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# Study on fluidized-bed pyrolysis of waste paper

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**Abstract:** A lab-scale fluidized bed is setup and pyrolysis experiments are carried out. When temperature ranges from 400 to 700 ℃, the yields of solid residue, bio-oil and syngas range from 36% to 18%, 19% to 30% and 9% to 42%, respectively, and the mass balance of pyrolysis ranges from 80% to 95%. At 400 to 700 ℃, the characteristics of bio-oil are similar and the heat value is about 10 MJ/kg. When the temperature is over 600 ℃, the yield of syngas increases approximately twice as much as that at 500 ℃. The yields of $CO_2$ and CO increase from 70 to 230 L/kg and 50 to 106 L/kg, respectively, while the yield of syngas only increases about 5% when the temperature increases from 600 to 700 ℃. The results indicate that the pyrolysis mechanism of waste paper is similar from 400 to 700 ℃, while the yield of syngas can be affected by secondary pyrolysis of bio-oil.

**Key words:** waste paper; fluidized bed; pyrolysis; syngas; bio-oil

Waste paper is one of the main components in municipal solid waste (MSW) and its mass percent is about 3% to 15% in developing countries, while it is 25% to 35% in developed countries[1-3]. Pyrolysis is expected to be an efficient means to recover energy from waste materials. Wu et al.[4-5] studied pyrolysis kinetics and the products by the use of the thermogravimetic analyzer. David et al.[6] studied pyrolysis kinetics at different heating rates by the use of a thermogravimetic analyzer. Much relative research was focused on studying the pyrolysis of biomass or other waste materials[7-13]. Most studies have been carried out in thermogravimetic analyzers but have seldom covered all products of pyrolysis. In this research, waste paper is pyrolyzed at 400 to 700 ℃ in a fluidized bed, and all products are analyzed, including solid residue, bio-oil and syngas.

## 1 Method

Waste cardboard is a typical kind of waste paper. This paper type acts as the feedstock with a size of about 2 mm × 5 mm × 5 mm. The proximate and ultimate analysis is reported in Tab. 1.

The fluidized-bed pyrolysis reactor is equipped with a steel tube of an inside diameter of 30 mm and a total height of 250 mm which is placed in an electrical heaters, as shown in Fig. 1. A K-type thermocouples is assembled at about 150 mm above the distributor. $N_2$ acts as a fluidized medium and the velocity is about 0.48 (N · m)/s. Sand is selected as bed material, the diameter of which is from 0.250 to 0.355 mm. Feedstock is fed intermittently from the top equipped with a valve. As soon as the feedstock is fed, the valve is closed quickly; waste paper is pyrolyzed and volatile products are introduced into the cooler rapidly; bio-oil is condensed and collected in vessels, and un-condensable syngas is collected in a gas-bag. The pyrolysis lasts about 2 to 3 min. Then the electrical heater and $N_2$ supplier are shut off synchronously. After the reactor is cooled, solid residue is collected. The precise flux of syngas is measured by a gas meter, which is made by Hangzhou Beta Gas Meter Co., Ltd. Un-condensable syngas is detected by Trace 2000 gas chromatography (GC) which is made by Thermo Finnigan in Italy. The heat values of feedstock, bio-oil and solid products are measured by a 5E-1AC/P oxygen bomb calorimeter provided by Kaiyuan Instrument Company in Changsha, China. Each experiment is repeated over 10 times and the average results are analyzed.

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**Tab. 1** Proximate and ultimate analysis of waste paper

| Proximate analysis/% | | | | $Q_{net,ar}$/(MJ·kg$^{-1}$) | Ultimate analysis/% | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $w(M_{ar})$ | $w(A_{ar})$ | $w(V_{ar})$ | $w(FC_{ar})$ | | $w(C_{ar})$ | $w(H_{ar})$ | $w(N_{ar})$ | $w(S_{ar})$ | $w(O_{ar})$ |
| 6.96 | 6.72 | 78.11 | 8.21 | 15.869 | 42.27 | 5.30 | 0.18 | 0.14 | 38.43 |

