



Hydrocarbon rich bio-oil production, thermal behavior analysis and kinetic study of microwave-assisted co-pyrolysis of microwave-torrefied lignin with low density polyethylene

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ABSTRACT

This study aims to enhance the quality of biofuel through microwave torrefaction pretreatment for lignin. Low density polyethylene (LDPE) was added as a hydrogen source during microwave co-pyrolysis along with the microwave-torrefied lignin (MTL). The thermal degradation behavior and kinetic study of MTL co-pyrolysis with LDPE by microwave-assisted heating was investigated as well. The results indicated that the hydrocarbon content in the bio-oil obtained from microwave co-pyrolysis of MTL and LDPE increased significantly (about 80%). It was also noticed that the aromatic hydrocarbon content increased from 1.94% to 22.83% with the addition of LDPE. Thermal behavior analysis and reaction kinetic study showed that the addition of LDPE into MTL had the effect of promoting thermal degradation and improving reaction rate during microwave-assisted pyrolysis.

1. Introduction

With the development of society and the increase of human activities, the energy has become increasingly serious. Due to the large consumption of petroleum resources which is non-renewable, it has been predicted that the world's petroleum resources will be exhausted by the year 2042 without considering the expected increase in the use of petroleum fuels (Abnisa and Wan Daud, 2014). In addition, the extensive utilization of fossil fuel resources has a direct correlation to the emission of harmful pollutants, such as sulfur dioxide, nitrogen oxides and carbon dioxide, which leads to a series of environmental problems such as the greenhouse effect, acid rain and air pollution. (Feng et al., 2018). At present, fossil fuels have gradually failed to meet the needs of human beings, and it is an urgent crisis that a new alternative energy source be found in order to alleviate the environmental pollution problems we face today (Xu et al., 2016a). Lignocellulosic biomass is considered to be one of the most important renewable resources on Earth, and the availability of lignocellulosic biomass is extremely abundant (Xu et al., 2016b). One of the most significant components in lignocellulosic biomass after cellulose is lignin, it is a kind of amorphous polymer widely existing in plants, which contains oxyphenyl-panol or its derivative structural units in its molecular structure

(Zhou et al., 2018a,b). The characteristics of the molecular structure of lignin indicate that it is the most recalcitrant components in lignocellulosic biomass and becomes a critical challenge for the bio-refinery industry. Lignin is typically derived from conventional pulp and paper industry and has a high availability. So far, most lignin is burned directly as a low grade fuel, and the molecular structure characteristics of lignin suggest that it has a great potential to be converted to bio-based fuels and chemicals such as aromatics hydrocarbons and phenols (Bu et al., 2012, 2014).

Biomass pyrolysis is a very complex chemical reaction process, which mainly includes the breaking of molecular bonds, isomerization and small molecule polymerization to generate solid phase, liquid phase and gas products (Mettler et al., 2012). In the pyrolysis process, there are mainly two heating forms: one is the traditional electric heating, and the other is the microwave heating (Morgan et al., 2017). Compared to the traditional heating, microwave heating converts electromagnetic field into heat energy at the molecular level through direct transformation induced heating (Sobhy and Chaouki, 2010). Microwave heating mainly has the following advantages: (1) the internal reaction of microwave heating is fast and uniform in that microwave radiation directly converts electromagnetic energy into intermolecular heat energy while traditional heating transfers heat from the outside to

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the inside of particulate matter (Zhang et al., 2016); (2) microwave heating is easy to control due to its instantaneous response when quickly starting and closing; (3) microwave-assisted heating does not require grinding of raw materials since it can deal with lumpy raw materials (Borges et al., 2014; Xie et al., 2014). Therefore, recently the application of microwave heating for biomass conversion for biofuels and bio-products has attracted increasing attentions (Cho et al., 2010; Bu et al., 2016).

