

# Fast Pyrolysis of Biomass in a Spout-fluidized Bed Reactor —Analysis of Composition and Combustion Characteristics of Liquid Product from Biomass

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**Abstract:** In order to gain insight into the fast pyrolysis mechanism of biomass and the relationship between bio-oil composition and pyrolysis reaction conditions, to assess the possibility for the raw bio-oil to be used as fuel, and to evaluate the concept of spout-fluidized bed reactor as the reactor for fast pyrolysis of biomass to prepare fuel oil, the composition and combustion characteristics of bio-oil prepared in a spout-fluidized bed reactor with a designed maximum capacity 5 kg/h of sawdust as feeding material, were investigated by GC-MS and thermogravimetry. 14 aromatic series chemicals were identified. The thermogravimetric analysis indicated that the bio-oil was liable to combustion, the combustion temperature increased with the heating rate, and only minute ash was generated when it burned. The kinetics of the combustion reaction was studied and the kinetic parameters were calculated by both Ozawa-Flynn-Wall and Popescu methods. The results agree well with each other. The most probable combustion mechanism functions determined by Popescu method are  $f(\alpha)=k(1-\alpha)^2$  (400~406 °C),  $f(\alpha)=1/2k(1-\alpha)^3$  (406~416 °C) and  $f(\alpha)=2k(1-\alpha)^{3/2}$  (416~430 °C) respectively.

**Keywords:** biomass; pyrolysis; spout-fluidized bed; liquid product; combustion characteristics

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## 1 INTRODUCTION

Biomass is a kind of widely distributive and environmentally friendly resource and the only renewable energy source that can be converted into liquid fuel. It is becoming a hot topic in the research of seeking alternative energy source to convert low quality and low volumetric energy density biomass resource to high quality and high volumetric energy density liquid fuel by developing appropriate liquefying method<sup>[1-3]</sup>. It is generally agreed that utilizing the biomass energy for preparing liquid fuel through fast pyrolysis is an effective way. Liquid product yield of the pyrolysis of the biomass in a spout-fluidized bed reactor can be obviously increased, compared with the ordinary fluidized bed reactor<sup>[4]</sup>. However, the liquid product is very complex due to the complexity of biomass in composition and structure and the complicated pyrolyzing process<sup>[5]</sup>. In this work, the analysis of composition and combustion characteristics of liquid product prepared in a spout-fluidized bed reactor were conducted in order to provide the fundamental data for

further investigation.

## 2 PRODUCTION OF LIQUID PRODUCT FROM BIOMASS

### 2.1 Experimental Apparatus

In general, pyrolysis of biomass involves three essential factors of high heating rate, medium reaction temperature (about 500 °C) and short residence time of the formed products. A set of experimental apparatus with a spout-fluidized bed reactor was established based on the cold flow experiments for the production of liquid product from biomass. Its structural parameters and flow sheet are featured of a cylindrical shell with 150 mm inner diameter, 1000 mm height of the space over the distributor plate, a  $\phi 45$  mm $\times$ 3 mm draft tube as a conduit inside the bed, and the shell end is a conical header (conical angle 90°).

The experimental tests indicated that the concept of spout fluidized bed and the designed laboratory installation can satisfy the requirements for pyrolysis of biomass<sup>[1]</sup>.

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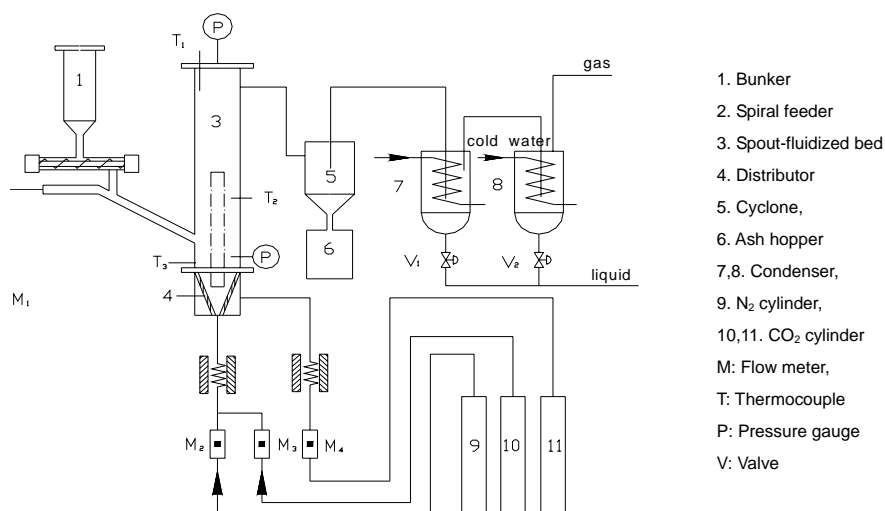


