

Continuous pyrolysis of pine sawdust at different pyrolysis temperatures and solid residence times



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ABSTRACT

In this work, the continuous pyrolysis of pine sawdust is performed with a screw reactor to investigate the influence of pyrolysis temperature and solid residence time on products and energy distribution. Gas chromatograph/mass spectrometer (GC/MS) and Fourier transform infrared spectroscopy (FTIR) were used to confirm the identities of bio-oil. The combustion kinetics of bio-char had analyzed by thermogravimetric (TG). The results of gas chromatograph showed that carbon monoxide is the main component in produced gas, and the maximum gas yield of 54.5% was obtained at the temperature of 900 °C. Compositional analysis of the oil products showed that phenols were the major components, and its proportion increased at higher temperatures and longer solid residence times. The activation energy of bio-char combustion is 461.10 kJ mol⁻¹ and 108.45 kJ mol⁻¹ in the ranges of 290–314 °C and 314–518 °C, respectively. The maximum of energy profit rate is 6.49% obtained at the temperature of 900 °C with the solid residence time of 6 min.

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1. Introduction

Biomass is an extremely abundant, various and inexpensive resource in the world. It is considered as one of the most plentiful and well-utilized sources of renewable energy. Compared to fossil fuels, biomass energy has been paid a great deal of attention in recent years due to the problem of environment pollution and energy shortage. The thermo-chemical conversion of biomass includes combustion, liquefaction, gasification and pyrolysis. Among them, pyrolysis is one of the promising thermo-chemical conversion routes. Biomass pyrolysis is the degradation of biomass by heat in the absence of oxygen, which produces gas, bio-oil and biochar [1], which have much potential value. As high value energy carrier, pyrolysis gas is suited for heat and electricity generation. Bio-oil can be used as fuel or chemical feedstock due to its higher energy density and abundant chemical compounds [2]. Biochar is utilized as the rough material of active carbon, reductant, adsorbent and soil amendment in industry and agriculture area [3].

In the pyrolysis process, the products of biomass pyrolysis are often influenced by factors such as feed materials, pyrolysis temperature, solid residence time, pyrolysis mode, reactor type, particle size, and so on. These effect factors were extensively investigate on distribution and component of pyrolysis products

[4–6]. In general, produced gas yield increases with pyrolysis temperature rising, while the bio-char decreased [7,8]. According to the feeding manner, biomass pyrolysis process can be classified into batch, semi-batch or semi-continuous or continuous processing. Different feeding manners result in the variation of heating rate, thermal history, and residence time, which have deep influence on the distribution of pyrolysis products. Dupont et al. [9] had investigated the continuous pyrolysis of softwoods conducted in an entrained flow reactor under high temperature (800–1000 °C) and fast heating condition (>500 K s⁻¹), they found that biomass pyrolysis was completed for the solid residence time more than about 0.3 s as the temperature greater than 900 °C. Lu et al. [10] studied the influence of temperature, residence time, and catalyst content with a batch type reactor, and their study indicated that high temperature or long residence time led to a deeper cracking of chemical bonds.

As pyrolysis is a precursor of other thermochemical processes (gasification and combustion), the mass and energy balance of pyrolysis are essential part to evaluate eventual product yield distribution. Some research papers report experiments of pyrolysis yield analysis [10–12]. The Fourier transform infrared spectroscopy (FTIR) and gas chromatograph/mass spectrometer (GC/MS) analysis are often used to investigate the composition of pyrolysis products. The components of bio-oil from different condensates analyzed by GC/MS shows that the chemical contents in bio-oil varied with the different condensation process based on the dew point of components [13]. FTIR are used to determine the variation of

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function group of bio-oil under different condensations. The mass and energy balances in biomass pyrolysis were studied by different methods. Olaleye et al. [14] have developed a dynamic model for biomass pyrolysis in a two-stage fixed bed reactor and the mass and energy balance were calculated with steam reforming reactor. Imam and Capareda [15] have reported the mass and energy distribution based on the calculation of pyrolysis products from switchgrass pyrolysis. More importantly, little information is known about the analysis of mass and energy distribution during the continuous pyrolysis of pine sawdust, which is a basis to evaluate the economic feasibility of pyrolysis technology. In this work, we quantify analysis the products distribution in pine sawdust pyrolysis, the influences of pyrolysis temperature and solid residence time on product yields were investigated, the product and energy distribution and energy profit rate was carried out in the continuous pyrolysis.

2. Materials and methods

2.1. Raw material

The raw material used in this study is pine sawdust, supplied by a timber mill in Dalian, China. The particle size of pine sawdust varies from 1 to 2 mm, after being crushed and ground. The proximate and ultimate analysis of sawdust samples are given in Table 1, which were carried out in an Elementar analyzer (VarioEL III, Germany) and an automatic proximate analyzer (SDTGA5000, Sundry, China), respectively. Oxygen content is obtained by difference to 100%. The calorific value of pine sawdust is performed by an oxygen bomb calorimeter.