Organic wastes refer to organic goods and materials which lost their original utilization value in the production, life and other activities, among which waste plastics are still store a large amount of energy (Panda et al., 2010). Besides, plastic wastes are rich in hydrogen compounds which might have good synergistic effects (such as increasing chemical selectivity) during its co-pyrolysis with biomass (Gunasee et al., 2017; Fan et al., 2017). Therefore, the combination of biomass and organic wastes to prepare biofuels is a great way to make full use of the renewable sources (Uzoejinwa et al., 2018). Although there were some research results about co-pyrolysis of lignin with plastic waste for biofuels production or the application of renewable sources (Devendra et al., 2016), there were still a few reports on microwave assisted pyrolysis/co-pyrolysis of lignin for biofuels (Duan et al., 2017).

Pyrolysis is affected by many factors including reaction temperature, catalyst and characteristics of raw materials (Balcik-Canbolat et al., 2017). Torrefaction pretreatment is a physical-chemical pretreatment method, also known as low temperature pyrolysis (Chen et al., 2011a). In this process, biomass produces many solid products with low water content and high heat value, and releases a large amount of CO and CO₂ as well as a small amount of volatile organic compounds simultaneously. The decomposition of biomass in the torrefaction process causes hydroxyl group (O–H) destroyed and hydrogen bond not formed, as a result, biomass becomes hydrophobic molecular structure finally (Karnjanakom et al., 2015; Rousset et al., 2011). Our previous study found that microwave co-pyrolysis of microwave torrefied rice straw with LDPE was able to enhance both quantity and chemical selectivity of major compounds such as hydrocarbons of bio-oil (Bu et al., 2018). However, to the best of our knowledge, so far it is still unclear about the mechanism of high quality bio-fuel production from co-pyrolysis of microwave torrefied lignocellulosic biomass with waste plastics. There is no report on the effects of microwave-assisted torrefaction on the microwave co-pyrolysis of lignin and LDPE and its thermal degradation behavior and reaction kinetics study analysis.

Therefore, in the present work, we are aiming to investigate the mechanism of bio-fuel production from microwave co-pyrolysis of microwave torrefied lignocellulosic biomass with LDPE using lignin as a model compound. The influence of MTL on products yield distribution and the chemical compositions of bio-oils were explored, and the thermal degradation behavior and kinetics study of MTL co-pyrolysis with LDPE were analyzed as well. This study provides a potential method to produce hydrocarbon rich bio-fuel production from organic waste resources.

2. Materials and methods

2.1. Materials

Lignin was acquired from Tokyo chemical industry Co. LTD., in Japan, low density polyethylene (LDPE) was used as a model compound for plastic waste from China Petro Co., Ltd.

2.2. Microwave torrefaction and microwave co-pyrolysis experiments

The microwave pyrolysis reactor was used to undergo microwave torrefaction pretreatment, the lignin torrefaction was performed under the reaction condition of 240 °C and 10 min. 40 g of lignin was put into a quartz flask and pretreated by torrefaction using with the microwave

reactor.

The microwave pyrolysis system was mainly composed of the following components: a 1.0kw, 50HZ microwave cavity (model: XO-100N, NanJing Xianou Instruments Manufacture Co., Ltd.), an infrared temperature sensor (model: IS-900AW, Guangzhou WAHOME Automation Equipment Co., Ltd.) and condensation system. The mass ratio of LDPE to lignin was 30%. The working process of microwave pyrolysis reactor is as follows: weigh the total raw material (LDPE and lignin torrefied) 30 g into a quartz flask, shake and mix it evenly, and then put the quartz flask into a microwave pyrolysis reactor; nitrogen was then added to the system before pyrolysis in order to ensure that the experiment was carried out in an oxygen free atmosphere. The gas flow rate was 50 mL/min and was sustained for 15 min prior to commencing the experiment; the input power of microwave heating was 750 W, and retention time was 12 min, the pyrolysis temperature was 550 °C. The products of bio-oil and syngas were collected after condensing, while the biochar remained in the quartz flask.