Fig.1 Flow sheet of experimental installation

## 2.2 Characteristics of Liquid Product

The product is featured with the following characters: acidic, dark brown in color, good fluidity and homogeneous, viscosity 40 CP (at 40°C), density 1.24 g/cm<sup>3</sup>, pH value 2.5, water content in the liquid product up to 30%. Table 1 lists the further analytical results. C<sub>d</sub>, H<sub>d</sub>, O<sub>d</sub> and N(S)<sub>d</sub> refer to the weight percentages of carbon, hydrogen, oxygen and total amount of nitrogen and sulfur on dry basis respectively, among which O<sub>d</sub> was calculated by difference. HHV<sub>d</sub>, stands for high heating value on dry basis.

**Table 1** Ultimate analysis of the liquid product

C <sub>d</sub> (%)	H <sub>d</sub> (%)	O <sub>d</sub> (%)	N(S) <sub>d</sub> (%)	HHV <sub>d</sub> (MJ/kg)
46.20	6.97	46.07	0.26	20.01

## 3 COMPOSITION OF LIQUID PRODUCT FROM BIOMASS

The liquid product was analyzed by GC-MS after

dehydration. The total ion flow chromatography is shown in Fig.2, and 14 organic compounds identified are shown in Table 2. They are mostly oxygen-containing aromatic compounds such as phenol, alcohol, fluorene, aldehyde and ketone.

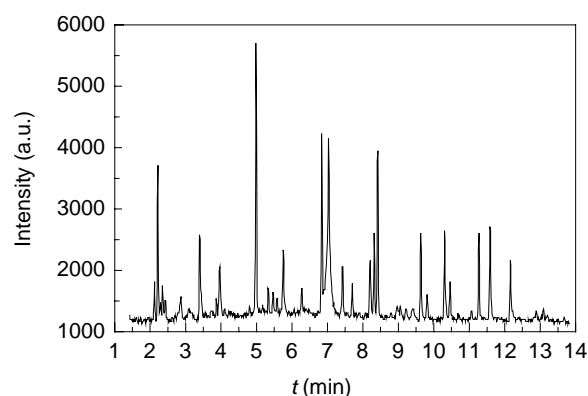


Fig.2 Total ion chromatogram of bio-oil

**Table 2** Organic chemicals in the bio-oil

No.	Chemical	Molecular formula	Molecular weight	Residence time (s)	Content (%)
1	9,9-bis[4-(4-nitrophenoxy)phenyl] fluorine	C <sub>37</sub> H <sub>24</sub> N <sub>2</sub> O <sub>6</sub>	592	4.1	2.77
2	1,2-benzenediol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	110	5.758	7.75
3	2,6-dimethoxy-phenol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	138	7.7	10.54
4	Vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	152	8.3	3.89
5	1,2,4-trimethoxybenzene	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	168	9.1	7.39
6	4'-hydroxy-3'-methoxy-acetophenone	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	166	9.558	2.67
7	4,7-dimethyl-5-decyne-4,7-diol	C <sub>12</sub> H <sub>22</sub> O <sub>2</sub>	198	10.07	3.71
8	1,2,3-trimethoxy-5-methyl-benzene	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	182	10.1	3.44
9	Butylated hydroxytoluene	C <sub>15</sub> H <sub>24</sub> O	220	10.2	6.71
10	2,6-dimethoxy-4-(2-propenyl)-phenol	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	194	11.0	3.73
11	4-hydroxy-3,5-dimethoxy-benzaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	182	11.5	4.77
12	2,6-dimethoxy-4-(2-propenyl)-phenol	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	194	12.333	3.66
13	4'-hydroxy-3',5'-dimethoxy-acetophenone	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	196	12.558	4.59
14	1-(2,4,6-trihydroxyphenyl)-2-pentanone	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	210	12.975	3.54

