

Study on vacuum pyrolysis of coffee industrial residue for bio-oil production

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Abstract: Coffee industrial residue (CIR) is a biomass with high volatile content (64.94 wt.%) and heating value (21.3 MJ·kg⁻¹). This study was carried out to investigate the pyrolysis condition and products of CIR using thermogravimetric analyser (TGA) and vacuum tube furnace. The influence of pyrolysis temperature, time, pressure and heating rate on the yield of pyrolysis products were discussed. There was an optimal pyrolysis condition: CIR was heated from normal temperature to 400 °C for 60 min, with 10 °C·min⁻¹ heating rate and a pressure of 30 kPa_{abs}. In this condition, the yields of bio-oil, char and non-condensable gas were 42.29, 33.14 and 24.57 wt.%, respectively. The bio-oil contained palmitic acid (47.48 wt.%), oleic acid (17.45 wt.%), linoleic acid (11.34 wt.%), octadecanoic acid (7.62 wt.%) and caffeine (5.18 wt.%).

1. Introduction

Biomass is a clean and renewable energy source leading to environmental, technical and economical benefits. With the concern of environmental protection, the energetic recovery of biomass via pyrolysis, gasification or combustion has attracted increasing worldwide interest. The pyrolysis is a thermal decomposition process producing char with ash content, volatiles and low molecular weight gases. Without char and volatiles oxidation or less, it's the better way to recycle energy from biomass (e.g. microalgae, wood, straw and coffee waste) (Bridgwater, 2012; Collard and Blin, 2014).

Coffee is considered as the second largest traded commodity in the world. Coffee plants are cultivated in over 70 countries with an average annual production of 8 million tons in the world (ICO, 2014). Coffee industrial residue (CIR) is the by-product from instant coffee manufacturing process, left behind at the factory. By the statistics, instant coffee production consumes around 20% of the global production of green coffee beans (González et al., 2013) and for each kilogram of instant coffee produced 0.91 kg of CIRs (Silva et al., 1998). In addition, the CIR contains great amounts of organic compounds (i.e. fatty acids, lignin, cellulose, hemi-cellulose and other polysaccharides) (Pujol et al., 2013), while its comprehensive utilization has become a new study in recent years. For example, CIR has been investigated for biodiesel production (González et al., 2013), as production of activated carbon (Tsai et al., 2012; Tehrani et al., 2015), as raw material of fatty acids (Cruz et al., 2014).

Pyrolysis can be achieved via heating under inert gas (e.g. nitrogen and argon) or vacuum. The former is frequently-used, but the latter (vacuum pyrolysis) has had a high interest for several years (Jongh et al., 2011; Fan et al., 2014). In this study, both of them were considered. The parameters of pyrolysis include feedstock, particle size, pyrolysis temperature, pressure, time and heating rate etc. In



general, different combinations of parameters lead to different product yields or chemicals. About pyrolysis conditions of CIRs, there were some studies from other researchers (Romeiro et al., 2012; Li et al., 2014; Tsai and Liu, 2013). The pyrolysis temperature and heating rate of CIRs had been discussed, but the effect of pyrolysis pressure and time were not considered. All of the reactors used inert gas for pyrolysis, leaving vacuum pyrolysis out of account.

This paper presents a study about pyrolysis of CIR, experimenting in thermogravimetric analyser at nitrogen atmosphere and tube furnace under vacuum. The thermogravimetry was carried out to investigate the changes of weight loss in pyrolysis. And the experiments in vacuum tube furnace were carried out for counting yields of products and providing bio-oil for characterization. The effect of pyrolysis factors on product yields were researched, including pyrolysis temperature, time, pressure and heating rate. Those results would make a contribution on the utilization of CIR.

2. Materials and methods

2.1. Materials

The coffee industrial residue (CIR) used for this study was collected from a coffee processing plant in Dongguan, Guangdong province, China. The original sample was oven-dried at 105 °C for 24 h and then became the sample of experiments in vacuum tube furnace. Dried CIR was grounded with a micromill (Yili QE-300, China) to pass through a 150 µm sieve, taken as the sample for characterization and thermalgravimetric analyzer.

