Discussion on the Analysis of Biomass Energy Utilization

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Abstract. In order to solve the problem of energy shortage and environmental pollution, eucalyptus is used as raw material to optimize the best process through dilute acid pre-treatment, enzymatic hydrolysis and fermentation, with xylose recovery rate, cellulose enzymatic hydrolysis rate, and total sugar yield as evaluation indicators. It has guiding significance for renewable biomass energy tree species to replace non-renewable petroleum-based raw materials to produce biobutanol, and the future development direction of biomass energy tree species production is looked forward. The pre-treatment process of eucalyptus with dilute sulfuric acid is optimized by response surface methodology. The effects of sulfuric acid concentration, solid-liquid ratio, reaction time and temperature on the pre-treatment effect are investigated with xylose recovery, cellulose enzymatic hydrolysis and total sugar yield as indicators. The results show that the pre-treatment effect of eucalyptus is the best when the concentration of H2SO4 is 0.52%(w/w), the pre-treatment temperature is 168 °C, and the time is 27min, and at this time, the xylose recovery rate is 87.58%. Then, under the optimum pre-treatment conditions, the effects of enzyme dosage and time on enzymatic hydrolysis are studied. The optimum enzymatic hydrolysis conditions are as follows: cellulase dosage 60FPU/g dry matter, and enzymatic hydrolysis for 36h. The cellulase hydrolysis rate can reach 90.82%, and the total sugar yield is 95.16%.

1. Introduction
Biomass renewable energy is currently a hot issue that has attracted much attention and research. Among all kinds of biomass renewable energy sources, forest biomass is an excellent alternative to fossil fuels because of its huge content (accounting for 90% of the earth's fixed energy) and can be used in many ways. And forest biomass energy is a kind of efficient clean energy, its carbon dioxide emissions are almost zero, and the environmental benefits are very high [1]. Zhou et al. (2016) predicted that by 2020, China's forest biomass energy resources could be utilized by about 1.2 billion tons, replacing the standard coal by about 804 million tons, and the carbon dioxide emissions generated by forest biomass energy replacing fossil fuels would reach 17.13 tons [2]. Therefore, if the efficient utilization of forest biomass energy resources can be realized, on the one hand, the dependence of human beings on fossil fuels can be reduced and the tense situation of energy supply can be alleviated; on the other hand, the use of this clean energy can reduce environmental pollution, contribute to improving climate warming, and achieve the harmonious development of economy and environment. China's forest biomass energy resources are rich in species, widely distributed, high combustion value, and have great potential for development and utilization. According to the data of the eighth forest inventory, there are about 16.4 billion cubic meters of living trees in China, with a forest area of up to 20.8 billion hectares, ranking
fifth in the world, and the area of planted forests remains the first in the world. China's forest carbon pool is about 21.4-28.1 billion tons of carbon, accounting for about 2% of the world's total carbon. However, at present, China's existing forest vegetation carbon storage accounts for less than half of the potential carbon storage, about 44%, which shows that China's terrestrial ecosystem carbon potential is still considerable.

2. State of the art
Since the 1990s, many foreign scholars have analyzed the demand and supply of biomass energy resources in different situations. Dias (2017) assessed Canada's forest biomass supply and the potential of reducing greenhouse gas emissions by using forest biomass energy fuels, and concluded that Canada's forest biomass energy supply was very deficient [3]. Kondziella (2016) used scenario simulation method to evaluate biomass energy potential considering environmental, technological and social factors, and the result was 50%-71% of theoretical potential [4]. Sikkema (2014) applied IWPB framework to study biomass energy potential considering biodiversity conservation, carbon storage balance and logging land conservation [5]. Nambiar et al. (2015) obtained the potential amount of forest biomass energy resources in China based on the survey data of some areas and the sixth forest inventory report, and discussed the availability of forest biomass energy resources from the aspects of forest multifunction, sustainable forest management and periodic resource supply [6]. Vangansbeke (2015) pointed out that the succession of soil communities after harvesting would lead to the decline of soil fertility, and the use of forest residues to supplement soil organic matter beforehand after harvesting would be beneficial for the maintenance of soil fertility level [7].

3. Methodology

3.1. Determination of moisture and dry matter content in eucalyptus
The raw materials are crude powder in 9FX-42 crop straw mill, then after fine powder in LK-400B portable mill, 20-mesh sieve is obtained. The moisture content and dry matter content in raw materials are determined by constant temperature method at 105 °C oven. Eucalyptus after crushing and sieving is mixed evenly. Take 5g and weigh (m1) it in an aluminium box (m0) which has been baked to constant weight. Then put it in an oven at 105 °C for 24 hours. Remove it and put it in a dryer to cool to room temperature and weigh it (m3). After weighing, the samples are put into the oven again, then removed after 1h and cooled in the dryer and weighed (m3). So repeatedly, until the difference between m3 and m0 is less than 0.002g, then the water content is calculated after drying. Each sample is repeated three times and the average value is taken as the calculated result.

