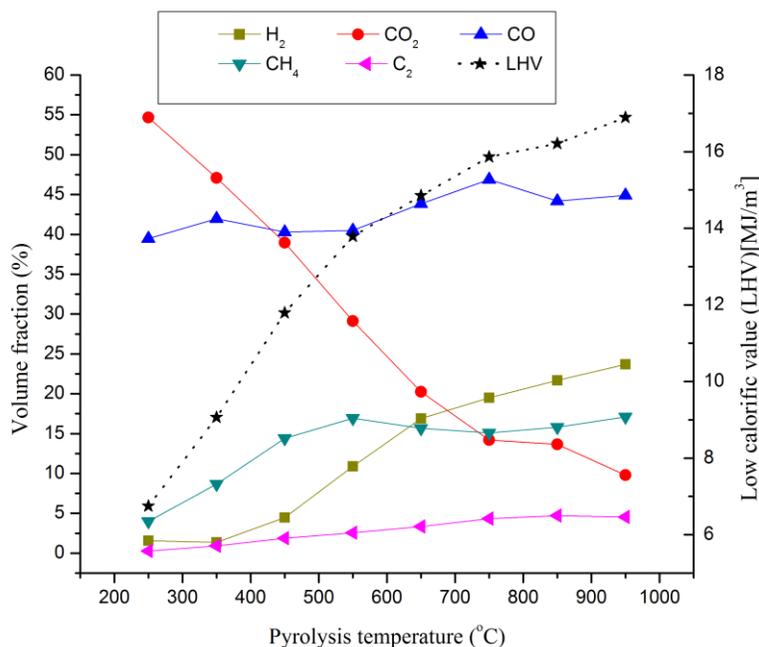


Fig. 5. Gaseous compositions of the sawdust briquette pyrolysis at different temperatures

A decrease in the fraction of CO<sub>2</sub> and a simultaneous increase in the productions of H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub> led to the LHV of the gaseous product increasing from 6.75 to 16.89 MJ/Nm<sup>3</sup> when the temperature increased from 250 to 950 °C. A slow increase was observed when the temperature was above 750 °C; therefore, the optimal operating temperature should not exceed 750 °C with the purpose of more economy. In the temperature range of 450 to 650 °C, the lower heating value of the gaseous product ranged between 11.79 and 14.85 MJ/Nm<sup>3</sup>, suggesting that the gaseous product from sawdust briquette pyrolysis can be used as a syngas. A good quality gaseous product with a low proportion of non-combustible components is directly available for generating power for civil and industrial usage. In this experiment, however, the percentage of CO<sub>2</sub> in the gas obtained from sawdust briquette was very high; therefore, a gas purification step, namely the abstraction of CO<sub>2</sub> would be needed to improve the quality of the gaseous product.

## CONCLUSIONS

1. Pyrolysis of sawdust briquette in a fixed bed was investigated across a broad range of temperatures (250 to 950 °C). The optimum operating temperature range was 450 to 650 °C considering the yields and properties of three kinds of products.
2. Increasing the pyrolysis temperature decreased the yield of briquette charcoal and increased the production of the gaseous product. The liquid yield firstly increased and then decreased as the temperature increased, reaching a maximum of 52.28% at 450 °C.
3. In the temperature range of 450 to 650 °C, the basic properties of briquette charcoal were comparable with wood charcoal and commercial briquette charcoal. FTIR spectrum of the briquette and charcoal indicated that the pyrolysis reaction of sawdust briquette mainly occurred when the temperature was below 750 °C. The surface of the briquette charcoal became more and more smooth and compact as the temperature increased.
4. At a low temperature (250 to 650 °C), the organic compounds identified from the pyrolysis oil mainly included many oxygenated compounds such as aldehydes, ketones, furans, and phenols. Nevertheless, the major compounds in the pyrolysis oil obtained at higher temperatures (750 to 950 °C) were aromatics with a single ring (benzene and indene) and polycyclic aromatic hydrocarbons (PAHS). The pyrolysis oil generated at 450 to 650 °C contained a large amount of phenolic compounds, such as guaiacol, 4-methyl guaiacol, 2-methoxy-4-vinylphenol, and (e)-isoeugenol, which are considered to be valuable chemical substances.
5. The main components of the gaseous product were CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>. Increasing the temperature decreased the volume fraction of CO<sub>2</sub> and increased the H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub> productions. The volume fraction of CO was not greatly affected by temperature. The low heating value of the gaseous product increased by increasing the temperature, and ranged between 11.79 and 14.85 MJ/Nm<sup>3</sup> for temperatures of 450 to 650 °C.

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