Process Optimization of Wood Particles Microwave Pyrolysis with Combined Production of Bio-Oil and Syngas

Sikan Wu*, Bo Chen, Yongyi Song, Xin Wang, Biao Zhang, Liping Zhao, and Kai Qiao
SINOPEC Dalian Research Institute of Petroleum and Petrochemicals, Dalian, LN 116043, CHINA

Abstract: Microwave is an alternative method which can rapidly pyrolyze biomass by thermal treating, and produce clean syngas and bio-oil products. In this research, the wood particles microwave pyrolysis process was proposed for preparing bio-oil and syngas production. The wood particles were first pyrolyzed by microwave reactor in the process, and then the bio-oil products were separated by cyclone separator and multi-phase separator, syngas products were prepared by steam reforming reactor and absorption tower. Kinetics for larch microwave thermogravimetry reactions were proposed and correlated with lab-scale experiments; the microwave pyrolysis process was simulated in Aspen HYSYS, and the results showed that when pyrolysis reaction temperature and microwave power were 900°C and 2.0 kW respectively, the maximum bio-oil and syngas production can be achieved. The H₂/CO and CO₂ content in syngas which can be used in chemical processes such as Fischer-Tropsch synthesis, can be controlled by the molar ratio function of steam and pyrolysis gas.

Key words: bio-oil, syngas, biomass, microwave, process simulation optimization

1 Introduction
The depletion of crude oil resources draws great research attention on renewable energy. Biomass is an alternative energy source because of low sulfur content renewability, and the capability of being converted into bio-fuels, materials or gases with zero carbon footprints. In recent years, significant progress has been made in the development of hydrotreating bio-oil[1], which enable the bio-oil to replace crude oil products. Moreover, the research on high efficiency catalyst is used for the hydrolysis of lignocellulosic biomass, which also has potential in the field of renewable chemical feedstock[2]. However, in addition to environmental pollution, the applications of traditional heating (pyrolyzing) method have problems on low utilization, slow heating speed and non-uniform heating, which affect the quality of products significantly.

Pretreatment has significant role in the conversion of biomass. Structurally, the bottleneck in biomass pyrolysis is mainly due to lignin seals and crystalline nature of cellulose[3]. Nonetheless, research has shown that microwave can significantly decreased parietal cell wall rate[4], which makes microwave pretreatment more economical and less energy consuming. Not only that, as a new thermal technology, microwave has been widely used in various fields[5-7]. The molecular friction caused by the thermal energy of microwave improves the heating speed and uniformity. Conventional studies of microwave pyrolysis of biomass mainly focus on straw[8-10], waste tea[11,12] and wood particles[13,14]; however, those studies only employed microwave as a heat source, few research efforts were spent on the reaction kinetics and process optimization.

The principle of microwave heating is very different from traditional heating, for example, when heating food in a microwave cooking oven, the friction of polar molecules inside the food(mainly water) convert electromagnetic energy into heat, so it is necessary to study the kinetics of microwave heating. By researching the reaction kinetics, the mechanism of microwave pyrolysis can be better explained, which is helpful to optimize the process. In this paper, a chemical process of biomass microwave pyrolysis for bio-oil and syngas production was proposed and opti-
2 Theory

2.1 Reaction networks

In general, plants, microorganisms, animals and their excreta all belong to the category of biomass, each biomass contains different cellulose, hemicellulose and lignin, the composition of products generated by their pyrolysis reaction is also different. Therefore, reasonable selection of biomass species is the key to energy conversion. For example, animal waste contains a certain amount of nitrogen, which is very helpful for the preparation of activated carbon. On the contrary, due to the addition of pesticides and fertilizers in the planting process, straw may lead to the generation of tar and gas. The specific product composition considered. In recent years, many researches have taken pure components such as acid, alcohol and phenol as the model of biological oil\(^{16}\), among which acetic acid is the most representative\(^{17}\). Therefore, acetic acid will also be used in this paper to replace the components of biological oil.

2.2 Reaction kinetics

In this paper, the apparent kinetics model was proposed by analyzing the reaction process. The following kinetic equations are used to describe the weight loss process.

\[ \frac{da}{dt} = k \alpha \]

Where \(a\) is the conversion rate; the reaction rate constant \(k\) can be expressed by the Arrhenius equation.

\[ k = A \exp(-\frac{E_a}{RT}) \]

In the formula, \(A\) is the pre-exponential factor and \(E_a\) is the activation energy. The specific expression of \(f(\alpha)\) can be obtained by analyzing and solving the thermogravimetric (TG) curve. In this paper, Coats-Redfern integration method is used to calculate the above two parameters.