#### 4 ANALYSIS ON THERMAL CHARACTERISTICS OF THE BIO-OIL

A thermal analyzer (STD 2960, V3.0F, TA Co., America) was used to analyse the thermal characteristics of the bio-oil. The results obtained under the following operation conditions are shown in Fig.3~6:

(1)  $N_2$  atmosphere, 50 mL/min flow rate, and 10 K/min heating rate.

(2)  $O_2$  atmosphere, 50 mL/min flow rate, 5, 10, 20 and 30 K/min heating rates respectively.

Figure 3 illustrates the different behaviors of the bio-oil when subjected to heating in  $N_2$  atmosphere and  $O_2$  atmosphere separately. Below 200°C TG curves are overlapped. This is because in this phase oxidation has not occurred and the process is dominated by vaporization of low boiling point compounds. Both curves show about 50% weight loss. This indicates that the bio-oil contains considerable amount of easily volatile components. Weight loss in  $O_2$  atmosphere is

slightly lower than that in  $N_2$  atmosphere when temperature is between 200 and 400°C. This might be because some  $O_2$  was combined with the biomass, which slowed down the devolatilization process. In this phase, weight loss was about 25%~30%. When temperature exceeded 400°C, the sample weight in  $O_2$  atmosphere was quickly reduced to almost zero within about 3 min while that in  $N_2$  atmosphere was only decreased smoothly and about 13% coke remained when the pyrolysis terminated at 600°C. It is apparent that in this phase the bio-oil was almost completely burned in  $O_2$  atmosphere with minute ash left<sup>[6-8]</sup>, while charring took place in  $N_2$  atmosphere. From Fig.4~6 we can find that peak temperature corresponding to the maximum weight loss rate rises in sequence of 409.55, 419.55, 442.37 and 445.71°C as heating rate rises in the order of 5, 10, 20 and 30 K/min. The peak temperature corresponding to the maximum exothermal peaks rises in the sequence of 426.59, 441.17, 472.29 and 478.26°C as heating rate rises in the same order as mentioned above.

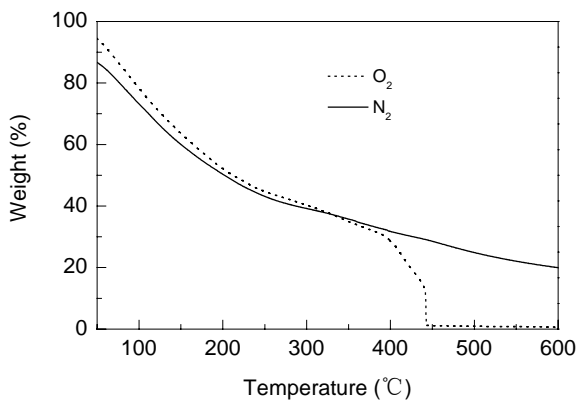


Fig.3 TG of bio-oil (10 K/min)