2.2. Experimental equipment and procedure

In this work, the continuous pyrolysis of pine sawdust was carried out in a screw reactor. The schematic diagram of the screw reactor is shown in Fig. 1. This reactor is composed of continuous feeding device, heating device and cooling device. A stirrer installs in feeding hopper to avoid bridging to ensure raw material flow into screw feeder. The heating device consists of a tubular heater, a temperature controller and a K-type thermocouple. The temperature of the heater is controlled by temperature controller and is monitored by a K-type thermocouple. The cooling device is a spiral glass condenser cooled by tap water. Pine sawdust is feed into the tubular heater reactor for pyrolysis by continuous feeding device. Biomass is decomposed into produced gas, bio-oil and bio-char. Bio-char is directly dropped in ash bucket, bio-oil is trapped in liquid container after a cooling unit, and produced gas is collected in air bags.

The continuous pyrolysis experiments of pine sawdust under different pyrolysis temperature and solid residence time are investigated. The pyrolysis temperature of experiments are conducted at 600–900 °C with the solid residence time of 6 min and feeding rate of 1.47 kg h⁻¹ in continuous mode. The frequency of electro-motor is modified to control the solid residence time inside the reactor. The solid residence time of experiments are performed in 3–7 min at pyrolysis temperature of 600 °C. Nitrogen with flow rate of 50 ml min⁻¹ serves as both the carrier gas and purging gas for biomass pyrolysis system. When the temperature of reactor reaches at a desired value, the raw materials are fed into the pyrolysis reactor continuously. As the reaction reaches a steady state after 30–40 min at each run, gas samples are collected every 5 min. The liquid and solid products are weighed after the experimental apparatus cooled down to the room temperature.

2.3. Product analysis

The pyrolysis products consist of thermal gas, bio-oil and bio-char. Thermal gas is the non-condensable phase of pyrolysis vapors. By contrast, bio-oil is condensable phase, consisting of water and oxygenated compounds. The bio-char is not volatilized in biomass fraction. The composition of gas was analyzed off-line by gas chromatograph (GC-7890, Shanghai, China). The component of bio-oil was detected with GC/MS analysis (HP6890/5973MS, American) and Fourier-transform infrared (FTIR) analysis (EQUINOX55, Germany). The temperature programming of GC/MS analysis was set up as follows: at first, the temperature was increased from normal temperature to 250 °C at 50 °C/min to gasification, and decreased to 170 °C at 5 °C/min. Then, the temperature increased to 240 °C at 10 °C/min, and maintained at 240 °C for 5 min. Bio-oil samples were extracted by organic solvent (CH₂Cl₂) to remove water before performing by FTIR analysis. CH₂Cl₂ in the oil phase was removed by rotary evaporators (RE-2000E). The proximate analysis and calorific value of bio-oil and bio-char were carried out in automatic proximate analyzer (SDTGA5000, Sundry, China) and oxygen bomb calorimeter, respectively.

3. Results and discussion

3.1. Products distribution

The determination of products distribution on continuous pyrolysis of pine sawdust under different pyrolysis temperature and solid residence time is given in Figs. 2 and 3. From Fig. 2, the bio-oil yield decreases from 51.7 to 18.0% when the pyrolysis temperature increases from 600 to 900 °C, while gas yield increases from 22.6 to 54.5%. It attributed to the secondary cracking of the pyrolysis vapors as well as the decomposition of the long chains macromolecules into smaller fragments at higher pyrolysis temperature. The char yield presents a little fluctuation trend in the range of 21.36–25.11%, appeared a relatively low amount. It might be caused by the more extensive primary decomposition of biomass and the secondary decomposition of the solid product at higher temperature. The similar tendencies of gas and oil yield with the temperature between 500 and 800 °C are reported by Lu et al. and Heidari et al. [10,16]. The variation of product yields demonstrated that higher pyrolysis temperature favors the production of gaseous product.

From Fig. 3, it can be seen that the bio-char yield is gradually decreased with the solid residence time increased from 3 to 7 min. The gas yield slightly decreases from 18.07 to 13.50% in the residence time of 3–4 min, and then increases to 24.48% at 7 min. The bio-oil yield is 28.86% in 3 min. It appeared maximum yield of 51.7% at residence time of 6 min. As solid residence time longer than 6 min, the bio-oil yield decreased to 46.97%. According to the pyrolysis product yield, pyrolysis process was divided into three stages with solid residence time. In the first stage (3–4 min), the pyrolysis product yields present a stable variation. This can be explained that shorter solid residence time results in incomplete pyrolysis and the secondary reaction is lack with the solid fast removed from the reactor. In the second stage (4–6 min), as the dominating reaction residence time, the bio-oil yield increases from 30.68% in the residence time of 4 min to 51.67% in 6 min; whereas, the char yield decreased from 44.01 to 21.36%. Compared to the first stage, longer pyrolysis time leads to more micro molecule gas produced from the decomposition of cellulose, hemicelluloses and lignin as well as the long chain and macromolecule organic compounds, which increase the yields of bio-oil and gases due to more volatiles release in its second cracking. In the last stage of reaction (greater than 6 min), the main raw materials had been decomposed and the residuals were cracked more thoroughly. The secondary reactions such as

Table 1
The proximate analysis and ultimate analysis of pine sawdust.

