# CHARACTERISTICS AND KINETICS OF BIOMASS PYLOLYSIS IN A MICRO FLUIDIZED BED REACTOR

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# CHARACTERISTICS AND KINETICS OF BIOMASS PYLOLYSIS

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**Abstract:** A Micro Fluidized Bed Reactor (MFBR) was developed to enable on-line pulse feeding and isothermal differential reaction of particle reactant. Application of the MFBR to biomass pyrolysis demonstrated that the resulting globe kinetics parameters were 11.77 kJ/mol and 1.45 $s^{-1}$ on the gas release characteristics, respectively.

**Keywords** Micro fluidized bed; Reaction kinetics; Biomass, Pyrolysis

## Introduction

Biomass is a renewable, $CO_2$-neutral energy resource, widely available and increasingly used as an alternative to fossil fuel for energy supply. The thermal conversion of biomass to produce fuel gas (mainly CO and $H_2$) via gasification, of which pyrolysis is the first step, is considered as a very promising process. However, biomass pyrolysis, or devolatilization, in general involves a complex set of chemical reactions, often influenced by physical transport processes. Identification and modeling of this important chemical and physical rate processes for different conditions are the basis for fundamental research and technology development of biomass thermal conversion.

By far, thermogravimetric (TG) was widely adopted to deduce the reaction kinetics through measuring the mass loss of a sample in the TG cell during a specified heating program. Many researchers revealed pyrolytic kinetics of different biomass using TG with different heating rate. The measurement might be differentiated the pyrolytic process of different components with low heating rate. However, it suffers seriously from the external gas diffusion in TG instrument. Meanwhile, the biomass fuel is essentially unsuitable to be tested in TG because the composition of the sample changes quickly with raising temperature in heating and the thermal conversion of biomass was usually carried out in fluidized bed reactor. Consequently, scientists designed various reactors other than TG to study the kinetics and reaction features of biomass pyrolysis, which includes mesh reactor [1], self stirred tank reactor[2] and fluidized /fixed bed reactors [3,4] of millimeters in diameter. These reactors, however, do not have standardized configuration and suffer still seriously from the influences of gas mixing and gas diffusion because the

reactors are usually too large to ensure the characteristics of micro reaction.

In this study, the Micro Fluidized Bed Reactor Analyzer (MFBR), which was developed in our previous research [5], was applied to biomass pyrolysis to investigate gas release characteristics at different reaction conditions. Meanwhile, the corresponding pyrolytic kinetics was also calculated on the characteristics of total gas products release.

## Experimental Section

**Beer lees Characteristics.** Beer lees from Beijing Beer Co. was studied. The same material was used by Hu et al. [6] in investigations of decoupling gasification behavior and the effects of mineral material during gasification. Table 1 presents the proximate and ultimate analysis for the particular sample of beer lees.

Table 1　Properties of the Beer lees

| Particle size | Proximate analysis（wt.%） | | | Ultimate analysis（wt.%） | | | |
|---|---|---|---|---|---|---|---|
| | $V_d$ | $A_d$ | $FC_d$ | $C_d$ | $H_d$ | $N_d$ | $O_d+S_d$ |
| 75-125 μm | 79.9 | 3.93 | 16.17 | 48.74 | 6.73 | 4.58 | 39.95 |
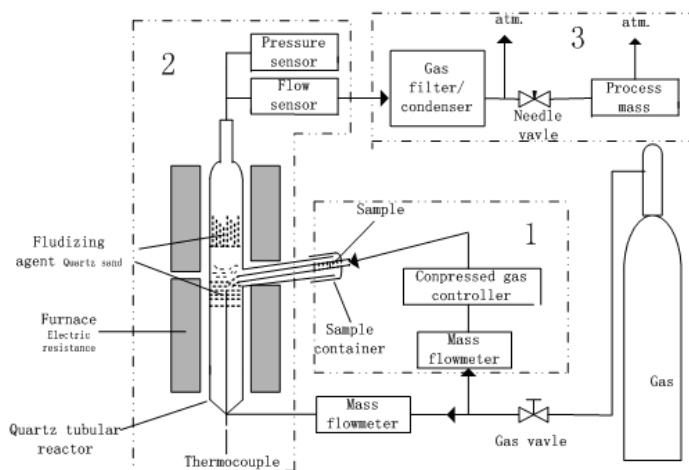