Coats-Redfern integral method is a widely applied method\(^{18,19}\). By assuming the expression of \(f(\alpha)\), it can solve the corresponding pre-exponential factors, reaction series and activation energy by TG curve.

One of the more common approach is to assume that \(f(\alpha) = (1 - \alpha)^n\), consider the heating rate \(\beta = \frac{dT}{dt}\), and then combine the equation (1) and (2)

\[ \frac{da}{dt} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) (1 - \alpha)^n \]

Take the logarithm of the left and right sides of the equation, after integration and phase shift, it can be obtained

When \(n \neq 1\)

\[ \ln\left[\frac{1 - (1 - \alpha)^{1-n}}{T^n(1-n)}\right] = \ln\left[\frac{A R}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \]

When \(n = 1\)

\[ \ln\left[-\ln(1 - \alpha)\right] = \ln\left[\frac{A R}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \]

For the reaction temperature region and activation energy \(E_a\) investigated in this experiment, \(2RT/E_a\) is much smaller than 1, so \(\ln[AR/(\beta E_a) (1 - 2RT/E_a)]\) in the right term of equation (4) and (5) can be regarded as a constant. In a general pyrolysis test, because the heating rate is controllable, \(\beta\) may be considered a constant. However, in the process of microwave pyrolysis, due to the influence of microwave power, the heating rate of biomass will fluctuate with the change of power. To explore the linear relationship between \(1/T\) and \(\ln\left[(1 - (1 - \alpha)^{1-n})/(T^n(1-n))\right]\) or \(\ln\left[(-\ln(1 - \alpha))/T^n\right]\), and then to fit the linear slope \(-E_a/R\) and intercept \(\ln[AR/(\beta E_a) (1 - 2RT/E_a)]\) to obtain the activation energy \(E_a\) and pre-exponential factor \(A\) respectively, the mathematical relationship between microwave power and heating rate should be proposed.

![Fig. 1 Reaction networks of biomass pyrolysis.](Image)
2.3 Process design of pilot-scale plant

Figure 2 was a design diagram of the process flow diagram of HYSYS. In process, the biomass pyrolysis will produce a certain amount of bio-char, and steam reforming reaction is a strong endothermic reaction. Considering the influence of energy consumption on economy, biomass pyrolysis reaction and steam reforming reaction can generally be carried out simultaneously in the same reactor. However, for controlling steam and raw material to facilitate the statistics of the process energy consumption, two modules Plug Flow Reactor (PFR) and Conversion Reactor (CR) were used to represent the two reaction processes in this study. PFR is designed for the known chemical and kinetic equation, which is suitable for biomass pyrolysis reaction to calculate the conversion rate. CR can simulate the steam reforming reaction by the metric relation in the chemical equation. In addition, due to the large microwave power required by pilot-scale, a single microwave source is not sufficient, incoherent combination technique of microwave power is applied in this study, and structure diagram of microwave reactor is shown in Fig.S1.

The raw materials were fed into the microwave reactor for pyrolysis reaction. Due to the high reaction temperature, the biological oil and pyrolysis gas will be transported into Multiphase Separator, and the bio-char generated by pyrolysis will be separated by Cyclone Separator. Bio-oil gradually condenses in the heat exchanger due to the decrease of temperature. Bio-oil products were separated through Multiphase Separator, and solid particles carried in the gas phase were also separated. The separated solids and gases together with steam entered the reforming reactor. At high temperature, the bio-char and steam may involve the following main reactions:

\[ C + H_2O = CO + H_2 \]  

CO + H_2O = CO_2 + H_2 \tag{7} 

C + CO_2 = 2CO \tag{8}

The bio-char was converted into H_2 and CO in the steam reforming reaction, which has the advantage of increasing the carbon conversion rate and the H_2/CO in the syngas. The reformed gas enters the absorption tower to remove CO_2, then the syngas products can be prepared by Separator.

Fischer-Tropsch synthesis is a process in which liquid hydrocarbons or hydrocarbons are synthesized from syngas under catalyst conditions. Too low H_2/CO and excessive CO_2 concentration will affect this process. Therefore, the reaction process established in this study requires that the H_2/CO of syngas is about 2 and the CO_2 concentration is less than 10 ppm.

3 Experimental

3.1 Sample preparation

The experimental larch waste samples were from Qingshan Forest Farm in Yichun, China. The samples were crushed and sieved into 20-40 mesh particles, and then placed in an air-dry oven and dried at 105°C for 24 h to remove moisture.