2.3. GC/MS analysis of bio-oil

The liquid product, crude bio-oil was collected after pyrolysis and condensation of the volatile products. The chemical composition of bio-oils was determined with an Agilent gas chromatography–mass spectrometer (GC/MS; GC, Agilent 7890 A; MS, Agilent 5975 C) with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm). The GC was programmed to heat to 40 °C for 5 min followed by heating to 300 °C at a rate of 5 °C/min. The split ratio was 50:1, and the sample quantity was 0.2 μL. The flow rate of the carrier gas (helium) was 0.6 mL/min. The MS detector was operated in the electron ionization mode (70 eV) with an ionization temperature of 230 °C. The mass spectra were recorded in the interval 30–550 *m/z*. The area percent method was used for the quantitation of the compounds present in the bio-oil. Identification of individual compounds was performed by comparing experimental mass spectra with those in the NIST Mass Spectral library.

2.4. FT-IR analysis of lignin and MTL

FT-IR analysis was conducted on lignin and microwave torrefied lignin samples using a Thermo Nicolet NEXUS 470 FT-IR System with DTGS Detector. The system specification has Wavenumber Range of 400–5000 cm⁻¹, a Spectral Resolution of 0.125 cm⁻¹ and Beamsplitters: KBr (375–7000 cm⁻¹). The samples were collected and prepared according to the instructions given by the manual and then entered for analysis.

2.5. Thermogravimetric analysis and lignin pyrolysis kinetic method

The thermal degradation behavior of different samples was carried out by a microwave-assisted thermogravimetric analyzer (Qingdao MAKEWAVE Instrument Co., Ltd) (Supplementary data). A known amount of the sample (about 1.5 g) was loaded into a quartz crucible, and the sample was heated from 25 °C to 550 °C at heating rate of 40 °C/min under a nitrogen flow of 40 mL/min, nitrogen was purged for 10 min to create an oxygen free atmosphere before pyrolysis reaction, and the input microwave power was set to 750 W during the experiment.

Coats-Redfern model is one of the most widely used method in non-isothermal kinetic analysis. This study adopted Coats – Redfern model to analyze the kinetics of co-pyrolysis of MTL and LDPE. The Coats-Redfern model applied to the following formula (Naqvi et al., 2015).

If $n = 1$,

$$\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT}$$

If $n \neq 1$,

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT}$$

where, α is the conversion rate; A is frequency factor (s^{-1}); E is the activation energy ($J \cdot mol^{-1}$); R is gas constant ($8.314 J \cdot mol^{-1} K^{-1}$); T is the reaction temperature (K); n is the reaction series; β is a constant rate of heating ($\beta = dT/dt$).

3. Results and discussion

3.1. FT-IR analysis of lignin and MTL

In order to investigate the effect microwave-assisted torrefaction has on molecular structure of lignin, raw lignin and MTL were characterized by FT-IR (Supplementary data). Results showed that both lignin and MTL had a wide absorption peak in the frequency range of $3650 cm^{-1}$ – $3200 cm^{-1}$ and acquired the strongest strength at $3450 cm^{-1}$, indicating that there were O–H functional groups both in lignin and MTL, the absorption peak of lignin was stronger than that of MTL. Additionally, the stretched peak produced in the range of frequency $1800 cm^{-1}$ – $1620 cm^{-1}$ in lignin and MTL showed that the absorption peak intensity of lignin was more evident than MTL, indicating that C=O functional groups existed in the samples and lignin obviously contained more C=O functional groups compared to MTL. This meant that MTL was more stable than raw lignin due to the high activity of C=O or carbonyl groups in the molecular structure of lignin (Pielhop et al., 2015; Renders et al., 2017). In the range of frequency $1300 cm^{-1}$ – $1000 cm^{-1}$, both lignin and MTL appeared to have strong stretching vibration peaks which were attributed to phenol C–O functional groups in the molecule. The vibration absorption peak intensity of MTL was stronger than that of lignin, suggesting that the content of phenol C–O functional groups in MTL increased. There were outward bending absorption peaks between $900 cm^{-1}$ – $700 cm^{-1}$ and the absorption peak strength of lignin was greater than that of MTL, which disclosed that there were aromatic hydrocarbon C–H functional groups in lignin and MTL, also suggesting that there existed higher content of aromatic hydrocarbon C–H functional groups in lignin. Moreover, there were also stretching vibration peaks in the frequency range of $750 cm^{-1}$ and $550 cm^{-1}$, implying that both lignin and MTL had phenolic O–H functional groups. At this stage, the absorption peak of MTL was stronger than that of lignin, which proved that there were plenty of phenolic O–H functional groups in MTL. The results of FT-IR analysis demonstrated that the structure of MTL was more stable than raw lignin, which might be illuminated by the repolymerization of unstable free radicals such as O–CH₃ and phenolic O–H during microwave-assisted thermal depolymerization of lignin, so less repolymerization will occur in further pyrolysis reaction (Li et al., 2007; Renders et al., 2017).