1: solid sample jet-transfer device; 2: micro fluidized bed reactor; 3: gas cleaning and determination

Figure 1　Schematic diagram of the experimal apparatus

**Apparatus and Procedure.**　Figure 1 shows a schematic diagram of the experimental apparatus. Experiment was performed generally with the following procedure. Three grams of quartz sand was put into each layer of the reactor, while the top layer was replaced from quartz sand to γ-$Al_2O_3$ (BET: 250$m^2$/g; average pore diameter: 7nm) with same particle size and volume in the carbon balance test using air as fluidizing gas. The sand particles were fluidized with a controlled fluidizing gas stream from 100 to 600 NmL/min at a temperature below 950℃. A 10-50 mg sample was then injected into the inside of the hot fluidized quartz sand particles with turbulent motion to initiate the reaction. Carbon combustion, as biomass pyrolysis

completed, was carried out at 800℃ by switching fluidizing gas from Ar to air. The carbon of char was calculated through the increment of $CO_2$ in off-gas. All the gas products could also be collected in the whole reaction stage using a gas bag and analyzed by GC (Micro GC 3000, Agilent).

**Results and Discussion**

**Carbon balances.**　It is difficult to do mass balance calculation because only the gas products were directly determined, leaving a considerable quantity of tar and ash unaccounted for. Carbon balance tests, as mentioned above, were carried out at 800℃ in the air atmosphere. The fluidized agent in the top layer of fluidized bed had replaced to γ-$Al_2O_3$ with high surface area and mesoporous structure to capture large molecules to minimize the formation of tar. The yield of carbon varied from 97% to 105%, as shown in Tab. 2, with changing of sample mass and gas flow rate. This suggests good stability and reproducibility of experiments in MFBR.

Table 2 Carbon yield of biomass combustion in MFBR

| Sample mass (mg) | Gas flow rate (NmL/min) | Yield C % |
|---|---|---|
| 20.5 | 100 | 103 |
| 23 | 200 | 105 |
| 30 | 300 | 97 |
| 20 | 400 | 101 |
| 25 | 500 | 98 |
| 30 | 600 | 99 |

**Influence of reaction temperature**

　　The pyrolysis of beer lees in MFBR was performed from 600-900℃ with flowrate of 300 NmL/min. The release patterns of the main gases differ noticeably from the experiments at fixed bed reactor with a slow heating rate. As shown in Fig. 2, the complete reaction time was greatly reduced with reaction temperature increasing. Meanwhile, the gas products were almost released at the same time except the early release of $CO_2$ at low temperatures, which suggests that the heating rate increased at high temperatures resulting in the lignin, hemicellulose and cellulose almost pyrolyzing simultaneously. The pyrolysis was completed in 10 s as reaction temperature exceeding 800 ℃, which was much shorter than the experiment in fluidized bed reactor with 80 mm diameter. These results also justified the fast reaction in MFBR for higher heating rate than that of large scale fluidized bed reactor.

　　The gas products were collected during the whole reaction, then analyzed using Micro GC. The results were illustrated in table 3. It was obviously that, as shown in this table, the total yield of gas products increased from 18.48 wt. % to 51.49 wt.% with temperature increasing, especially for CO, accounting for 50% of total gas yield,