2.2. Characterization of Materials

2.2.1. Proximate analysis. The moisture analysis was conducted according to DD CEN/TS 14774-3: 2004. The ash content was determined according to DD CEN/TS 14775: 2004. The volatile matter content was analyzed according to DD CEN/TS 15148: 2005. The fixed carbon was calculated using Eq.(1).

$$FC = 100\% - V - A - M \quad (1)$$

where FC , V , A and M are the content (wt.%) of fixed carbon, volatile, ash and moisture, respectively.

2.2.2. Ultimate analysis. The C, H, N and S contents in the sample were measured using an elemental analyzer (Perkin Elmer Series II 2400, USA). The O content was calculated using Eq.(2).

$$O = 100\% - C - H - N - S - A - M \quad (2)$$

where O , C , H , N , S , A and M are the content (wt.%) of O, C, H, N, S, ash and moisture, respectively.

2.2.3. Heating value. The higher heating value (HHV) was determined by an isothermal-jacket bomb calorimeter (SHR-15, China).

2.3. Non-isothermal thermogravimetric analysis

The experiments were carried out on a thermalgravimetric analyzer (Henven HCT-3, China). Pyrolysis was performed under a carrier gas flow (nitrogen) of 30 mL·min⁻¹, with a sample mass of approximately 10 mg, which was heated up to 800 °C at a heating rate of 10 °C·min⁻¹.

2.4. Pyrolysis

2.4.1. The experiments in thermogravimetric analyser. The experiments in thermogravimetric analyser were implemented before the experiments in vacuum tube furnace, in order to study the changes of weight loss on different pyrolysis conditions. The experiments were performed using a thermalgravimetric analyzer (Henven HCT-3, China). The sample was approximately 10 mg in each experiment. Pyrolysis was conducted with variable temperatures (300–500 °C), heating rates (5–25 °C·min⁻¹) and pyrolysis times (60 or 120 min) under a nitrogen gas flow of 30 mL·min⁻¹.

2.4.2. The experiments in vacuum tube furnace. The experimental setup is shown in Fig. 1. The tube furnace (SK-G06123K, China) consists of a 1 m long quartz tube (diameter 60 mm), heated by well-insulated, controllable heating elements. The quartz tube is connected to condensation pipes, bottles and a circulating water vacuum pump. The circulating water vacuum pump removed the organic vapors and other gas products from the reactor through the condensation pipes. The condensable vapors were then condensed in the vacuum traps and recovered as liquid, but non-condensable gas was absorbed by alkaline (NaOH) liquor in the third bottle or escaped. A control program was used to control the heating rate, final pyrolysis temperature and pyrolysis time, and the valve before circulating water vacuum pump was used to control pyrolysis pressure.

The experiments were conducted in batch runs with variable temperatures (300–500 °C), heating rates (5–20 °C·min⁻¹), pyrolysis times (20–100 min) and pressures (10–50 kPa_{abs}). Once the quartz tube was loaded (quartz boats with 40 g of dried CIR), heating started after the quartz tube was sealed and evacuated to the desired operating pressure. The quartz tube was natural cooling after control program finished. The setup was stopped cooling when the control program was over, but under vacuum until the sample temperature reached low temperature (approximately 100 °C). Then the quartz boats with char and the bottle with bio-oil were removed and weighed. As the empty quartz boats and bottle had been weighed, the weights of char and bio-oil were obtained. At last, the yields of char, bio-oil and non-condensable gas were estimated using Eqs.(3)–(5).

$$\eta_s = \frac{m_s}{m_0} \times 100\% \quad (3)$$

$$\eta_L = \frac{m_L}{m_0} \times 100\% \quad (4)$$

$$\eta_G = \frac{m_G}{m_0} \times 100\% = \frac{m_0 - m_s - m_L}{m_0} \times 100\% \quad (5)$$

where η_s , η_L and η_G are the yield (wt.%) of char, bio-oil and non-condensable gas, respectively; m_0 , m_s , m_L and m_G are the weight (g) of sample, char, bio-oil and non-condensable gas, respectively.