Raw material	Proximate analysis (wt%) ^{ad}				Ultimate analysis (wt%)					HHV (MJ/kg)
	Volatile matter	Fixed carbon	Ash	Moisture	C	H	O ^a	N	S	
Pine sawdust	76.85	18.88	0.34	3.93	44.75	6.31	42.94	1.68	0.05	18.47

^{ad} Air dried.

^a By difference.

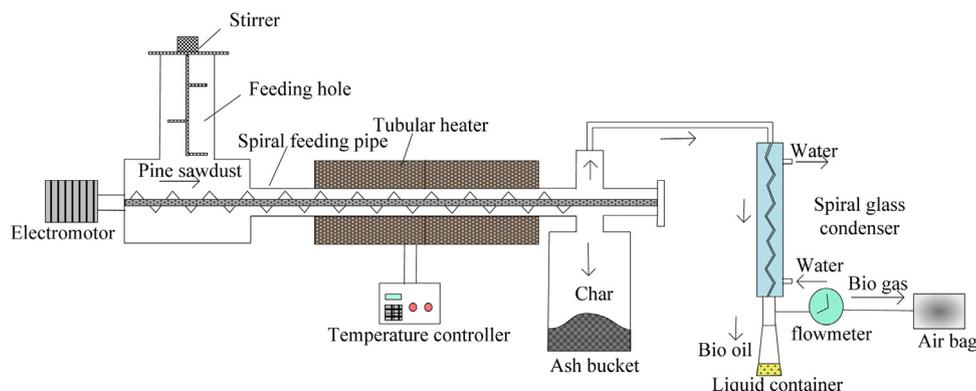


Fig. 1. Schematic diagram of the screw reactor.

thermal cracking, repolymerization, and recondensation are occurred, and therefore, less bio-oil and more gas were produced [17]. In this work, the solid residence time of 6 min is the optimal solid residence time of bio-oil extracted from pine sawdust pyrolysis. The similar trend of product yield also can be observed in the work published by Mayor and Williams [18], who investigated the fast pyrolysis of loblolly pine biomass under different residence times.

As shown in Figs. 2 and 3, mass losses ranging from 2.4 to 11.8% are calculated. The maximum of mass loss is 11.8% obtained at the temperature of 600 °C with the solid residence time of 4 min. The mass loss may result from some high boiling liquid products deposited in the piping of the system and little solid product remained in screw feeder pipe. Another possible source for mass

loss is the high volatile material in bio-oil vaporized at room temperature and the unmeasured light hydrocarbons of gas lead to the measured value is lower than the actual value.

3.2. Gas composition

The composition of gas under different temperatures is shown in Fig. 4. As observed in Fig. 4, the gas is mainly made up of carbon monoxide, which composition varies from 45.74 to 47.19%, resulted from the enhancement of decarbonylation reaction. H₂ content increases from 10.45% at 600 °C to 25.59% at 900 °C, which produced by the cracking and rearrangement of aromatic bonds at higher temperature (>500 °C) [19]. The CO₂ decreases from 24.87 to 10.06% with the increasing pyrolysis temperature. This is because

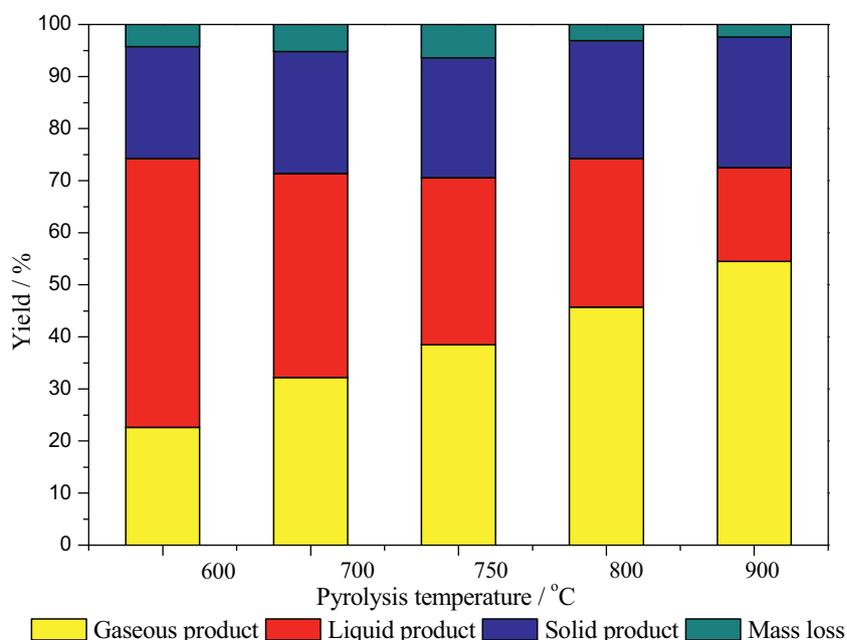


Fig. 2. The effect of pyrolysis temperature on product distribution.