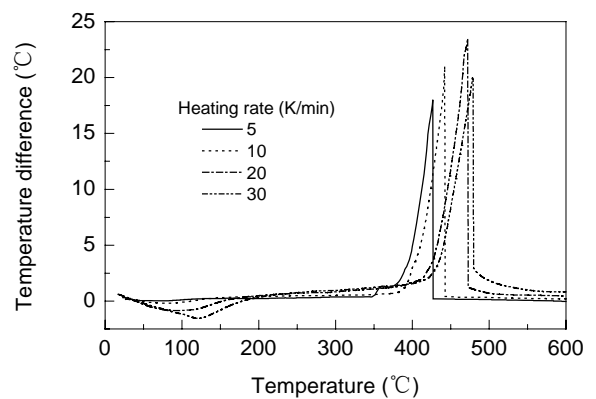


Fig.4 DTA of bio-oil at various heating rate

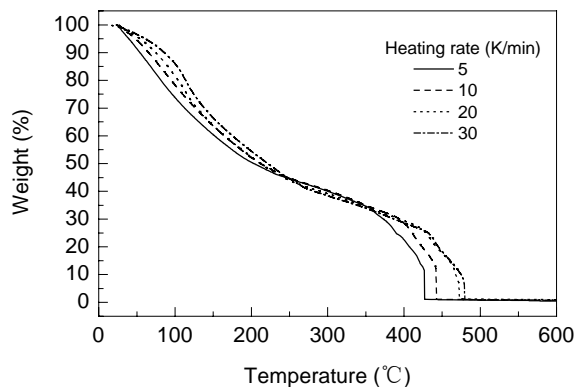


Fig.5 TG of bio-oil at various heating rates

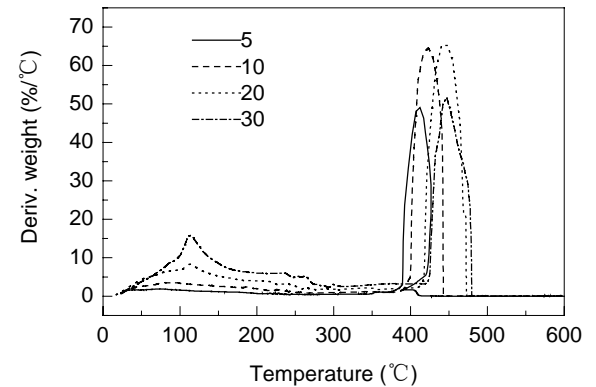


Fig.6 DTG of bio-oil at various heating rates

## 5 PYROLYSIS AND COMBUSTION KINETICS OF PYROLYZED BIO-OIL

Both Ozawa–Flynn–Wall method<sup>[9]</sup> and Popescu method<sup>[10]</sup> were employed to calculate the pyrolysis and combustion kinetic parameters and the most probable mechanism functions for describing the combustion reaction in the temperature scope of 400~430 °C were also selected from the 22 kinetic functions as listed in literature<sup>[11]</sup>.

The calculated activation energy,  $E$ , from both methods agrees well with each other and on the whole the value rises along with conversion ratio increasing (see Tables 3 and 4). When the conversion ratio is less than 0.3, the process is dominated by vaporization of low boiling point compounds, which thus results in low activation value (less than 100 kJ/mol). When the conversion ratio is up from 0.4 to 0.5, the activation energy is about 150 kJ/mol, which corresponds to the pyrolysis of some bio-oil components. When the conversion ratio is from 0.7 to 0.9, the activation energy value is also about 150 kJ/mol, which corresponds to the combustion of the bio-oil. Surprisingly, when the conversion ratio is from 0.6 to 0.7, the calculated activation energy is either negative or incredible (extremely low correlation coefficient). This might be due to the multi-type reaction mechanisms co-existing in this transition phase (from pyrolysis to combustion)

**Table 3** Activation energy  $E$  calculated with Ozawa–Flynn–Wall method

$\alpha$	$E$ (kJ/mol)	$R$
0.1	55.99	-0.9945
0.2	64.56	-0.9949
0.3	93.82	-0.9523
0.4	122.11	-0.9246
0.5	189.95	-0.9118
0.6	-180.11	0.9111
0.7	164.8	-0.5136
0.8	182.73	-0.9905
0.9	155.55	-0.9932

**Table 4** Kinetic parameters calculated with Popescu method

$\alpha_n \sim \alpha_m$	$E$ (kJ/mol)	$\ln A$	$R$
0.2~0.1	59.72	18.2624	-0.9947
0.3~0.2	90.56	26.8464	-0.9655
0.4~0.3	111.71	30.8698	-0.9356
0.5~0.4	160.96	41.0664	-0.9253
0.6~0.5	-305.68	-71.2962	0.4442
0.7~0.6	-142.35	-28.4708	0.4628
0.8~0.7	166.25	30.9187	-0.9749
0.9~0.8	127.87	25.3023	-0.9793

Note:  $A$ ,  $R$  and  $\alpha$  denote pre-exponential factor, correlation coefficient and conversion ratio respectively.