3.2. The effect microwave torrefaction has on product distribution during microwave co-pyrolysis

Fig. 1 shows the effect of microwave torrefaction on product yield distribution during microwave co-pyrolysis of lignin and LDPE, results indicated that the bio-oil yield had a slight decrease for bio-oil obtained from co-pyrolysis of MTL and LDPE comparing with MTL pyrolysis independently (~17% vs. 20%). The yield of syn-gas increased with the addition of LDPE into MTL in the pyrolysis process, however, no significant difference was observed for volatiles yield (the yield of bio-oil and syn-gas) for MTL pyrolysis independently and MTL co-pyrolysis with LDPE, which might be illuminated by the competitive reaction between liquid and gas (Bu et al., 2016). As a result of this, the syn-gas derived from co-pyrolysis increased from 36.13% to 38.90%. The existence of LDPE during pyrolysis may be able to generate more non-condensable gases such as H₂ and short chain olefins (Zhang et al., 2016b).

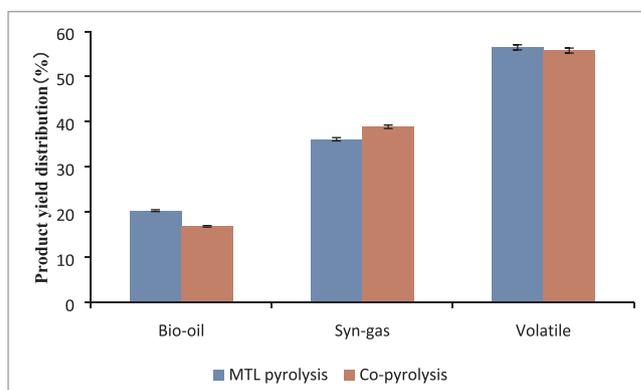


Fig. 1. Product yield distribution of MTL under different reaction conditions.

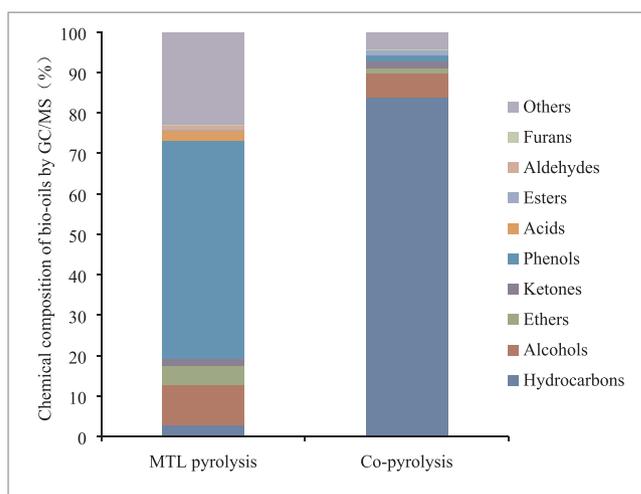


Fig. 2. Chemical composition of bio-oils from MTL under different reaction conditions by GC/MS analysis.

