Estimation Method of Biomass Energy Reserves in China: A Case Study of Corn Straw

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Abstract: Nowadays, biomass resources are the best choice to replace fossil resources. Energy development in biomass is mainly through pyrolysis of biomass. At present, no one has estimated how much biomass energy there is for a country. In this article, taking corn as an example, China as the production country, the potential biomass resources in China are speculated, in which Lignocellulose is the main experimental biomass and pyrolyzed to obtain biomass energy. The most common method of biomass energy conversion is isothermal conversion. The first-order reaction model is used for kinetic analysis of the conversion. The sample is subjected to powder falling pyrolysis at 480 degrees. In order to overcome the regional differences in China, the data of 30 degrees north latitude are used. Finally, the reaction time and the total amount of biomass energy available for development and utilization in China in 2020 are obtained.

Keywords: biomass energy, pyrolysis, isothermal conversion method.

1. Foreword
Today, fossil resources such as oil, coal and natural gas are facing depletion. At the same time, global problems such as environmental pollution caused by the use of fossil resources are becoming increasingly prominent, forcing us to find renewable resources to replace fossil resources in order to continue people’s current social life and strive for the realization of sustainable development of human society. Biomass energy is an energy form with biomass as the carrier, that is, an energy form in which solar energy is stored in biomass in the form of chemical energy through photosynthesis of plants. It is the only renewable resource containing C and H elements currently available except fossil resources and is the best choice to replace fossil resources [1].

At present, biomass energy technology has become one of the major hot topics in the world, and has attracted the attention of governments and scientists from all over the world, such as Japan’s sunshine plan, India's green energy project, and the energy farm in the United States [2]. Before that, many people have studied pyrolysis and overcome the most basic technical problems. Against this background, it is necessary to understand how much biomass energy can be used in a country. Taking China for example, since the end of 1990s, China has decided to increase its investment in funds and expand the policy support for the development and application of biomass energy [3]. In the future, China, a large energy-consuming country, will have more eyes on biomass resources. However, little effort has been made to estimated the total biomass energy that a country can produce.

The energy development in biomass mainly takes the form of biomass pyrolysis. Biomass pyrolysis refers to the thermochemical process in which biomass is rapidly heated and decomposed under anoxic
or limited oxygen conditions, and pyrolysis steam is rapidly condensed to obtain a liquid product as the main product, and non-condensable gases and solid products as by-products [1].

The pyrolysis equation is generally described by the following equation:

\[
\frac{da}{dt} = A e^{-E/RT} f(\alpha)
\]  

This equation describes the relationship among the degree of conversion \(\alpha\), activation energy \(E\), and temperature \(T\) [4]. Here, \(A\) refers to the pre-exponential factor \((s^{-1})\), \(R\) is the ideal gas constant \((J/(mol K))\), and \(T\) is the reaction temperature \((K)\). This equation is usually determined by thermogravimetric analysis (TGA) [5]. However, there are many methods such as integral and differential methods to solve the activation energy \(E\) value by knowing the conversion degree on the basis of experiments. The fact proves that the integral method is more accurate than the differential method. The value of \(E\) and \(A\) will not be described in more detail here [6].

Lignocellulose is the main source of biomass. Its main components are 35%-50% cellulose, 25%-30% hemicellulose and 15%-30% lignin [1]. Corn stover, one of the most representative biomass, is a typical lignocellulosic biomass. At present, there is still no way to systematically predict for the whole country or region. This paper will take corn as an example, China as the production country, lignocellulose as the main experimental biomass, and use physical model to analyze the data of conversion rate and activation energy across the country to speculate the potential biomass resources in China.

2. Methods

The most common way of biomass energy conversion is isothermal conversion method, which can be divided into two categories, integral and differential isothermal conversion method. According to Brown and Gallagher [7], isothermal conversion method has been adopted by many major thermal equipment manufacturers. The author also states the application of this concept in various processes with great success. According to Starink [8], the conversion rate of all isothermal conversions is based on an equation, i.e. the conversion rate is related to the temperature function and the actual conversion rate, which can be written as (2) [6].

\[
\frac{dx}{dt} = f(\alpha) k(T)
\]  

In the above formula, the temperature function is generally assumed to be expressed as follows:

\[
k(T) = A e^{-E/RT}
\]  

For the two parts of isothermal transformation method, integral method and differential method, the author takes logarithm for the above two equations and obtains their linear expressions [8]. This method does not use the mathematical approximation of temperature integration, but uses the linear expression of the equation under constant heating rate after taking logarithm to determine the reaction rate of the same reaction stage at different rates. If you do not use the logarithmic method, but directly integrate the above equation, you will get the integral expression:

\[
\int_0^x f(\alpha) \frac{dx}{f(\alpha)} = \frac{A}{B} \int_T^{\infty} e^{-\frac{E}{R T}} dT = \frac{A}{B} \int_u^{\infty} \frac{e^{-u}}{u^2} du
\]  

The term containing \(u\) in the formula is called temperature integral, and the integral method is usually more accurate than the differential method.