exhibited larger increase extent. However, the yield of $CO_2$ changed slightly and maintained around 8 wt.% from temperature 700 to 900℃, which represents the carboxyl or ester functional group could completely degrade at high temperatures. The yields of hydrocarbon compounds (C1-C3) increased from 4.71 to 11.68 wt. % with the increase of temperature from 600 to 800℃, while decreased to 10.49 wt. % at 900℃. The variation trend of hydrocarbon compounds' yields elucidates that high temperature promote the cracking of tar to form hydrocarbons, while the cracking rates of hydrocarbons are also increased, especially when temperature exceeded 800℃. Hydrogen was definitely increased with temperature increasing for both cracking of tar and gas products. The high yields of gas during the pyrolysis were due to higher heating rate and good mass transfer of MFBR.
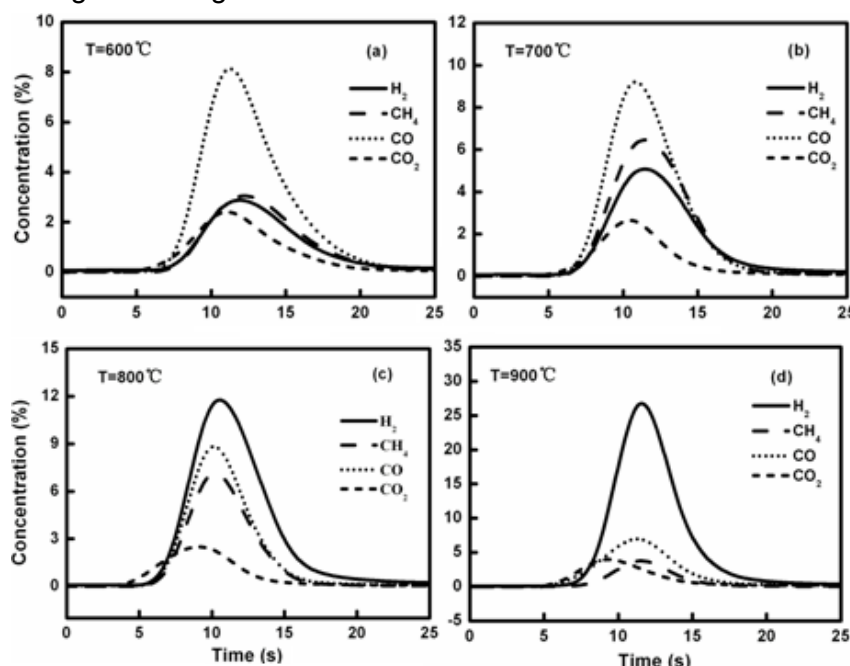


Figure 2 Gas release characteristics in MFBR

Table 3 Products distribution at different temperature

|  | Pyrolysis Yields wt.% lees | | | |
| --- | --- | --- | --- | --- |
|  | 873K | 973K | 1073K | 1173K |
| H2 | 0.10 | 0.32 | 0.75 | 1.67 |
| CO | 7.45 | 19.90 | 23.70 | 31.32 |
| CO2 | 6.22 | 7.81 | 9.10 | 8.01 |
| C1-C3 | 4.71 | 11.64 | 11.68 | 10.49 |
| total permanent gas | 18.48 | 39.67 | 45.23 | 51.49 |
| Carbon in remains | 10.23 | 9.49 | 6.40 | 5.84 |

The carbon yields in remains at different temperatures were obtained using combustion method by instantaneous switching Ar to air at 800℃ and calculated

through the increment of CO and $CO_2$ in the total gas. The carbon yields in remains decreased from 10.23 to 5.84 wt. % with temperature increasing, which were much smaller than fixed carbon of biomass(16.17 wt.%), suggesting more volatiles discharged in these reaction conditions. It is demonstrated that good mass transfer and higher heating rate promote the biomass pyrolysis and release of volatiles.

**Influence of flowrate of fluidizing gas**

Figure 3 shows the total gas conversion versus reaction time at different fluidizing gas flowrates below terminal velocity of quartz. The complete reaction time decreased with flowrates increasing, and achieved to 10 s as flowrate exceeding 300 NmL/min at 800℃. It is obvious that, the reaction rate could be expressed by the slope of curve, the slop of curve changed slightly at high flowrates, which represents the high gas velocity accelerates the reaction rate and greatly weakens the limitation of external diffusion.
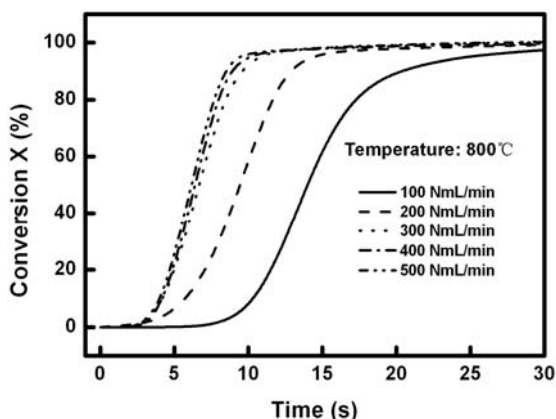