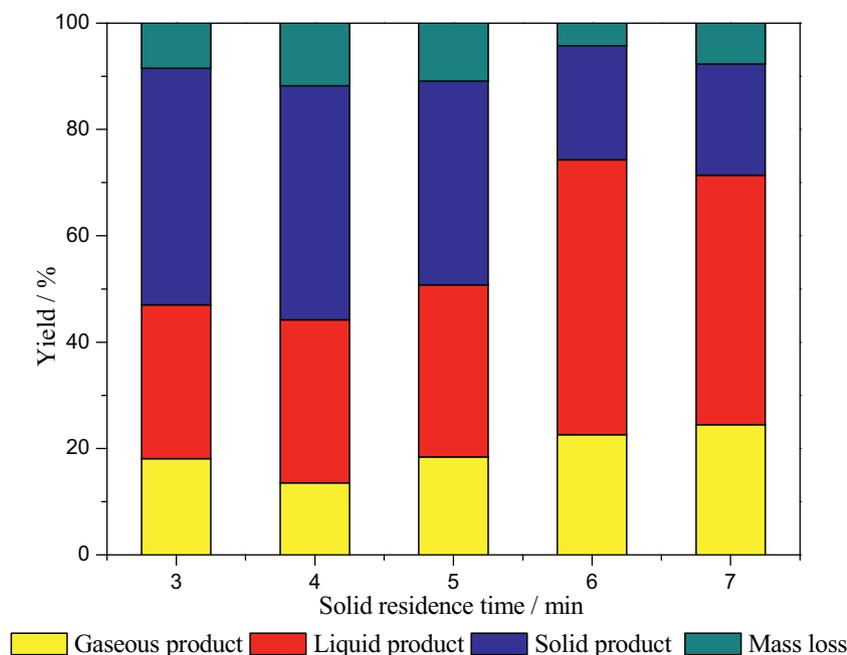


Fig. 3. The effect of solid residence time on product distribution.

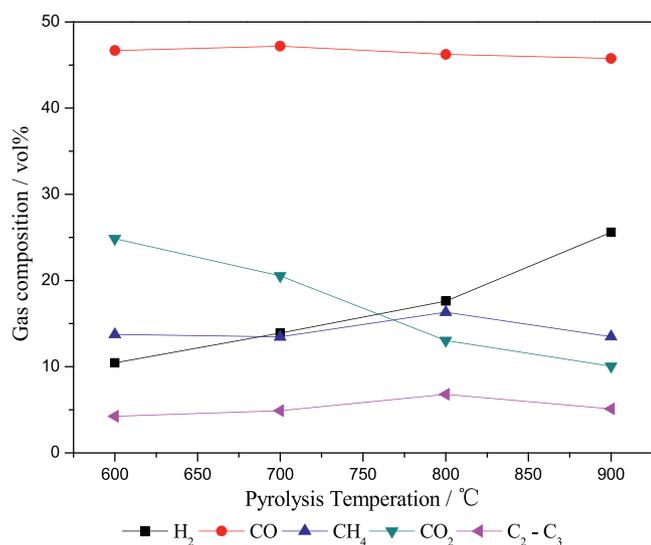


Fig. 4. Influence of pyrolysis temperature on gas composition.

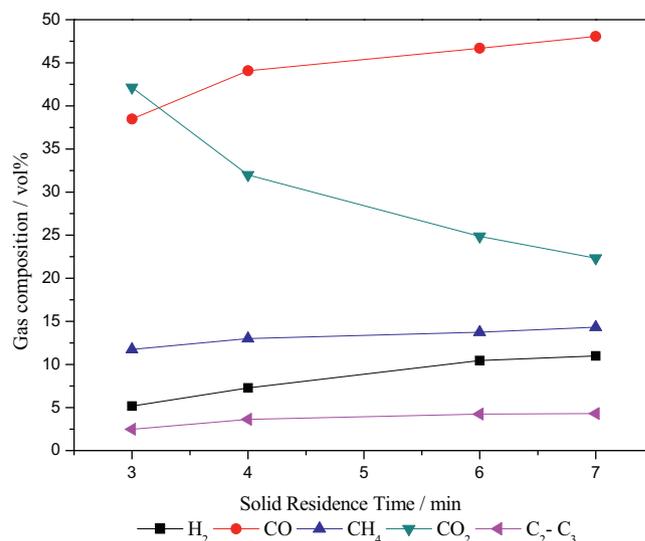


Fig. 5. Influence of solid residence time on gas composition.

the majority of CO₂ is produced by decarboxylation reaction at relatively low temperature [20]. The concentration of CH₄ presents a slight rising between 600 and 800 °C, and decreases with the further increased temperature. The decline of CH₄ yield might be attributed to the reaction of CH₄ and oxygen to produce acetylene at higher temperature [10]. The maximum content of C₂-C₃ is 6.81% obtained at 800 °C, so its amount is negligible with the pyrolysis temperature ranging from 600 to 900 °C. The content variation of gas composition agrees with the results of Fagbemi et al. who have studied the pyrolysis product yield from three biomasses [21]. Moreover, they indicated that high temperature favored H₂ production by the dehydrogenation of higher hydrocarbons.