\[
\text{water content\%} = \frac{m_1 - m_3}{m_1 - m_0} \times 100
\]

\[
\text{dry matter content\%} = 1 - \text{water content\%}
\]

3.2. Determination of ash content in eucalyptus
0.5g of the sample after the determination of dry matter content is weighed (m1) in a constant crucible (m0) and carbonized to smokeless in an electric furnace and then put into a muffle furnace. The temperature is controlled at 575 °C and heated for 24 hours. After cooling to 200 °C, the crucible is moved into the dryer, and the sample is cooled to room temperature and weighed (m3). Replace the sample back to muffle furnace and repeat it until the weight change two times is less than 0.3mg. Each sample is repeatedly weighted three times and the average value is taken as the calculated result.

\[
\text{ash content\%} = \frac{m_1 - m_3}{m_1 - m_0} \times 100
\]
3.3. Determination of protein content in eucalyptus

The protein content in eucalyptus is determined by Kjeldahl method. 0.100g sample is weighed and put into the digestive tube. 10.000g anhydrous potassium sulfate, 0.500g copper sulfate and 20mL concentrated sulfuric acid are added. In the fume hood, it is digested to a transparent light green colour and distilled, absorbed and titrated on a fully automatic Kjeldahl Nitrogen Meter. Each sample is repeated three times and the average value is taken as the calculated result.

\[
\text{protein content}\% = \frac{\text{Total nitrogen content} \times 6.25}{\text{Dry weight of eucalyptus samples}} \times 100
\]  

(4)

3.4. Determination of cellulose, hemicellulose and lignin content in eucalyptus

The two-step acid hydrolysis method is adopted. Step 1: accurately weigh 0.300g sample to be measured and put it into the test tube, add 3.0mL 72% H2SO4 solution, and mix in a whirlpool. Put the test tube in a 30 °C water bath to maintain 60min and mix it with swirl once 5~10min. Step 2: take the test tube out of the water bath and add 84mL deionized water to dilute the sulfuric acid concentration from 72% to 4%. Continue to put it in the sterilizing pot at 121°C for 1 hour, and then drain it. Glucose and xylose are determined by high performance liquid chromatography (HPLC) after filtrate is filtered through 0.22μm filter membrane, used for calculating the content of cellulose and hemicellulose. The acid soluble lignin (ASL) is determined by ultraviolet-visible spectrophotometry. The acid insoluble lignin (AIL) is determined after filtrate residue is dried to constant weight at 105°C. The AIL contain acid-insoluble ash and acid-insoluble protein, which are neglected because of its small content. Each sample is repeated three times and the average value is taken as the calculated result.

Because the second step of two-step acid hydrolysis is carried out in a high-pressure sterilizing pot at 121°C, a standard sugar recovery test is needed. Selection of standard sugar concentration should be close to the corresponding sugar concentration in the sample. Repeat the second step, and determine the standard sugar recovery concentration of known concentration by HPLC to calculate the recovery coefficient of monosaccharide.

\[
\text{Cellulose content}\% = \frac{C_i \times V \times 0.9}{\alpha \times m} \times 100
\]  

(5)

\[
\text{Hemicellulose content}\% = \frac{C_i \times V \times 0.88}{\beta \times m} \times 100
\]  

(6)

\[
\text{ASL content:} \text{ the filtrate is measured under 320nm and its absorbance is compared with 4% sulfuric acid. The sample is diluted with contrast, so that the absorbance is 0.2~1.0 and the dilution is recorded. Each sample is repeated three times and the average value is taken as the calculated result.}
\]

\[
\text{ASL}\% = \frac{OD_{320} \times V \times n}{\varepsilon \times m} \times 100
\]  

(7)

\[
\text{AIL}\% = \frac{m_1 \times 100}{m}
\]  

(8)

\[
\text{Lignin content}\% = \text{ASL}\% + \text{AIL}\%\]

(9)
4. Results and discussion

4.1. Composition determination of eucalyptus wood

Eucalyptus glucan, xylan, protein and other components are determined by two-step acid hydrolysis and Kjeldahl method. The contents of each component are shown in Table 1.

| Composition | Glucan | Xylan | Lignin | Protein | Ash content |
|-------------|--------|-------|--------|---------|-------------|
| %           | 35.85  | 17.41 | 21.61  | 2.80    | 3.40        |

It is known from Table 1 that the main components of eucalyptus raw materials are glucan, xylan and lignin, with contents of 35.85%, 17.41% and 21.61%, respectively. In addition, there is a small amount of arabinose 0.70%, and other sugars such as mannose are not detected. In addition to these three components, eucalyptus wood also contains 2.80% protein, 3.40% ash and other substances.