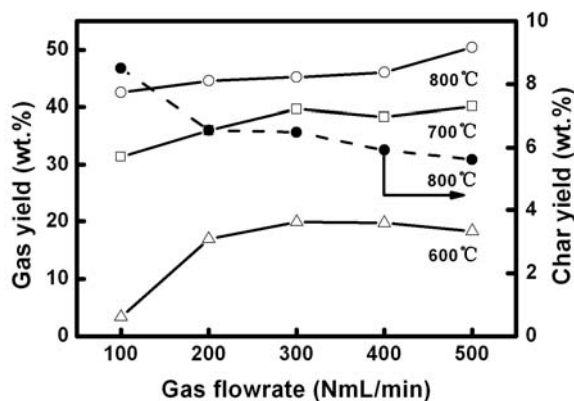Figure 3 Relative conversion vs reaction time in MFBR at different



Figure 4 Products yields versus gas flow rates in MFBR

Figure 4 shows the gas yields variation versus flowrates at different temperature. The gas yields increased with reaction temperature increasing for high temperature promoting the pyrolysis of biomass and the second pyrolysis of tar, which was also illustrated in table 3. Meanwhile, as shown in figure 4, the gas yields were also influenced by the flowrates of fluidizing gas. For example, at 600℃, the yield was only 3.38 wt. % at 100 NmL/min, a big increase to 16.92 wt. % at 200 NmL/min, and then changed slightly as flowrates exceeding 300 NmL/min. The possible reason was that quartz in MFBR could not fluidized well with 100 NmL/min at 600℃, superficial gas velocity (0.014 m/s) < Umf (0.022 m/s), which might resulted in the lower heating rate of beer lees in this operating conditions. The above both reasons resulted in the decrease of gas yield at lower flowrates. Meanwhile, at high temperatures, the yields of gas changed slightly with flowrates increasing, which suggests that the influence was reduced for the almost same fluidizing state at these flowrates. The carbon yields in remains, which was calculated on the amount of $CO_2$

by combustion of the pyrolysis remains, were decreased from 8.50 to 5.62 wt.% with fluidizing gas flowrates increasing at 800 ℃. These results were also suggest that the high gas velocity promote the violate transfer resulting in less carbon remaining, which was more closed to real situation in fluidized bed reactor.

**Calculation of pyrolytic Kinetics of beer lees**

The pyrolysis kinetics of beer lees in MFBR was calculated using the release characteristics of mono-gas component and total gas at 500-900 ℃ with flowrate of 300 NmL/min. For micro-fluidized bed reactor the diffusional and non-isothermal effects can be negligible in these conditions so that the pyrolysis reaction in the MFBR can be considered to be under isothermal conditions. Conversion of beer lees pyrolysis (X) was calculated by

$$X = \left. \int_{t_0}^{t} C_i \times u dt \middle/ \int_{t_0}^{t_e} C_i \times u dt \right. \times 100\% \quad , \tag{3}$$

where Ci denotes the concentration of gas (i) or total gas, u refers to the flow rate of effluent gas, and $t_0$, t and $t_e$ represent the initial stage (time 0), time t and end stage, respectively.

The kinetic parameters of biomass pyrolysis reaction in isothermal process, as lot of literature reports [5,6], were generally calculated using the shrinking core model. This model suggests that the reaction rate can be related to the unreacted surface area or remaining amount of reactant. The model can be expressed with Eq. (4), where n is the reaction order and k(T) is the reaction rate constant defined by the Arrhenius equation (5):