Fig. 5 shows the influence of solid residence time on gas composition. The composition of CO₂ presents a sharply decline trend, which decreases from 42.12 to 22.33% in the solid residence time of 3 and 7 min. However, CO increases from 38.49% at 3 min to 48.07% at 7 min. This indicated long residence time provided

opportunity for secondary cracking to occur, and more macromolecular compounds were decomposed for CO releasing. H₂ content slightly increases from 5.18 to 10.98% gradually with prolonging residence time. The higher partial pressure of CO might favors to H₂ production according to Eq. (1). As observed, CH₄ and C₂-C₃ yield all presents a slightly increase trend, which the variation of concentration is within 2.5%, indicating that the solid residence time has not obviously influence on the production of CH₄ and C₂-C₃.



3.3. Bio-oil composition and characterization

Bio-oil is a considerably complex oil-water mixture, which consists of water, phenols, ketones, aldehydes, etc. The FTIR spectrums of bio-oil at different pyrolysis temperature are shown

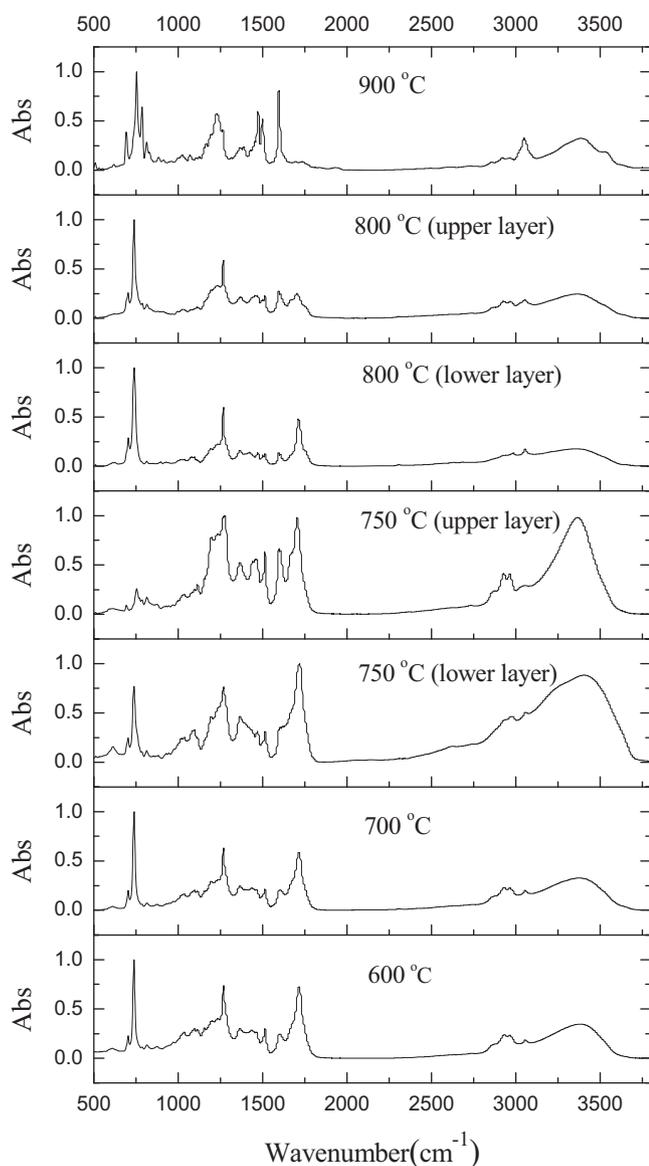


Fig. 6. The FTIR spectrum of bio-oil at different pyrolysis temperature.

in Fig. 6. Liquid products present obvious layering at 750 °C and 800 °C. The upper and lower layers of liquid products were sampled and analyzed, respectively. As observed in Fig. 6, the aromatic-H (Ar-H) deformation vibration band at 650 cm^{-1} , the Ar (C=C) stretching vibration band at 1500, 1600 cm^{-1} and the Ar-H stretching vibration band at 3030–3070 cm^{-1} corresponds to the presence of benzene ring. The presences of phenol (C–O) stretching vibration band at 1200 cm^{-1} and benzene ring are representative of phenols, indicated that were the prominent components of bio-oil at 600–900 °C. The O–H stretching vibration bands at 2800–3050 cm^{-1} reflects the existence of alcohols at the temperature ranging from 600 to 750 °C. According to the carbonyl (C=O) stretching vibration band at 1650–1850 cm^{-1} , bio-oil has no carbonyl at 900 °C compared to other temperatures, representing the absence of ketones or aldehydes. The presence of ester (C–O–C) stretching vibrations (1030–1300 cm^{-1}) and C=O stretching vibrations (about 1735 cm^{-1}) indicates the absence of ester in bio-oil at the temperature of 800 and 900 °C. As seen in Fig. 6, the functional groups of bio-oil in upper layer are corresponding to that in lower at same temperature.

