Pyrolysis behavior of basswood by TG

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Abstract. The pyrolysis behavior of basswood was studied by thermogravimetric analysis (TG). Thermodynamic analysis of basswood at heating rate of 10, 20, 30, 90 K/min in N2 atmosphere was investigated. The pre-exponential factor and the activation energy were calculated by means of Li Chung-Hsiung method. The most possible mechanism function f(α) has been established. Basswood activation energy is 63.0-78.4 kJ/mol. The result shows that activation energy of fast pyrolysis in 90 K/min is least. Fast pyrolysis is available for energy saving and chemical action.

1. Introduction

Biomass is a huge amount of renewable resources, which is considered as the organic matter produced by plants through photosynthesis. The most important advantages of biomass are such as renewable, resource-rich and environment-friendly. Therefore, biomass is considered to be the main energy source for substitute of the decreasing fossil fuel resources. [1]. In particular, wood can be used as energy by developed thermochemical technology[2]. Different ways of biomass thermochemical conversion, including pyrolysis, gasification and liquefaction, were studied. The pyrolysis of biomass has been an intensive research topic in the past three decades, because it can produce liquid fuels, syngas and even high value-added chemicals. Biomass pyrolysis is usually carried out through a series of complex reactions. In order to better understand the pyrolysis process of biomass, the pyrolysis behavior of three main components was studied by predecessors.

Basswood is the main material of furniture in northern China and a typical waste of wood industry. Since the end of 1970s[3], thermogravimetric analysis (TG) has become a good technique for analyzing evolved gases. The key to the advantage of this technology is to extract multiple information during a TG operation, such as the change of sample mass loss with temperature. However, comparison of fast pyrolysis and slow pyrolysis, the different of former and latter at their pyrolysis process.

2. Experimental

2.1. Materials

Basswood sawdust is collected from furniture factories. Basswood sawdust was isolated by vibrating screen and tested by 100 meshes (grain diameter <0.15 mm). Before screening, the samples were dried at 105 °C for 3 hours.
2.2. Methods
Carbon, hydrogen and nitrogen contents were measured by a vario micro cube elemental analyzer produced by elementar company in Germany. The oxygen content was obtained through deducting the C, H and N contents from 100%. Table 1 shows the ultimate analysis data of sawdust. The pyrolysis behavior of biomass was studied by thermogravimetric analysis (TGA). Biomass was pyrolyzed in TGA. In order to reduce the difference of heat diffusion and mass transfer, the mass of wood sample is kept at about 3.5 mg. The experimental samples were heated at 30-950 °C at heating rates of 10 °C/min, 20 °C/min, 30 °C/min and 90 °C/min, respectively. Using 99.99% pure nitrogen with flow rate of 70 ml/min as carrier gas can not only remove condensate and gas product in time, but also provide inert environment for pyrolysis, thereby reducing any secondary gas-phase interaction.

| Sample  | C    | H    | O    | N    |
|---------|------|------|------|------|
| Basswood | 48.855 | 6.428 | 44.717 | 0    |

3. Results and discussion

3.1. Thermogravimetric analysis of basswood
As shown in Figure 1, the TG and DTG curves of basswood with heating rates (20 °C/min.) are obtained. Through the curve analysis of Fig. 1, the heating process of basswood can be roughly divided into several steps: The first step lasts until about 250 °C, mainly when water is removed. In the second step, the most light volatile substances are produced between 250 and 400 °C. This stage is usually identified in the literature as the degradation of hemicellulose and cellulose. The high temperature peak is mainly due to the degradation of cellulose, while the shoulder is due to the degradation of hemicellulose at low temperature. In the third step, a peak could not be observed due to the degradation of lignin. Heavy volatile compounds are produced at this stage. It is usually recognized as the decomposition of lignin, which proceeds very slowly and covers a wide temperature range.