2.5. Characterization of bio-oil

In characterization of bio-oil, pH meter (Leici PHS-25, China) was used to determine the pH of bio-oil. Dynamic viscosity of bio-oil was determined by rotary viscometer (Changji NDJ-8S, China). Moisture of bio-oil was measured using infrared moisture meter (Guanya SFY-20A, China). Organic matters in the bio-oil were analyzed by gas chromatography/mass spectrometry (GC/MS: Agilent 7890A/5975C, USA). A HP-5MS capillary column (30 m×250 μm×0.25 μm) was employed to separate the constituents. Bio-oil was diluted in acetone and passed through the organic filter membrane (aperture size 0.22 μm) using an injector, then 0.2 μL sample solution was injected into column at 250 °C, with a split ratio of 10:1. Helium was used as carrier gas at flow rate of 20 mL·min⁻¹. Oven temperature was programmed from 100 to 240 °C at 10 °C·min⁻¹, held at initial and final temperatures for 2 min. The detector and ion source temperature were 150 °C and 230 °C, respectively.

3. Results and discussion

3.1. Characterization of Materials

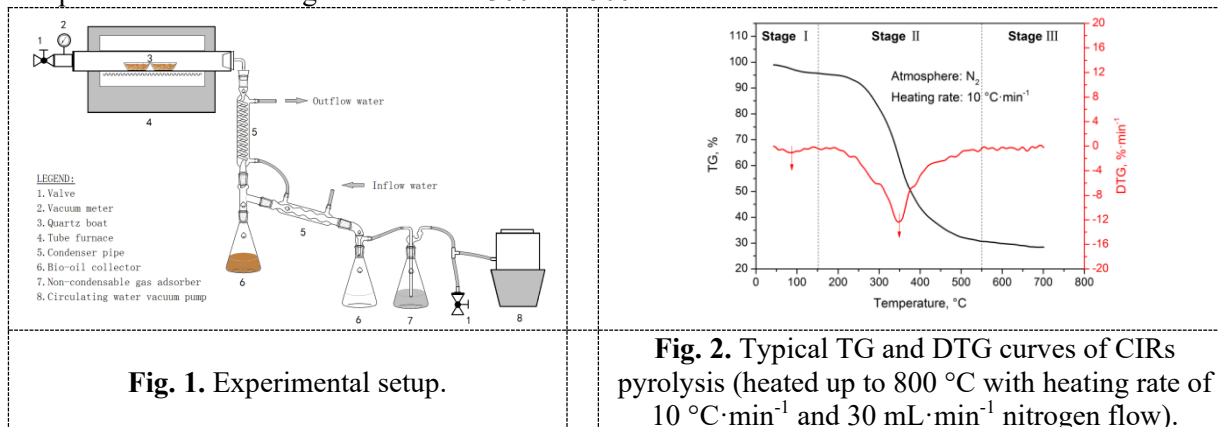
The results of proximate analysis, ultimate analysis and heating value about CIR were presented in Table 1. The volatile content of CIR is very high (approximately 65 wt.%), implicating high yield of bio-oil in pyrolysis. The CIR contains numbers of fixed carbon (about 21 wt.%), which would make a contribution to the yield of char in pyrolysis. In ultimate analysis, the main elements are C (46.62 wt.%) and O (23.90 wt.%). The higher heating value of CIR is 21.3 MJ·kg⁻¹, closed to wood (about 20 MJ·kg⁻¹) (Skreiberg et al., 2011), between sewage sludge (3–16 MJ·kg⁻¹) and coal (approximately 30 MJ·kg⁻¹) (Otero et al., 2002). In short, the CIR is an energy source containing much organic matter, and it's quite significant to recycle energy from CIRs with pyrolysis technology.

Table 1. Proximate analysis, ultimate analysis and heating value of the CIR (dry basis).