Table 2

Main chemical compounds of bio-oil at different pyrolysis temperature analyzed by GC/MS.

Compound	Content percentage (%)				
	600 °C	700 °C	750 °C	800 °C	900 °C
Phenols	45.812	48.723	49.090	49.936	62.955
Ketones	25.328	22.652	15.425	1.715	0
Aldehydes	14.946	11.240	4.814	1.136	0
Acids	6.197	10.518	11.200	2.747	0
Alcohols	3.604	3.306	0.631	0	0
Esters	4.113	1.621	1.864	0	0
Aromatic hydrocarbon	0	29.852	15.620	42.196	37.046

Table 3

Main chemical compounds of bio-oil at different solid residence time by GC/MS.

Compound	6 min	3 min
Phenols	48.723	32.511
Ketones	22.652	20.047
Aldehydes	11.240	9.809
Acids	10.518	25.800
Alcohols	3.306	0
Esters	1.621	2.060
Aromatic hydrocarbon	29.852	2.570

In order to simplify the complexity of liquid products, the results of GC/MS can be mainly separated into seven fractions based on the functional groups of compounds. The main chemical compounds in bio-oil analyzed by GC/MS at different pyrolysis temperatures are presented in Table 2. As can be observed from Table 2, the increase of pyrolysis temperature affects the amount of chemical compounds in liquid product. It is well known that phenols are the main component of bio-oil produced by the depolymerization of lignin macromolecules of the raw material. The results are agreement with the works of Amutio et al. [20] despite of the pyrolysis temperature of their experiments varied from 400 to 600 °C. In addition, with the pyrolysis temperature increasing, the amount of phenols increases from 45.81% at 600 °C to 62.96% at 900 °C. The content of ketones and aldehydes decreases with the increase of pyrolysis temperature. This is because that higher temperature favors unsaturated bonds condensation and secondary cracking of ketones and aldehydes [22]. The yield of alcohols decreases from 3.60% of 600 °C to 0.63% of 750 °C. The yield of ester is relatively low, which the maximum yield is 4.11% obtained at 600 °C. No alcohols and ester compounds in bio-oil have been detected between 800 and 900 °C, and this might be due to the degree of cracking reaction increases with the rising temperature. The acids content increases in the range of 600–750 °C, and decreases at the pyrolysis temperature of 800 °C. It is noteworthy that aromatic hydrocarbon is also regarded as the main component of liquid product at the temperature of 800 and 900 °C. Furthermore, the primary component of liquid product obtained at 900 °C were phenols and aromatic hydrocarbon, but no ketones, aldehydes, acids, alcohols and esters were presented in it. These results are in agreement with the results of FTIR. Uzun and Kanmaz [19] reported that the main components of bio-oil obtained at the temperature of 500 °C with a reaction time of 5 min were ketones, phenols, carbonyls as well as carboxylic acids, whose study was performed in a well-swept resistively-heated fixed bed under the nitrogen atmosphere.

Table 3 presents the main chemical compounds of bio-oil at different solid residence time with the pyrolysis temperature of 700 °C analyzed by GC/MS. As seen in Table 3, the main chemical compounds of bio-oil at different solid residence time are similar in the case of same pyrolysis temperature. Therefore, solid residence time have not great effects on the composition of bio-oil inferred from these results.

Table 4
The calorific value of bio-oil at different pyrolysis temperature and solid residence time.

	Pyrolysis temperature/°C					Solid residence time/min				
	600	700	750	800	900	3	4	5	6	7
HHV ^{ar} (MJ kg ⁻¹)	17.87	18.76	19.89	17.13	13.63	13.76	14.85	17.85	17.87	17.89

Table 5
Influence of pyrolysis temperature and solid residence time on char properties.