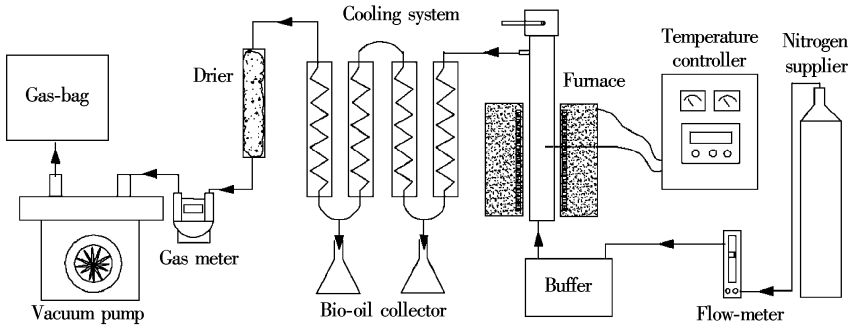


**Fig. 1** Illustration of fluidized-bed pyrolysis reactor

## 2 Results and Discussion

### 2.1 Mass balance

In the analysis of mass balance, four kinds of products are considered: solid residue, bio-oil, syngas and moisture in syngas. The mass balance at different temperatures is displayed in Fig. 2. When the temperature increases from 400 to 700 ℃, the yield of solid residue, bio-oil and syngas changes from 36% to 18%, 19% to 30% and 9% to 42%, respectively. The mass balance of pyrolysis ranges from 80% to 95% approximately.

The mass balance increases with the increase in temperature, and reaches about 95% when the temperature is 700 ℃. It is because every experiment lasts 2 to 3 min, or if it lasts over 3 min, that the syngas will be diluted by $N_2$ and it will cause more errors in detection. Waste paper cannot be pyrolyzed completely in 2 to 3 min at lower temperatures (400 to 500 ℃). The reaction is going on before it is cooled and collected and then some mass is missed. When the temperature is over 600 ℃, pyrolysis can almost finish in 2 to 3 min, and less mass is missed during cooling, so the mass balance can reach over 90%.

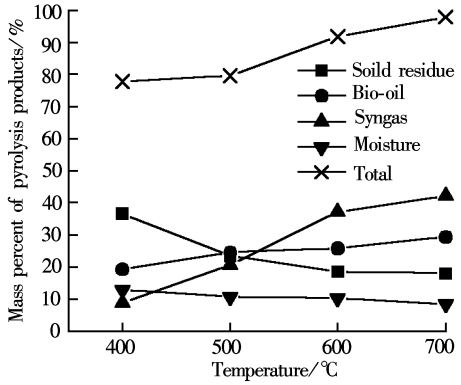


**Fig. 2** Mass balance at different pyrolysis temperatures

### 2.2 Characteristics of solid residue

The characteristics of solid residue are reported in Tab. 2. With the increase in temperature, the percents of volatile carbon and hydrogen decrease. It indicates that pyrolysis can be fulfilled more completely at higher temperatures. The mass percent of solid residue ranges from 36% to 18% approximately. It is much higher than the results of cellulose pyrolysis[12], which is probably caused by two reasons: ① There are some incombustible additives in the waste cardboard; furthermore, the ions such as $K^+$, $Na^+$, $Ca^+$ etc. in additives facilitate char forming during pyrolysis[13–15]; ② The size of the feedstock is much larger than that of other thermogravimetic experiments[4–5], which causes more char production[6, 16].

**Tab. 2** Proximate and ultimate analysis of solid residue at different pyrolysis temperatures

| Temperature/℃ | Proximate analysis/% | | | | $Q_{net,ar}$/ | Ultimate analysis/% | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $w(M_{ar})$ | $w(A_{ar})$ | $w(V_{ar})$ | $w(FC_{ar})$ | (MJ·kg$^{-1}$) | $w(C_{ar})$ | $w(H_{ar})$ | $w(N_{ar})$ | $w(S_{ar})$ | $w(O_{ar})$ |
| 400 | 5.11 | 18.35 | 41.99 | 34.54 | 16.242 | 51.83 | 2.17 | 0.49 | 0.23 | 21.82 |
| 500 | 4.69 | 28.51 | 39.03 | 27.77 | 14.198 | 45.50 | 1.49 | 0.47 | 0 | 19.34 |
| 600 | 3.44 | 36.17 | 32.98 | 27.42 | 13.276 | 46.92 | 1.24 | 0.29 | 0.14 | 11.81 |
| 700 | 4.41 | 37.33 | 30.46 | 27.80 | 11.282 | 45.27 | 1.11 | 0.37 | 0.21 | 11.31 |

### 2.3 Characteristics of bio-oil

The bio-oil is brown, which is shown in Fig. 3(a). It is different from the bio-oil of wood pyrolysis, as shown in Fig. 3(b), which will be analyzed in another paper. It is hydrophilic and volatile, and when it is heated, it will be polymerizated intensively. The

moisture percent is about 45% and the heat value is about 10 MJ/kg, as shown in Tab. 3. The characteristics of bio-oil are similar at 400 to 700 ℃, which indicate that the mechanisms of pyrolysis are also similar at this range of temperature.