Proximate analysis (wt.%)				Ultimate analysis (wt.%)					Higher heating value (MJ·kg ⁻¹)
Moisture	Volatile	Fixed carbon	Ash	C	H	O	N	S	
6.98	64.94	21.03	7.05	46.62	8.87	23.90	5.64	0.94	21.3

3.2. Non-isothermal thermogravimetric analysis

Fig. 2 shows the typical TG and DTG curves of CIRs pyrolysis. TG curve indicates the relation between temperature and weight, and its derivative with respect to time is DTG curve, which shows the change speed of weight over time. The pyrolysis process could be divided into three stages: stage I (0–150 °C), stage II (150–550 °C) and stage III (550–800 °C). In stage I, there was a small weight loss that represented the evaporation of water, corresponding to a peak in DTG curve. Stage II was characterized by a major mass loss, approximately 65% of total weight, which was caused by the release of organic matters. And only one syncretic peak was observed in DTG curve. During stage III, the loss of weight was very slow, while the carbonization of pyrolysis residues was underway. Deduced from DTG curve in non-isothermal thermogravimetric analysis, the optimum pyrolysis temperature for CIRs might be between 300 and 500 °C.



3.3. Product yields on different pyrolysis conditions

3.3.1. Effect of pyrolysis temperature. Fig. 3a shows the changes of weight loss from the sample pyrolysis at different final temperatures. The weight of final solid products decreased as temperature increased, i.e. from 49.21 wt.% at 300 °C to 35.22 wt.% at 400 °C. The loss components were moisture and volatile, and different volatiles volatilized according to temperatures. The weight loss curves of different temperatures coincided at earlier stage as their heating processes were the same. And the curves of 450 °C and 500 °C completely coincided, which indicates that all volatiles had been lost. However, the final weight of 400 °C and 450 °C curves were much closed, which means that most volatiles had been lost at 400 °C.

Fig. 4a presents the yields of char, non-condensable gas and bio-oil from CIRs pyrolysis at different temperatures. As temperature increased, the yield of char decreased from 60.00 wt.% at 300 °C to 27.24 wt.% at 500 °C, and the yield of bio-oil increased to a maximum (approximately 43 wt.%). During the sample pyrolysis, it included the evaporation of water, the escape of volatiles and the charring of solid product. At 400 °C, the yield of bio-oil had been closed to 43 wt.%, that is to say, nearly all volatiles had gone out. Moreover, the charring of solid product had happened to a certain degree, while higher temperatures (450 or 500 °C) caused the loss of char. Therefore, the optimum pyrolysis temperature of CIRs was 400 °C, which was much closed to pyrolysis temperature (380 °C) of a study about soluble coffee ground (Romeiro et al., 2012).

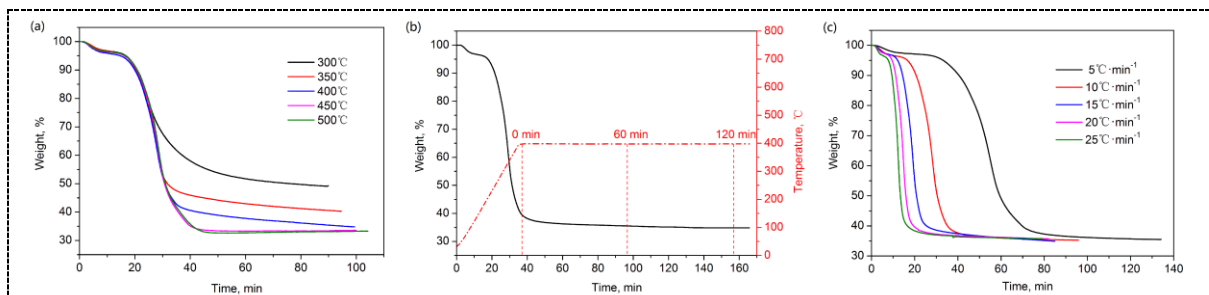


Fig. 3. Weight loss curves of CIRs pyrolysis: (a) at different final temperatures (with $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate and $30\text{ mL}\cdot\text{min}^{-1}$ nitrogen flow); (b) for different time (with $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate to $400\text{ }^{\circ}\text{C}$ with $30\text{ mL}\cdot\text{min}^{-1}$ nitrogen flow); (c) with different heating rates (heated up to $400\text{ }^{\circ}\text{C}$ for 60 min with $30\text{ mL}\cdot\text{min}^{-1}$ nitrogen flow).