2.1. First-order reaction model

The first-order reaction model is based on the assumption [9] that the reaction occurs uniformly throughout the carbon particles, and the conclusion is obtained by studying the combustion of coal and pine sawdust. The first-order reaction model is the most effective mechanism to describe the first stage of biomass oxidation and coal combustion. It is described by the function:

The above calculation is independent of the model, so further dynamic analysis is necessary. Based on the above method, three models are proposed to describe the coke conversion process [6]:

\[
x = 1 - x
\]
2.2. RPM
RPM is widely used in modeling of coal char gasification, and this model is widely used in the interpretation of gas-solid reaction rate data. This model can fully express the maximum increase of conversion rate without using any adjustable additional parameters. The expression is:

\[ f(x) = \frac{s}{1 - \epsilon} (1 - x) \sqrt{1 - q \ln (1 - x)} \]  

(6)

Wherein the structural parameters are described as follows:

\[ \varphi = \frac{4\pi L (1 - \epsilon)}{s^2} \]  

(7)

Wherein \( s \) is the initial area per unit volume, \( \epsilon \) is the initial porosity of the material, and \( L \) is the initial segment length per unit volume. The RPM model is the most widely accepted structural model for predicting pore surface area development during gasification and combustion of porous coal chars.

2.3. Contraction nuclear model
The shrinking core model is widely used to describe the dissolution, leaching or reaction process of solid particles. It has a wide range of applications, such as hydrometallurgy, bacterial leaching of minerals, combustion of coal particles and catalyst regeneration [10]. The reduction reaction is taken as an example to illustrate the shrinking core model. The reduction reaction is a typical gas-solid phase reaction and is gradually promoted from outside to inside. There is a shrinking core of unreacted materials in the reduced ore until the end of the reaction. The reduced solid product layer is attached to the solid reactants, and has the same shape and volume as the raw ore, with negligible change. The ore is denser and looser after reduction. Diffusion of gas in the product is much easier than in raw ore. People idealize the above characteristics and construct a reaction model, which is called shrinking core model. The model is actually expressed as:

\[ f(x) = \frac{s(1 - x)^h}{(1 - \epsilon)} \]  

(8)

Wherein \( s \) is the initial surface area per unit volume, \( \epsilon \) is the initial porosity, and \( h \) is the shape factor of the grain geometry.

In this paper, the first-order reaction model, which is the most commonly used model, will be adopted to study the conversion of biomass mainly from corn.

3. Results and discussion
China will produce a total of 2.61 \times 10^8 tons of corn in 2020 [11]. The ratio of corn straw output (kg) to corn is usually 1.2: 1 [11]. Therefore, the total tons of corn stalks produced in China in 2020 can be estimated.

Now we have to select the experimental data. As China is a country with a large cross-latitude and the geographical environment of different regions is quite different, I need to assume that the conversion of corn stalk biomass in the whole country will be carried out under the same environment. The average environment will be calculated using the regional data of China at 30 degrees north latitude, because this position is just at the average latitude of south and north China. In addition, Pakistan's Punjab Province is also located in the region with latitude 30 degrees north, which is equivalent to the data of China. Therefore, the experimental data of Punjab Province can be used to select the value of \( E \) and \( A \) [12].