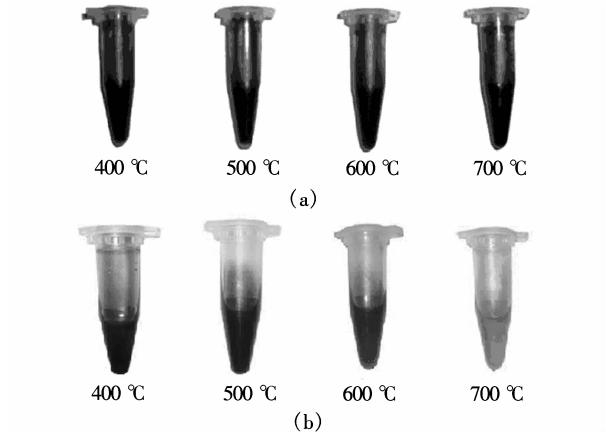


**Fig. 3** Bio-oil from different pyrolysis temperatures. (a) Bio-oil of waste paper pyrolysis; (b) Bio-oil of wood pyrolysis

**Tab. 3** Characteristics of bio-oil from different pyrolysis temperatures

| Temperature/℃ | Ultimate analysis/% | | | Moisture percent/% | $Q_{net,ar}$/(MJ·kg$^{-1}$) |
|---|---|---|---|---|---|
| | $w(C_{ar})$ | $w(H_{ar})$ | $w(N_{ar})$ | | |
| 400 | 23.99 | 3.24 | 0.28 | 44.94 | 10.151 |
| 500 | 23.54 | 3.12 | 0.23 | 46.80 | 9.805 |
| 600 | 23.93 | 3.11 | 0.22 | 47.36 | 10.252 |
| 700 | 23.35 | 3.27 | 0.22 | 45.03 | 10.099 |

### 2.4 Analysis of syngas

The yields of the main components in syngas are reported in Tab. 4 ($N_2$ and $H_2O$ are free). 600 ℃ seems to be a notable inflexion for waste paper pyrolysis in a fluidized bed. When the temperature is over 600 ℃, the yields of syngas increase approximately twice as much as that at 500 ℃. The yields of $CO_2$ and CO increase from 70 to 230 L/kg and 50 to 106 L/kg, respectively. Generally, the proportion of components in syngas is approximately consistent at 400 to 700 ℃. This indicates that the mechanisms of pyrolysis are similar, which corresponds to the analysis above.

**Tab. 4** Yields of pyrolysis gases of waste paper at different temperatures

| Temperature/℃ | Yields of components/(L·kg$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | $y(CO_2)$ | $y(CO)$ | $y(H_2)$ | $y(CH_4)$ | $y(C_2H_6)$ | $y(C_2H_4)$ |
| 400 | 32.11 | 11.25 | 9.66 | 0.23 | 0 | 0.29 |
| 500 | 70.68 | 50.02 | 7.51 | 1.36 | 0.21 | 0.58 |
| 600 | 232.81 | 106.27 | 7.06 | 6.08 | 0.68 | 2.07 |
| 700 | 244.94 | 130.85 | 11.04 | 7.90 | 0.76 | 3.67 |

## 3 Conclusions

1) When pyrolysis temperature ranges from 400 to 700 ℃, the yields of solid residue decrease from 36% to 18%, while that of bio-oil and syngas increase from 19% to 30% and 9% to 42%, respectively.

2) 600 ℃ is a notable inflexion of waste paper pyrolysis in a fluidized bed. When the temperature is over 600 ℃, the yields of syngas increase sharply and reach about twice as much as that of the yields at 500 ℃.

3) The experiments indicate that the pyrolysis mechanism of waste paper is similar from 400 to 700 ℃, while the yield of syngas can be affected by secondary pyrolysis of bio-oil.

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# 废纸流化床热解特性试验研究

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**摘要**:在自行设计的流化床实验台上进行废纸热解实验研究. 当热解温度从400 ℃升高到700 ℃时,固体残渣产率从36%降低到18%,而热解油、热解气产率分别从19%增加到30%和9%增加到42%. 实验的质量平衡达到80% ~95%. 各温度下,液体产物特性相似,热值都为10 MJ/kg左右,说明在此温度范围内,热解反应机理相似. 当反应温度从500 ℃提高到600 ℃以上时,热解气产量几乎提高一倍,其中$CO_2$与CO产量分别从大约70 L/kg提高到230 L/kg和50 L/kg提高到106 L/kg;而温度从600 ℃提高到700 ℃时,热解气产量仅提高5%. 研究表明,热解油的二次裂解会影响热解气产量.

**关键词**:废纸;流化床;热解;合成气;生物油

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