Table 1 showed the industrial analysis and elemental analysis before and after pyrolysis of the sample. It can be seen from the table that the volatiles of wood particle raw material are as high as 78.03%, which makes it easy to generate combustible gas and liquid during pyrolysis. It is conducive to the preparation of bio-oil and syngas products from biomass. From the perspective of elemental analysis, larch particles have a carbon-oxygen ratio close to 1, and a
certain amount of hydrogen, which has a very important influence on the preparation of CO and H₂ in the syngas. By comparing the industrial analysis and elemental analysis data, it can be seen that larch has a good effect on the preparation of syngas and biological oil products by pyrolysis. The analysis of the structure of bio-oil products, which is shown in Fig. S2-S4, also be proved that the bio-oil produced by microwave heating is a good and easily modified liquid fuel.

3.2 Thermo gravimetric experiment

Figure 3 are the photos and schematic diagram of microwave thermogravimeter used in this study. This equipment is the Mobile Lab Workstation series microwave materials

| Table 1 | Industrial analysis and elemental analysis of larch particles. |
|---------|---------------------------------------------------------------|
|         | Industrial analysis (%) | Elemental analysis (%) |
|         | M₀ | A₀ | V₀ | FC | C  | H  | O  | N  | S  |
| before  | 6.59| 1.70| 78.03| 13.68| 44.97| 5.41| 41.01| 0.24| 0.08|
| after   | 5.16| 6.60| 2.66| 85.58| 84.06| 0.94| 2.84| 0.32| 0.08|

Fig. 3 Microwave thermogravimeter. a: external; b: internal; c: schematics.
experiment platform produced by Tangshan Nayuan Microwave Thermal Instrument Manufacturing Co., Ltd. Different from traditional thermogravimeter, microwave thermogravimeter adopt microwave as heating method, which is mainly used for the investigation of biomass pyrolysis kinetics under microwave heating condition. The TG curve of biomass pyrolysis can be obtained by the equipment, where TG curve represents the change of wood particle mass with temperature.

Since the ability of a material to absorb microwave is determined by its dielectric properties and the average power of microwave, the functional relationship is given by

$$P_{av} = \omega \varepsilon_0 \varepsilon''_{eff} E V$$

Where $P_{av}$ is the average absorbed power; $\omega$ is the angular frequency (rad/s); $\varepsilon_0$ is the dielectric constant for the free space; $\varepsilon''_{eff}$ is the effective dielectric loss; $E$ is the intensity of the electric field (V/m); $V$ is volume (m$^3$).

Therefore, microwave gravimetric test is different from conventional thermogravimetric method, which requires a certain volume of raw material samples. In this test, 50 g larch particle samples were placed on the triangular bracket of the microwave thermogravimeter balance. After the balance value was stable, the high-temperature thermocouple was inserted and the top screw was locked to ensure the microwave cavity is completely sealed. An inert gas of 0.05 ml/min was then injected from the top gas inlet for 10 min. Set the microwave power required for the test, turn on the microwave power switch, and record the weight loss rate of the sample.

3.3 Model Correlation

Figure 4 showed TG curve and heating curve of pyrolysis of wood particles at different power. It can be seen from Fig. 4 that 200°C-600°C is the main weight loss temperature zone of larch particles under different power microwaves.

Because larch particles contain a certain amount of ash, the weight loss rate of larch particles is about 90% in this temperature zone without ash. Although the trend of each thermogravimetric curve and the residual weight are roughly the same under the different microwave powers, the heating rate generally increases with the increase of power. Considering the influence of heat transfer hysteresis effect, the initial weight loss temperature of the TG curve in Fig. 4 is constantly shifted to the right. The calculation of the narrow temperature range is mainly concerned with the major weight loss region of the biomass, and therefore an expression of the heating rate $\beta$ in this region needs to be established.

Since the temperature changes with time in the major weight loss zone shows a trend similar to the linear relation. In order to facilitate the fitting of the kinetic equation, cubic spline difference method is adopted for the relational expression between time and temperature in Table 2. The slope in the relational expression is the heating rate $\beta$ in the narrow temperature range used to calculate the kinetics.