3.3. GC/MS analysis of bio-oil

Fig. 2 shows the GC/MS analysis results for the chemical composition of bio-oils from MTL under different reaction conditions. The typical composition of bio-oils include aldehydes, ketones, carboxylic acids, esters, ethers, phenols, alcohols, hydrocarbons, furans, and some unclassified compositions. Results showed that the major chemical compounds of bio-oils were hydrocarbons, phenols, alcohols, ethers and acids, which approximately accounted for 77–95% of the bio-oils. The content of phenols was the highest up to 53.78% in pyrolysis of MTL, while the content of hydrocarbons was only 2.93%. In comparison, the hydrocarbons content from MTL co-pyrolysis with LDPE significantly increased to 83.86%. The main components of hydrocarbons were long-chain hydrocarbons, such as 1-Tridecene, 3-Tetradecene, (E)-, and cyclic hydrocarbon, such as Naphthalene and Cyclopropane. It was noticed that phenols content decreased significantly from 53.71% for microwave pyrolysis of MTL to 1.37% for microwave co-pyrolysis of MTL and LDPE. The chemical selectivity indicated that most phenols were phenols monomers such as phenol, guaiacols and their derivatives. This might be explained that most of phenolic monomers were converted to hydrocarbons and aromatic hydrocarbons during co-pyrolysis reaction under the performance of hydrogen donor from the cracking of LDPE. Alcohols were another important component in the obtained bio-oils. The content of alcohols for bio-oil from MTL pyrolysis and MTL and LDPE co-pyrolysis was 9.80% and 6.02%, respectively, most of which were long chain aliphatic alcohol and Benzofuranol. The results revealed that in the bio-oil obtained from MTL pyrolysis, the acid content was up to 2.61%, while the acid content in the bio-oils from