Figure 1. TG and DTG curves of basswood

3.2. Kinetics of biomass pyrolysis
Consistent with other authors, weight loss events of cellulose, hemicellulose and lignin are considered non-interactive. With the hypothesis that biomass solid samples are decomposed by single-stage irreversible reaction in inert atmosphere, the rate constant of chemical reaction is expressed by Arrhenius equation, i.e. $k=A\exp(E/RT)$, and the reaction rate is expressed by biomass conversion rate, $\alpha$, it can be expressed as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} (\frac{E}{RT}) f(\alpha)$$ (1)
In the literature, the kinetic parameters is obtained by Li Chung-Hsiung method. If $RT/E << 1$, equation (6) can change to equation (7). According to formula (7), a beeline with gradient equal to $-E/R$ can be drawn with $\ln \left[ G(\alpha)/T^2 \right]$ as ordinate and $1/T$ as abscissa. As the integral function of percent conversion, $G(\alpha)$ is related to the mechanism of controlling reaction and the shape and size of reaction particles. This study was used to estimate the reaction mechanism from the dynamic TG curve.

Table 2 shows ten different representations of $G(\alpha)$ for the different solid state mechanisms, which were used in this work to evaluate reaction mechanisms by using Li Chung-Hsiung Method from dynamic TG curves. If the most precise function is used, the linear regression analysis with $\ln \left[ G(\alpha)/T^2 \right]$ as dependent variable and $1/T$ as independent variable has the highest correlation coefficient. Therefore, $E$ (the activation energy) can be obtained from the gradient of the regression line, and $A$ (the pre-exponential constant) can be derived from the nodal increment of the regression line. Table 3 shows linear regression analysis of different solid mechanism at 20K/min heating rate in basswood pyrolysis. From Table 3, we can see that first-order reaction assumption is best mechanism. And then the values of activation energy and pre-exponential constant could be derived as it shows in Table 4.

From Table 4, we can see that basswood activation energy is 63.0-78.4 kJ/mol. It is lower than literature [4], which said furniture sample is 134.32-155.76 kJ/mol in an inert atmosphere. Because the wood and slower heating rate is different. Two sample both shows that activation energy of fast pyrolysis in 90K/min is least. Fast pyrolysis is available for energy saving and chemical action.
Table 3. The results from the mechanism model at the main pyrolysis stage on basswood

| Mechanism | a       | b         | R         | SD        |
|-----------|---------|-----------|-----------|-----------|
| A2        | -6.65678| -3988.55863| -0.99828  | 0.02937   |
| A3        | -9.36322| -2263.62457| -0.99746  | 0.02022   |
| C1        | 1.46253 | -9163.36074| -0.99876  | 0.05714   |
| C2        | -6.51093| -3368.04018| -0.81581  | 0.29898   |
| D1        | 10.54953| -15583.8219| -0.99093  | 0.26466   |
| D2        | 11.90359| -16704.63466| -0.99489  | 0.21225   |
| D3        | 12.87541| -18065.92276| -0.99787  | 0.14795   |
| D4        | 11.21687| -17153.91652| -0.99613  | 0.18956   |
| R2        | -1.15507| -8104.43212| -0.99602  | 0.09084   |
| R3        | -0.95034| -8439.83962| -0.99743  | 0.0759    |

Table 4. Kinetic parameters of wood pyrolysis in N2 at heating rates: 10, 20, 30 and 90Kmin−1 using Li Chung-Hsiung method

| Kinetic parameters | Basswood | Heating rate (K min−1)/mesh |
|--------------------|----------|------------------------------|
|                    | 10/100   | 20/100 | 30/100 | 90/100 |
| f(α)               | 74726.79 | 76147.53 | 78448.34 | 62972.89 |
| E                  | 312528   | 791140.3 | 1662667  | 192688.4  |
| A                  | -0.9932  | -0.9988  | -0.9989  | -0.9956   |
| R                  | -0.9932  | -0.9988  | -0.9989  | -0.9956   |

4. Conclusions
1. In this study, ten different solid-state reaction mechanisms were compared, and the best reaction mechanism was inferred from the dynamic TG curve. First-order reaction assumption is best mechanism in main weight loss stage of basswood through higher correlation coefficient of linear-regression analysis.

2. Basswood activation energy is 63.0-78.4 kJ/mol.

3. The result shows that activation energy of fast pyrolysis in 90K/min is least. Fast pyrolysis is available for energy saving and chemical action.

Acknowledgement
The authors are grateful for the support by Natural Science Foundation of Tianjin City (CN) (16JCQNJC08200) and Tianjin Agriculture University science and Technology Development Fund (2016NYB09).

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