Through consulting the literature, we found that about 45% of bio-oil liquid products can be obtained by fast pyrolysis at about 480 degrees, which is the highest liquid yield. In the end, the conversion rate of this reaction will reach about 85% [12]. If the improved solid heat carrier circulating fluidized bed technology is adopted, a higher gas yield can be obtained above 700 degrees[13]. However, considering that the pyrolysis of corn stover can be conveniently carried out in a large scale nationwide, the reaction is carried out at 480 degrees. We will assume that the falling pyrolysis method is used throughout the country, and the reaction flow is shown in figure 1 [13]:
During the powder drop pyrolysis experiment, the installed reaction tube has an inner diameter of 90mm and a height of 2000mm, and is internally provided with a plurality of layers of adjustable baffles. The straw powder added from the feeder 5 is entrained by nitrogen and pyrolyzed while falling down. The pyrolyzed oil and gas are separated from the semi-coke in the lower section of the reactor 8 and dedusted before entering the condenser 10. Condensate and gas are collected separately, and char is collected by the lower tank. Pyrolysis products contain 45% bio-oil, 25% semi-coke and 30% gas (including 38%CO₂, 32%CO, 13%CH₄, 9%C₆H₁₂, 7% H₂) [13].

The following data are processed. Table1 is the experimental data of Pakistan [14]:

| X     | E       | A       |
|-------|---------|---------|
| 0.3   | 29.8    | 2.68    |
| 0.4   | 35      | 1.53    |
| 0.45  | 35.3    | 1.405   |
| 0.5   | 32.6    | 1.435   |
| 0.55  | 34.8    | 1.61    |

Perform linear fitting on the data in the table, and convert E, A into E(x) and A(x), so as to minimize the difference between the fitting result and the absolute value of the experimental data. The function is represented in figure 2 and figure 3:

The fitting result of E is $E = 4937.1x^4 - 6199.4x^3 + 2283.4x^2 - 113.59x - 14.253$, and the result of A is $A = 44.726x^2 - 42.137x + 11.282$. Then, we brought formulas (5) and (3) into formula (2) and rearranged them to obtain:

$$\int_0^t dt = \int_0^{0.05} \frac{1}{(44.726x^2 - 42.137x + 11.282)e^{-\frac{4937.1x^4 - 6199.4x^3 + 2283.4x^2 - 113.59x - 14.253}{RT}(1 - x)}} dx$$

Using excel to perform numerical integration on the above formula, with each interval of 0.05, the value of $t = 10.02s$ will play an important role in considering the cost for calculating the large-scale use of corn stover to obtain biomass energy in the country. It is necessary to carefully consider how...
much time and cost it takes for each machine in each region to burn how many samples. Only by knowing the cost can one know whether the result will bring benefits.

Now, the elemental analysis of corn straw is carried out again. The results show that the element C accounts for 49.27%, H accounts for 6.55%, N accounts for 1.56% and O accounts for 42.62% [14] in the corn straw. The final products of the reaction are hydrogen, nitrogen, carbon dioxide, carbon residue and water, in which water and carbon dioxide will continue to react with the carbon residue to produce carbon monoxide. Thus, the reaction can be described as:

\[
2C_{49.27}H_{6.55}N_{1.56}O_{42.62} \rightarrow^{Heated} 655H_2 + 156N_2 + 8524CO + 1330C \tag{11}
\]

Among these products, hydrogen can be directly used as an energy source. From the above equation, it can be known that \(6.14 \times 10^{-2} \text{kg}\) of hydrogen can be obtained from 1kg of reactants. However, we only need to react 85% of every 1kg of reactants, so the \(6.14 \times 10^{-2} \text{kg}\) of hydrogen here actually needs to consume \(6.14 \times 10^{-2} \text{kg}\) of corn straw. According to the aforementioned annual output and proportion, we can obtain a total of \(3.13 \times 10^{11} \text{ kg}\) of corn straw in one year. Taking these samples to participate in the reaction, through chemical equation, we can calculate a total of \(1.63 \times 10^{10} \text{kg}\) of hydrogen in the product. The calorific value of hydrogen is \(1.43 \times 10^8 \text{J/kg}\), which means that
1.43x10^8 J of heat can be released per 1 kg of hydrogen burned, so we can finally get 2.34 × 10^{18} J of energy. This is the ideal biomass energy that can be obtained from corn stalks throughout China in 2020. This value is approximately equivalent to 7.98 × 10^{10} kg of standard coal using the official standard calculation method [15] in China.

4. Conclusion

In this article, we obtained two calculation results. On the one hand, we calculated that the potential biomass energy available from corn stover in China in 2020 is approximately equivalent to about 80 million tons of standard coal. This data is very considerable. Therefore, the implementation of this scheme in China is very beneficial, and this method can also be used to evaluate biomass energy in other countries or regions. On the other hand, we get the reaction time in 30°N, which is 10.02s. The data can be used to calculate economic problems in commercial production in the future.

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