$$dX/dt = k(T) \times (1-X)^n \quad , \tag{4}$$

$$\ln(k(T)) = \ln(A) - \frac{E}{RT} . \tag{5}$$

**Globe gas kinetics**

Figure 5 converts the data of conversion versus reaction time into the correlation of ln(dX/dt) and ln(1-X). The entire curve for a given temperature can be divided into three parts denoting three reaction stages. The first part (right side) belongs to the sample heating stage. As pyrolysis was complete on the surface, a layer of carbon and ash were formed around the biomass particle, the reaction shifted into the second stage, the major period to implement the decomposition. Once the intra-particle gas diffusion completely controlled the reaction and the reactant was close to complete depletion, the reaction rate decreased to the minimal value with the progress of reaction. This refers to the start of the third reaction stage.
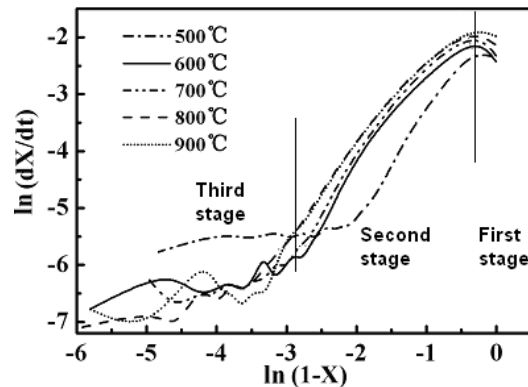
Figure 5 Correlation of ln(dX/dt) and ln(1-X) for total gas in MFBR.

The data of the second reaction stage shown in Fig. 5 are subject to a good linear fitting of ln(dX/dt) with ln(1-X) to define the reaction order n and rate constant k(T) for different temperatures (illustrated in Tab. 4), which shows that a linear correlation coefficient r reached 0.99 for all temperatures.

The apparent activation energy and frequency factor of the globe kinetics was also calculated using Arrhenius equation on the reaction constants at different temperatures. The E and A are 11.77 kJ/mol and 1.45 1/s, respectively, which were much lower than TG tested values between 30 and 235 kJ/mol for E, $3.29 \times 10^4$ and $5.98 \times 10^4$ for A. The smaller of activation energy shows that the reaction rates in the MFBR was much faster than in TG, while the much smaller frequency factor represents the effective collision of reactant molecules was greatly reduced resulting in the decrease of probability of secondary reaction, verifying that the MFBR allowed good mass and heat transfer as well as good measurement of the reaction rate and kinetics compared to TG. The kinetics parameters were also slightly less than the values of fast pyrolysis of biomass in large CFB reactor[7], which represents the kinetics in MFBR could reflect the reaction in large fluid bed reactor, meanwhile, also shows good heat and mass transfer for rapid mixing in MFBR.

Table 4   Reaction order and rate constant of gas components

| T (℃) | ln（k(T)） | n | R | Kinetics parameters | |
|---|---|---|---|---|---|
| 500 | -1.47 | 1.86 | 1.00 | E (kJ/mol) | A (1/s) |
| 600 | -1.22 | 1.62 | 0.99 | | |
| 700 | -1.07 | 1.62 | 0.99 | 11.77 | 1.45 |
| 800 | -0.98 | 1.52 | 0.99 | R=.99 | |
| 900 | -0.82 | 1.62 | 0.99 | | |

## Conclusions

In order to overcome shortcomings of thermogravimetric (TG) methods (e.g. not enabling sample feed at a specified temperature and suffering from gas diffusion in

TG cell), the so-called micro-fluidized bed reaction analyzer (MFBR) was developed to be a standard reaction analysis tool for biomass thermal conversion reactions. The combustion of beer lees using mesoporous α-Al$_2$O$_3$ as fluidizing agent justified that the reliability and repeatability of MFBR system. Measurement of pyrolysis of biomass in MFBR identified a time of about 10 s above 800℃ to finish pyrolysis reactions, which is much closer to the theoretically expected time in comparison with the other literature reports from using fluidized beds of tens of millimeters in diameter. Meanwhile, the high gas yields and less carbon in remains during pyrolysis suggest that the excellent mass transfer in MFBR promoted the volatile release and the fast heating rate in MFBR facilitate the biomass pyrolysis and the gas formation.

The globe kinetics parameters on total gas evolution were obtained using shrinking core model, the reaction order was around 1.62, and the activation energy and frequency factor were 11.77 kJ/mol and 1.45 1/s, respectively. The resulting values for the pyrolysis were obviously lower than those measured from TG and fixed bed reactor and slightly lower than those measured from large scale CFB reactor. The suppressed external diffusion limitations and higher heating rate prevailing in MFBR were responsible for all these kinetics parameters. All of these show in fact the capability and superiority of the MFBR for analyzing biomass pyrolysis, and it is believed that these data would provide deep insight into the pyrolysis mechanics. These findings from the biomass pyrolysis in MFBR exhibit a great potential in the thermal conversion of biomass or other fuel.

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