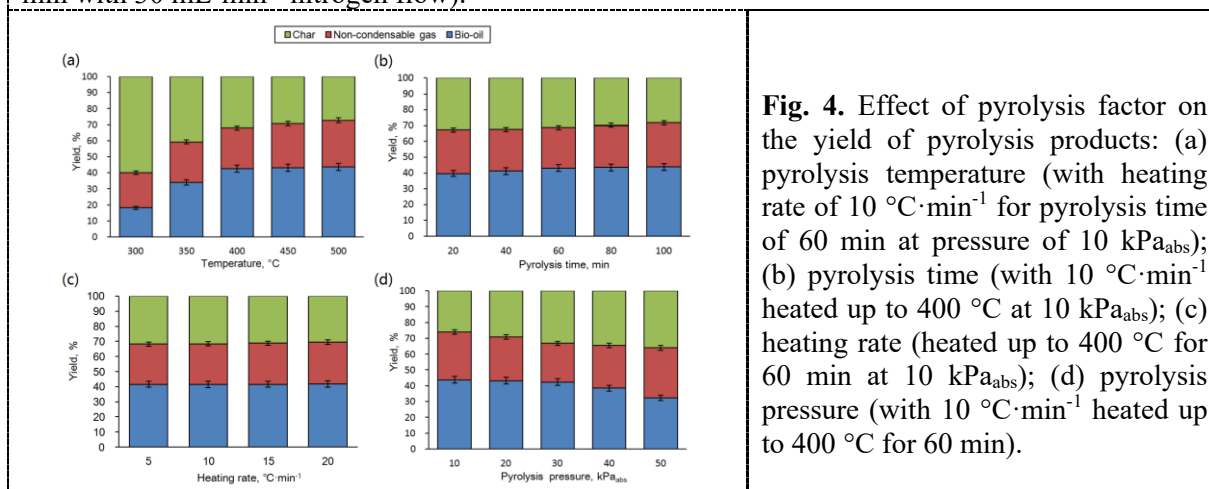


Fig. 4. Effect of pyrolysis factor on the yield of pyrolysis products: (a) pyrolysis temperature (with heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ for pyrolysis time of 60 min at pressure of $10\text{ kPa}_{\text{abs}}$); (b) pyrolysis time (with $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heated up to $400\text{ }^{\circ}\text{C}$ at $10\text{ kPa}_{\text{abs}}$); (c) heating rate (heated up to $400\text{ }^{\circ}\text{C}$ for 60 min at $10\text{ kPa}_{\text{abs}}$); (d) pyrolysis pressure (with $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heated up to $400\text{ }^{\circ}\text{C}$ for 60 min).

3.3.2. Effect of pyrolysis time. Fig. 3b presents the changes of weight loss from the sample pyrolysis related to pyrolysis time. The weights of solid product were 38.95 wt.% in 38 min (0 min at final temperature), 35.52 wt.% in 98 min (60 min at final temperature) and 34.84 wt.% in 158 min (120 min at final temperature), respectively. In other words, the pyrolysis of samples had been finished when the weight decreased to 35 wt.%.

Fig. 4b shows the yields of char, non-condensable gas and bio-oil from CIRs pyrolysis with different pyrolysis times. With pyrolysis time extended, the yield of char decreased slowly, and the yield of bio-oil increased to a maximum. More pyrolysis time, more heat and mass transfer happened, such as the evaporation of water, the escape of volatiles and the charring of solid product. Water and volatiles became bio-oil after cooling, and the solid turned to char, while charring too long caused the decrease of char. When pyrolysis time was 60 min, all volatiles had separated out, thus the yield of bio-oil reached a maximum value. As a result, the optimum pyrolysis time of CIRs was 60 min.

3.3.3. Effect of heating rate. Fig. 3c shows weight loss curves of the sample pyrolysis with different heating rates. The final weights of all curves were about 35 %, which means that the yield of solid product was not affected by heating rate. Except curve of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, curves converged between 40 and 60 min, in other words, their pyrolysis processes began to synchronize. Obviously, the heating rate determined the speed to reach final pyrolysis temperature, but was not necessary to be too high as heat and mass transfer also needed some time.