The results of biomass thermogravimetric experimental data are shown in Fig. 5. It is obvious that the main stages of biomass pyrolysis reactions are suitable for the descrip-

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**Table 2**  The change of temperature with time at each power.

| Microwave power | Relational expression | Temperature range |
|-----------------|----------------------|------------------|
| 0.5 kW          | $T = 1.4766t - 93.74380$ | $317.2^\circ C < T < 616.3^\circ C$ |
| 1.0 kW          | $T = 1.4947t - 242.1636$ | $215.4^\circ C < T < 648.2^\circ C$ |
| 1.5 kW          | $T = 1.7923t - 147.5517$ | $185.9^\circ C < T < 712.2^\circ C$ |
| 2.0 kW          | $T = 1.7842t - 39.5210$  | $337.0^\circ C < T < 687.9^\circ C$ |

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Fig. 4  Experimental results of wood particles at different microwave power. a: Thermogravimetric curves; b: heating curves.
tion of first-order kinetics.

The first-order kinetic fitting of biomass pyrolysis is shown in Table 3. The linear correlation coefficients of the regression equations obtained are all above 0.9, the result is credible.

4 Results and Discussion

After obtaining the characterization kinetics of biomass pyrolysis, the reaction at different powers can be simulated by PFR in Aspen HYSYS. Considering the process economy, due to the high energy consumption of microwave, and the synthesis gas prepared needs to adjust H₂/CO through steam reforming, the water and electricity consumption of the whole process is a relatively concerned standard. For products, the production rate of biological oil and the quality of syngas are two important indicators. Especially for syngas, the application of Fischer-Tropsch synthesis has certain requirements for CO₂ content and H₂/CO.

### 4.1 Calculation and optimization

Comparing the results of different reaction temperatures and microwave power, the basic parameters of the simulation process were listed in Table 4. All simulation results discussed in this paper were based on it.

Figure 6 showed the simulation results of the amount of bio-oil and syngas products prepared at different reaction temperatures. When the microwave power is low (< 1 kW),
Biomass pyrolysis produces few products and hardly changes with temperature. When the microwave power is high (>1 kW), the amount of bio-oil and syngas produced increases with temperature and power. Because of high pyrolysis temperature, biomass rapidly gasifies and generates bio-char. Under high temperature, the microwave absorption performance of bio-char is far greater than that of biomass itself. Therefore, biomass can be further gasified. The bio-oil produced will be partially pyrolyzed and can also promote the increase of gas volume. Therefore, to prepare more target products, it is necessary to control the reaction temperature and microwave power.

Table 5 showed the product yield at the optimum temperature of different microwave power. Figure 7 showed the simulation results of the flow ratio of steam to gas required to adjust H2/CO at different reaction temperatures with different power. It can be seen from the figure that the effect of microwave power on the amount of steam is much larger than the reaction temperature. When the microwave power is low (≤1 kW), the simulation results show that the reaction of biomass microwave pyrolysis is incomplete, resulting in low H2 content in the gas. At this time, the steam flow required for H2/CO regulation of syngas decreases with the increase of microwave power. When the microwave power is high (>1 kW), as the increase of microwave power leads to the increase of gas production, the pyrolysis bio-char content is reduced, and the limit value of H2/CO is reduced too. Therefore, if a higher H2/CO ratio of 2 with <10 ppm CO2 content, it is necessary to ensure a molar ratio of steam to gas products of 0.335.

### 5 Conclusion

In this paper, the kinetics of larch under different microwave powers were correlated by microwave thermogravimetry, and a technological process for preparing bio-oil and syngas from wood particles by microwave pyrolysis was designed. To explore the optimal technological conditions of the process, Aspen HYSYS was used to optimize the process. Since microwave reactors and steam reforming reactors need to consume electricity and steam in the process, the water and electricity energy consumption is the focus of optimization.

Microwave power, reaction temperature and the molar ratio of steam to product gas were investigated. The pyrolysis reaction temperature and microwave power of 900°C and 2.0 kW, respectively, are excellent process conditions, at which time the maximum bio-oil and gas production can be obtained. The H2/CO and CO2 content in syngas can be controlled by the molar ratio function of steam and pyrolysis gas. In this case, to obtain a synthesis gas having a H2/CO ratio of 2 with <10 ppm CO2 content, it is necessary to ensure a molar ratio of steam to gas products of 0.335.

### Acknowledgements

The authors would like to thank the financial supports from Natural Science Foundation of China (Grant Nos. 61671319 and 61627803) and National Key R&D Program of China (Grant Nos. 2018YFA0209400 and 2018YFA0209404).
Fig. 7  Simulation results of steam at different reaction temperatures. a: 500°C; b: 600°C; c: 700°C; d: 800°C; e: 900°C.

Supporting Information
This material is available free of charge via the Internet at http://dx.doi.org/jos.69.10.5650/jos.ess20011

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