	Proximate analysis (%wt)					HHV _{ar} (MJ kg ⁻¹)
		Volatiles	Moisture ^{ad}	Ash	Fixed carbon	
Temperature (°C)	600	27.04	3.53	6.32	63.11	27.71
	750	22.75	7.2	3.99	66.06	27.03
	800	18.19	7.85	7.85	66.11	25.93
	900	13.34	3.55	6.38	76.73	27.54
Solid residence time (min)	3	42.88	6.5	4.3	46.32	24.95
	4	38.42	6.29	2.01	53.28	24.63
	6	27.04	3.53	6.32	63.11	27.71
	7	19.33	1.38	3.96	75.31	28.66

The calorific value of bio-oil at different pyrolysis temperature and solid residence time is given in Table 4. The calorific value of bio-oil shows a slight rise between 600 and 750 °C, and decreased when the pyrolysis temperature further increase. The decrease in calorific value of bio-oil may result from more volatile matters were decomposed to non-condensable gas, and accordingly less macromolecular compound were condensed into bio-oil. The maximum calorific value of bio-oil was 19.89 MJ kg⁻¹ obtained at 750 °C with the solid residence time of 6 min. When solid residence time is longer than 5 min, the calorific value of bio-oil is similar. These results indicate that solid residence time has not obvious effect on the calorific value of bio-oil when it is greater than 5 min.

3.4. Bio-char characterization

The presence of volatile matter in bio-char indicates that the incomplete thermal degradation occurs in the pyrolysis process [13]. Table 5 presents the proximate analysis and calorific value of bio-chars at different temperature and solid residence time. It can be observed from Table 5, with the pyrolysis temperature increases, volatile content decreases from 27.04 to 13.34%, but the

Table 6
The kinetic analysis of char.

Temperature range (°C)	E (kJ/mol)	Correlation coefficient, R ²
290–314	461.10	0.9574
314–518	108.45	0.9739

content of fixed carbon increases from 63.11 to 76.73%. These might be due to the secondary cracking reaction increases with pyrolysis temperature rising, contributed to an increase in the cracking of combustible composition of biomass. The residual solids have lower volatile content and higher fixed carbon content compared to the raw material. The same variations of volatile and fixed carbon contents are appeared with the increase of solid residence time. These results indicated that high temperature and longer solid residence time are beneficial to the release of volatiles and production of fixed carbon. The same trends also were observed in the work published by Gheorghe et al. [23]. As observed in Table 5, moisture and ash content are relatively low in comparison with fixed carbon and volatile content. The maximum calorific value of bio-char is 28.66 MJ kg⁻¹ obtained at the temperature of 600 °C with the solid residence time of 7 min. Compared to the raw material, bio-char

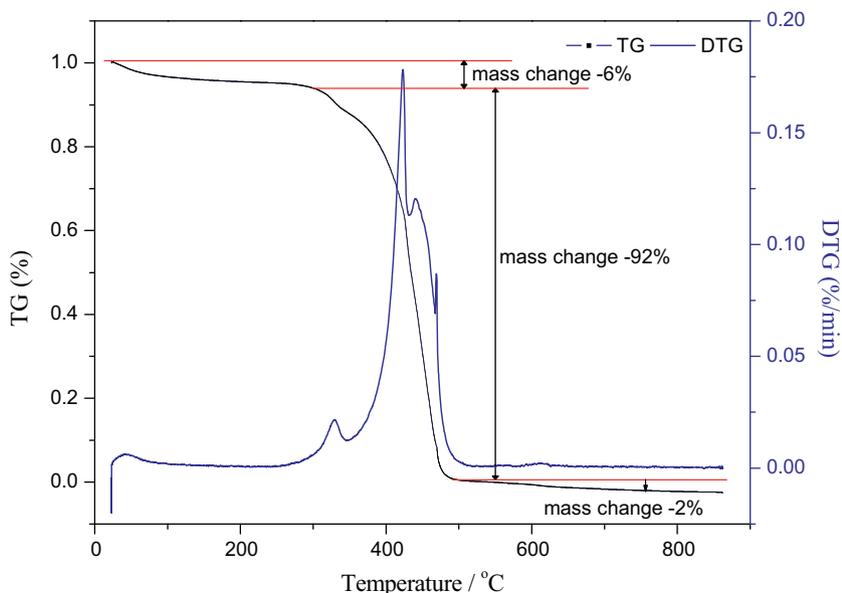


Fig. 7. TG and DTG curves for bio-char.

Table 7
Energy distribution of pyrolysis products under different pyrolysis temperature and solid residence time.

	Temperature (°C)	Residence time (min)	Feeding rate kg h ⁻¹	Energy content (%)			Energy profit rate (%)
				Gaseous	Liquid	Solid	
	600		1.47	16.12	49.99	32.05	-1.84
	700			25.54	39.81	31.64	-3.01
	750			33.69	34.52	33.72	1.93
	800			46.21	26.53	31.76	4.50
	900			55.80	13.25	37.44	6.49
		3	2.98	8.47	21.50	60.05	-9.98
		4	2.40	8.20	24.67	58.62	-8.52
		5	1.94	9.45	31.28	45.44	-13.83
		6	1.47	16.12	49.99	32.05	-1.84
		7	1.20	18.43	45.46	32.64	-3.65

has a higher calorific value under different pyrolysis temperature and solid residence time, indicated that the bio-char can be used as solid fuels.