As shown in Fig. 4c, the yields of char, non-condensable gas and bio-oil from CIRs pyrolysis with different heating rates were almost the same. That is to say, the heating rate did not influence product yields. However, the operating instruction manual of vacuum tube furnace suggests that the heating rate should be less than or equal to $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, in order to prolong furnace life. Based on the small-

sized experiments, $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ was suitable. Consequently, the optimum heating rate of tube furnace for CIRs pyrolysis was $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

3.3.4. Effect of pyrolysis pressure. The experiments were just carried out in the vacuum tube furnace, because the thermogravimetric analyser in this work could not control pressure. Fig. 4d illustrates the yields from pyrolysis of CIRs as a function of pressure. As pyrolysis pressure reduced from 50 kPa_{abs} to 10 kPa_{abs}, the char yield decreased from 36.03 wt.% to 25.98 wt.%, and the bio-oil yield increased from 32.34 wt.% to 43.81 wt.%, while a maximum value was approximately 43 wt.%. This is an intuitive result, since it is commonly accepted that at higher pressures, there will be more recondensation reactions which would lead to more of the vapors becoming trapped on the char, thereby increasing the char yield. At the lower pressure, volatiles extract from tube faster, and there are fewer reactions of volatiles bringing about more bio-oils. A possible mechanism could be that higher gas density as a result of higher pressure improves the number of reactions between gases and solids, and causes char yield decreased (Jongh et al., 2011). Among 10 kPa_{abs}, 20 kPa_{abs} and 30 kPa_{abs}, the bio-oil yields were almost the same, but char yield at 30 kPa_{abs} was the greatest and 30 kPa_{abs} was the easiest to achieve. For this reason, the optimum pyrolysis pressure of CIRs was 30 kPa_{abs}.

3.3.5. Product yields on the optimal pyrolysis condition. Among pyrolysis factors, pyrolysis temperature and pressure are more important since they had most significant effect on yields of products. Pyrolysis time should be enough ensuring the sufficient transfer of mass and heat. And heating rate is allowed to adjust on the basis of machinery and equipment. According to results above, the optimal pyrolysis factors of experiments were $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (heating rate), 400 $^{\circ}\text{C}$ (pyrolysis temperature), 60 min (pyrolysis time) and 30 kPa_{abs} (pyrolysis pressure). On the optimal condition, the yields of char, non-condensable gas and bio-oil were 33.14, 24.57 and 42.29 wt.%, respectively.

3.4. Characterization of bio-oil

The bio-oil was from CIRs pyrolysis on optimum condition. It was an acidic liquid (pH=3.12), so its reservoir must be acid-proof. The dynamic viscosity of bio-oil was $3.6\text{ mm}^2\cdot\text{s}^{-1}$, which was much higher than water with a dynamic viscosity of $1.0\text{ mm}^2\cdot\text{s}^{-1}$. Simultaneously, the moisture of bio-oil was 17.86 wt.%, while it should be noted that the higher water content contributed to the lower viscosity. The problem of bio-oil translocation must be considered when comes to industrialized application. GC/MS was employed to identify the chemical compounds presenting in bio-oil. Table 2 provides the major chemical constituent of bio-oil. The chemical compounds were palmitic acid (47.48 wt.%), oleic acid (17.45 wt.%), linoleic acid (11.34 wt.%), octadecanoic acid (7.62 wt.%) and caffeine (5.18 wt.%). These organic matters have value to chemical industry.

Table 2. Major chemical constituent of bio-oil on optimum condition.

NO.	Retention time (min)	Chemical compound	Area (%)	Quality (%)
1	8.7	Pentadecane	3.42	96
2	12.8	Caffeine	5.18	97
3	13.2	Hexadecanenitrile	2.76	96
4	13.4	Methyl palmitate	2.53	98
5	13.8	Palmitic acid	47.48	95
6	15.4	Linoleic acid	11.34	94
7	15.5	Oleic acid	17.45	95
8	15.7	Octadecanoic acid	7.62	99
9	15.8	Octadecanamide	2.22	93

4. Conclusions

According to experimental results, the optimal pyrolysis condition was as follow: dried CIRs were heated from normal temperature to 400 $^{\circ}\text{C}$ for 60 min, with $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate, under a pressure of 30 kPa_{abs}. In this condition, more bio-oil and char were prepared and less non-condensable gas was

exhausted, in other word, yields of product were well-content. The bio-oil has value to chemical industry, containing a large number of palmitic acid and oleic acid.

Acknowledgments

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