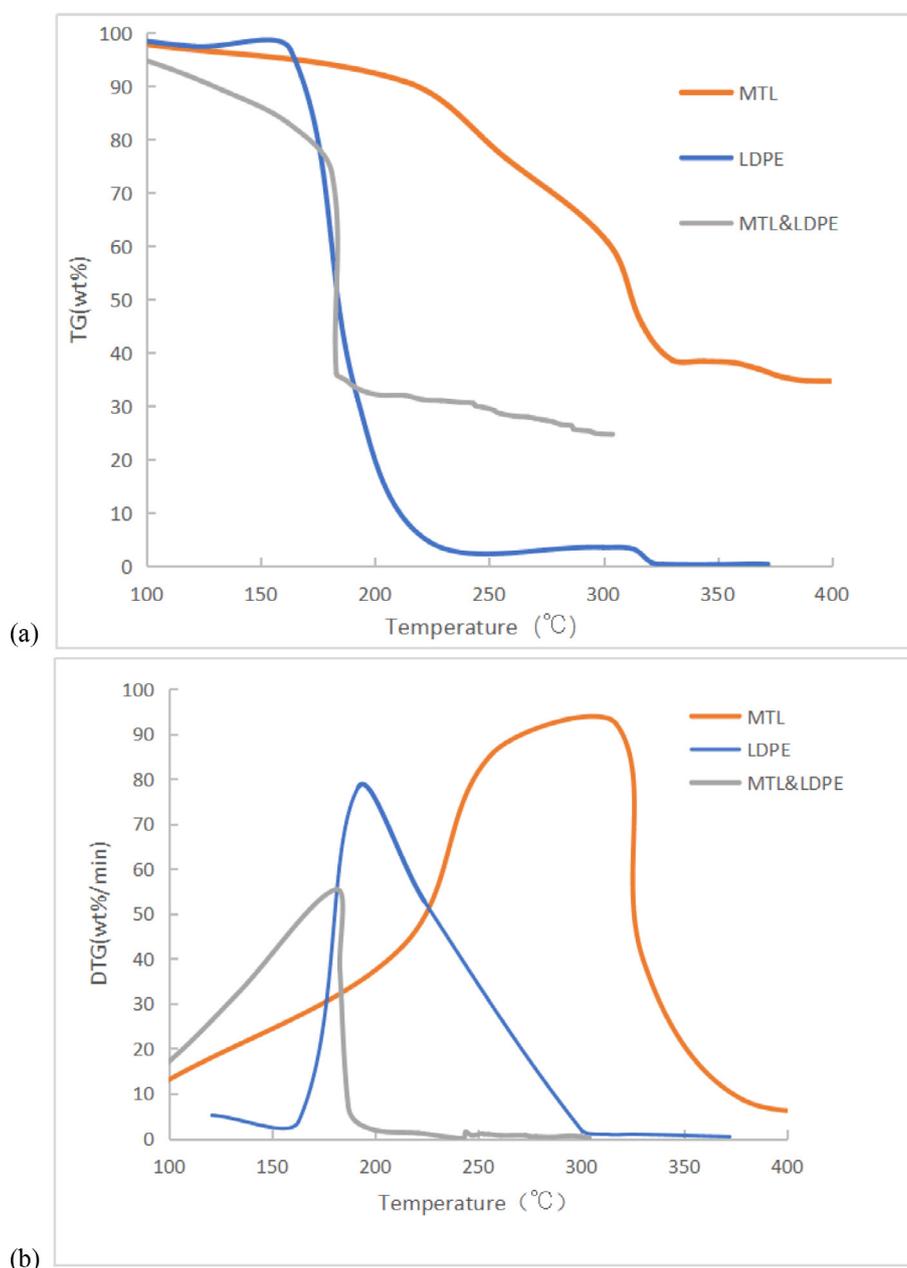


Fig. 3. (a) Thermogravimetric (TG) curves for MTL under different microwave pyrolysis conditions; (b) Derivative thermogravimetric (DTG) curves for MTL under different microwave pyrolysis conditions.

co-pyrolysis was significantly lower (0.15%). On the base of GC/MS results, the addition of LDPE in MTL pyrolysis could significantly increase the hydrocarbons content and reduce the phenols in the bio-oils.

Besides, aromatic hydrocarbons all accounted for a large part of hydrocarbons in the obtained bio-oil. With the addition of LDPE during MTL pyrolysis, the content of aromatic hydrocarbons dramatically increased to 22.83% from 1.94% of the bio-oil. High selectivity to aromatic hydrocarbons should have a close relationship with the co-feeding of LDPE during microwave co-pyrolysis of MTL and LDPE (Zhang et al., 2016b). GC/MS analysis disclosed that the aromatic hydrocarbons were mainly composed by alkyl derivatives of Benzene, Naphthalene and its alkyl such as methyl and ethyl derivatives. In bio-oil obtained from co-pyrolysis of MTL and LDPE, the selectivity for alkyl derivatives of Benzene and Naphthalene and its derivatives was 26.11% and 44.5%, respectively.

3.4. Thermal degradation behavior analysis

Fig. 3 shows the thermogravimetric (TG) curves and derivative thermogravimetric (DTG) curves for MTL, LDPE, MTL and LDPE under different pyrolysis conditions by microwave-assisted heating. In the process of MTL pyrolysis and its co-pyrolysis with LDPE using microwave thermogravimetric analyzer, it was observed that there was no change for the recorded temperature when pyrolysis temperature reached 400 °C, which might attribute to that the pyrolysis of all samples completed at this time. Besides, the weight loss of MTL or MTL co-pyrolysis with LDPE was almost ignorable due to that lignin was pre-treated via microwave torrefaction at 200 °C. As a result, the reaction temperature of thermal degradation behavior analysis was in the range of 100–400 °C as shown in Fig. 3. Fig. 3(a) gives TG curves of different samples by thermogravimetric analyzer. It revealed the smooth thermal decomposition process of MTL individually, mainly in the temperature range of 150–350 °C, which kept about 40% solid residue; The thermal

Table 1
Kinetic parameters of different samples.