**Table 5** The most probable mechanism functions with Popescu method

Temperature scope (°C)	Reaction order	Differential function expression
400~406	2	$(1-\alpha)^2$
406~416	3	$(1/2)(1-\alpha)^3$
416~430	3/2	$2(1-\alpha)^{3/2}$

and thus it makes the presupposition of these two methods no longer tenable. The most probable mechanism functions chosen with Popescu method for describing the combustion at 400~430 °C are shown in Table 5 which indicates that the combustion is a chemical reaction control process, but reaction order is different in different temperature ranges.

## 6 CONCLUSIONS

(1) 14 main organic compounds in the liquid product from fast pyrolysis of biomass at 480 °C were identified by GC-MS. They are mostly oxygen-containing aromatic compounds such as phenol, alcohol, fluorene, aldehyde and ketone.

(2) Thermal analysis of the liquid product indicated that it was easy to vaporize and burn, and the residue of its combustion was minute.

(3) Thermal kinetics analysis indicated that calculated activation energy values by using Ozawa–Flynn–Wall method and Popescu method are consistent with each other. The most probable mechanism functions for describing combustion at 400~430 °C were also selected from 22 kinetic functions which indicated that the combustion was a chemical reaction control process.

### REFERENCE:

- [1] Chen M Q. Preparation of Liquid Fuel through Pyrolysis of Biomass in a Conduit-spouting Fluidized Reactor. [D]. Shanghai: East China University of Science and Technology, 2003. 2–10 (in Chinese).
- [2] Chen M Q, Yan Y J, REN Z W, et al. Preparation of Liquid Fuel through Fast Pyrolysis of Biomass in a Spout-fluidized Reactor with a Draft Tube [J]. J. East China University of Science and Technology, 2004, 30(2): 143–147 (in Chinese).
- [3] Bridgwater A V. Principles and Practice of Biomass Fast Pyrolysis Process for Liquids [J]. Fuel Process. Technol., 1999, 51(1): 3–22.
- [4] Ren Z W, Xu Q, Chen M Q, et al. Fast Pyrolysis of Biomass in Fluidized Bed to Produce Liquid Fuel [J]. J. Solar Energy, 2002, 23(4): 462–466 (in Chinese).
- [5] Aguado R, Olazar M, San Jose M J, et al. Pyrolysis of Sawdust in a Conical Spouted-bed Reactor: Yields and Product Composition [J]. Ind. Eng. Chem. Res., 2000, 39(6): 1925–1933.
- [6] Vitolo S, Seggiani M, Frediani P, et al. Catalytic Upgrading of Pyrolysis Oils to Fuel over Different Zeolites [J]. Fuel, 1999, 78: 1144–1159.
- [7] Kok M V, Okandan E. Effect of Crude Oil Type and Heating Rate on

- Combustion of Crude Oil-Lignite Mixture [J]. Fuel, 1992, 71: 1499-1503.
- [8] Chen M Q, Li L, Yao Y J, et al. Hydrodynamics of Sawdust in a Spout-fluid Bed with a Draft Tube: Effect of Draft Tube Length [J]. J. East China University of Science and Technology, 2003, 29(1): 26-30 (in Chinese).
- [9] Xu G H, Yuan J. Common Thermal Analyzers [M]. Shanghai: Shanghai Science and Technology Press, 1990. 93-94 (in Chinese).
- [10] Popescu C. Integral Method to Analyze the Kinetics of Heterogenous Reactions under Non-isothermal Conditions [J]. Thermochim. Acta, 1996, 285(2): 309-323.
- [11] Pan Y X, Guan X Y, Feng Z Y. A New Method Determining Mechanism Function of Solid State Reaction [J]. J. Inorg. Chem., 1999, 15(2): 247-251 (in Chinese).