To evaluate the combustion feature of bio-char as potential solid fuel, combustion kinetics of bio-char were investigated by thermogravimetric (TG). Fig. 7 shows the TG and DTG curves for char as a function of the temperature at a heating rate of 10 °C min⁻¹ at air atmosphere. Three regions exist in the TG curves. The first region is the weight loss of 6% at the temperature lower than 290 °C, mainly relating to the volatilization of inherent moisture and volatile materials in hemicelluloses [24]. The second region occurs in the temperature between 290 and 480 °C, about the weight of 92% sharply losing, mainly due to the thermal decomposition of cellulose and lignin in bio-char. As we all know, the composition of cellulose occurs over the temperature between 300 and 400 °C, and the lignin starts to decompose at a wider temperature range of 280–500 °C [24,25]. The similar trend of weight loss is reported by Lu et al. [10]. After 480 °C, the last weight loss is only 2%, resulted from the reaction of residual material. Table 6 shows the kinetic analysis of char combustion, and the results indicates that the activation energy of each stage is 461.10 kJ mol⁻¹ and 108.45 kJ mol⁻¹ in the ranges of 290–314 °C and 314–518 °C, respectively. According to the high correlation coefficient, we have realized that the first order reaction model fitted the experimental data.

4.1. Energy analysis and distribution

The energy distribution of pyrolysis products and energy profit rate under the different pyrolysis temperature and solid residence time are presented in Table 7. The energy of feedstock and products was evaluated using higher heating value. The heat input from the heater system was not considered in the calculation of energy balance. The energy profit rate was calculated by the heating value of products and feedstock, as given by Eq. (2). From Table 7, the energy of gaseous product increases from 16.12% at 600 °C to 55.80% at 900 °C, but the contents of liquid product energy present an inverse trend, which decreases from 49.99 to 13.25% with the temperature increase from 600 to 900 °C. The energy of solid product shows a stable variation, which varies from 31.64 to 37.44%.

$$\text{Energy profit rate} = \frac{\text{Product energy} - \text{feedstock energy}}{\text{Feedstock energy}} \quad (2)$$

The energy distribution reveals that the energy gain and loss occurred in pyrolysis process. The energy profit rate declines from -1.84 to -3.01% at the pyrolysis temperature between 600 and 700 °C. Then the energy profit rate increase from 1.93 to 6.49% at the pyrolysis temperature ranging from 750 to 900 °C indicating that product energy is greater than feedstock energy, which may

be explained that more energy from heater system is converted into the product energy at higher temperature.

The feeding rate influences the solid residence time, which determined the extent of biomass decomposition. According to the variation of product energy content in Table 7, we find that the energy content of solid product shows a larger variation of 28%. The variations of gaseous and liquid product energy content are consistent with the product yield variation. The maximum energy loss is obtained with 13.83% at the solid residence time of 5 min with the pyrolysis temperature of 600 °C. As shown in Table 7, the energy profit rate is positive indicating that product energy is greater than feedstock energy.

In the view of economic feasibility, as shown in Table 7, there are three pyrolysis products, pyrolytic gas, liquid, and solid residuals. The pyrolytic gas was rich in combustible component, e.g., H₂, CO, CH₄ and C₂–C₃, and the liquid and solid products also have high heating value. From 750 to 900 °C, the total heating value of pyrolysis products could supply enough energy for pyrolysis process. Specially, only the pyrolytic gas can supply maximum half energy of pyrolysis demand. Additionally, the liquid and solid residues also have many ways of high value utilization. For example, the redundant liquid can be used as raw material in chemical, medicine industry based on its rich certain chemical content contained, such as phenols, ketones, acids, etc. The solid, bio-char can be used as precursor of activated carbon preparation, and also it is a good agent of soil amendment.

5. Conclusion

In this study, the continuous pyrolysis of pine sawdust was carried out in a screw reactor to investigate products and energy distribution and energy profit rate under different pyrolysis temperature and solid residence time. CO was the dominating composition at the pyrolysis temperature between 600 °C and 900 °C with solid residence time ranging from 3 to 7 min. GC/MS and FTIR analysis of bio-oil showed that the main component of bio-oil were phenols. The maximum calorific value of bio-oil reached 19.89 MJ/kg at the temperature of 750 °C with the solid residence time of 6 min. The TG and DTG curves of bio-char combustion presented that the activation energy was 461.10 kJ mol⁻¹ and 108.45 kJ mol⁻¹ in the ranges of 290–314 °C and 314–518 °C, respectively. Bio-char have lower volatile content and higher fixed carbon content compared to the raw material. The maximum calorific value of bio-char was attained at 600 °C with 7 min, which indicated that longer solid residence time benefits higher heat value bio-char production. The maximum yield of gas was obtained at 54.5% at a temperature of 900 °C with solid residence time of 6 min. The energy distribution revealed that the maximum energy profit rate reach 6.49% at the pyrolysis temperature of 900 °C with 6 min solid residence time.

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