Sample	Reaction order (n)	E	ln A	R ²
MTL	1	21.51	-3.83	0.91
	2	38.27	1.23	0.83
	3	64.35	7.63	0.93
LDPE	1	43.82	3.31	0.81
	2	81.83	14.87	0.88
	3	149.67	34.76	0.96
MTL & LDPE	1	29.06	0.18	0.84
	2	53.39	8.31	0.87
	3	71.86	15.06	0.95

decomposition process of LDPE displayed that the decomposition of LDPE quickly completed within the range of 160–250 °C, however, there was no solid remained in the thermal decomposition process comparing with MTL. It was obviously observed that there were two stages for co-pyrolysis of MTL and LDPE, the thermal decomposition of MTL and LDPE co-pyrolysis mainly occurred in the temperature range of 100–190 °C, the first stage started from 100 to 170 °C, the second stage was from 170 to 200 °C, and the solid residue was about 30%. This might be illuminated by the synergistic effect of LDPE and lignin during co-pyrolysis which shifted the mainly thermal degradation of MTL and LDPE to lower reaction temperature, the addition of LDPE into MTL had a certain role in promoting thermal degradation during microwave pyrolysis.

Fig. 3(b) described the DTG curves of different samples during microwave-assisted pyrolysis. It can be seen from the DTG curves that one smooth and broad peak at the temperature range of 250–320 °C was observed for the DTG curves of MTL pyrolysis. The DTG curve of LDPE pyrolysis only appeared one sharp peak, corresponding to the temperature of 192 °C and the mass loss of 78.17%. The DTG result of MTL and LDPE co-pyrolysis revealed that one peak was at the temperature of 181 °C, and the mass loss was 55.34%. The results indicated that the thermal degradation of MTL was more complex than LDPE and their co-pyrolysis, the addition of LDPE during microwave pyrolysis of MTL caused the temperature to a lower temperature area. These results can be attributed to the synergistic effect between MTL and LDPE during co-pyrolysis, which was in good agreement with previous report (Xiang et al., 2018).

3.5. Reaction kinetics analysis of co-pyrolysis of MTL and LDPE

Kinetic parameters obtained by microwave-assisted thermogravimetric analyzer pyrolysis using Coats-Redfern model to calculate included apparent activation energy (E) and pre-exponential factor (ln A), as shown in Table 1. The kinetic parameters from Table 1 indicated that MTL pyrolysis or its co-pyrolysis with LDPE were both third order reactions, the R² of them was 0.93 and 0.95, respectively, the apparent activation energy was 64.35 kJ/mol and 71.86 kJ/mol, respectively, the pre-exponential factor (ln A) was 7.63 and 15.06, respectively, though the addition of LDPE during MTL microwave pyrolysis increased the activation energy to some extent, it was also observed that there was an obvious increase for the frequency factor with the addition of LDPE compared to microwave pyrolysis of MTL individually. The influence of the change of frequency factor on the rate of decomposition (k) was much more significant than the influence of the change of activation energy, indicating that the addition of LDPE is beneficial for improving the reaction rate of MTL pyrolysis via microwave-assisted heating. This might be explained by a decrease in the reaction rate of other steps with the addition of LDPE, but an increase for the rate of reaction for rate determining step (Bu et al., 2019).

4. Conclusions

In this study, the microwave co-pyrolysis of microwave torrefied lignin with LDPE was investigated, FTIR analysis showed that the microwave torrefied lignin was more stable than raw lignin. GC/MS analysis revealed that the addition of LDPE during microwave pyrolysis of MTL made hydrocarbons and aromatic hydrocarbons dramatically increase to 83.86% and 22.83%, respectively, while phenols were decreased significantly. The reaction rate for co-pyrolysis of MTL and LDPE was improved obviously comparing with MTL pyrolysis individually by microwave-assisted heating.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2019.121860>.

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