4.2. Effect of pre-treatment time on xylose recovery, cellulase hydrolysis rate and total sugar yield

After processing eucalyptus for 10min, 15min, 20min, 25min and 30min, enzymatic hydrolysis is carried out for 48h. The changes of xylose recovery, cellulose hydrolysis rate and total sugar yield after hydrolysis are obtained as shown in Figure 1.

![Figure 1. Effect of pre-treatment time on xylose recovery, cellulase hydrolysis rate and total sugar yield](image)

It can be seen from Figure 1 that xylose recovery, cellulase hydrolysis and total sugar yield increase with time in a certain period of time, and reach the maximum at 25 minutes. It also shows that the hydrolysis yield of cellulose increases with the prolongation of reaction time in a certain period of time, indicating that longer pre-treatment more destroys the supra-molecular structure of lignocellulose in raw material, which is beneficial for cellulase. With the prolongation of the reaction time, the three both decrease simultaneously, so the time should not be too long.

4.3. Effect of sulfuric acid concentration on xylose recovery, cellulase hydrolysis rate and total sugar yield

Eucalyptus is pre-processed with 0.1%, 0.3%, 0.5%, 0.7% and 0.9% dilute sulfuric acid for 48 hours, and its fermentable sugar concentration is determined. The changes of xylose recovery, cellulose hydrolysis and total sugar yield are investigated as shown in Figure 2.
Figure 2. Effect of sulfuric acid concentration on xylose recovery, cellulase hydrolysis rate and total sugar yield

As can be seen from Figure 2, xylose recovery, cellulase hydrolysis rate and total sugar yield increase with the increase of acid concentration at a lower sulfuric acid concentration. When sulfuric acid concentration is 0.5%, xylose recovery reaches 78.74%. The maximum value of cellulase hydrolysis rate and total sugar yield appear to be delayed. When acid concentration is high, xylose recovery, cellulase hydrolysis rate and total sugar yield show a downward trend. The reason may be that when acid concentration is too high, mono-saccharides such as glucose in hydrolysate will be further degraded to furfural and other substances. At the same time, the increase of acid concentration will cause equipment corrosion and later treatment costs. Taking these factors into consideration, 0.5% acid concentration is selected to optimize the later stage parameters.

4.4. Effect of temperature on xylose recovery, cellulase hydrolysis rate and total sugar yield

Eucalyptus is pre-processed at different pre-treatment temperatures and then enzymatically hydrolyzed for 48 hours. The concentration of fermentable sugar, xylose recovery, cellulose hydrolysis rate and total sugar yield are determined after the hydrolysate is obtained. The changes of xylose recovery, cellulose enzymatic hydrolysis and total sugar yield are shown in Figure 3.

Figure 3. Effect of pre-treatment temperature on xylose recovery, cellulase hydrolysis rate and total sugar yield
It can be seen from Figure 3 that in the dilute acid pre-treatment process, the three factors increase with the increase of reaction temperature. When the reaction temperature is 170°C, the xylose recovery, cellulase hydrolysis rate and total sugar yield are 81.53%, 69.88% and 77.13%, respectively. Continuously increasing reaction temperature, the three show a downward trend or a slight increase, probably because mono-saccharides such as reducing sugar will aggravate dehydration to produce fermentation inhibitors such as 5-HMF, levulinic acid and formic acid at high temperature.

4.5. Results analysis

From the optimization of pre-treatment, enzymatic hydrolysis, detoxification and butanol fermentation based on enzymatic hydrolysate, the following conclusions are obtained: the pre-treatment conditions of dilute sulfuric acid are optimized according to response surface method, and the optimum pre-treatment conditions are determined as follows: pre-treatment time 27min, pre-treatment temperature 168°C, acid concentration 0.52%, and solid-liquid ratio 1:10. Under these conditions, xylose recovery rate is 87.58%, cellulase hydrolysis rate is 90.82%, and total sugar yield is 95.16%. After the optimum pre-treatment process is determined, the amount of cellulase used in the enzymatic hydrolysis process is optimized. The results show that the highest cellulase hydrolysis rate is 91.55% when the amount of cellulase is 60FPU/g dry matter.

5. Conclusion

Eucalyptus raw materials, the research objects, are pre-treated with dilute acid at high temperature. The effects of dilute acid pre-treatment conditions (pre-treatment time, pre-treatment temperature, acid concentration and solid-liquid ratio) on enzymatic conversion are optimized by response surface method. The chemical composition of the samples is investigated to further study acid pre-treatment, which lays a foundation for studying the mechanism of improving the conversion rate of biomass feedstock. The quadratic polynomial mathematical model of the effect of acid pre-treatment on the subsequent enzymatic hydrolysis conversion is established by response surface optimization with acid concentration, pre-treatment time and pre-treatment temperature as variables, and the model has significant significance (P<0.05). The optimal acid pre-treatment conditions are: acid concentration 0.52%, time 27min, and temperature 168°C. Under these conditions, xylose recovery rate is 87.58%, cellulase hydrolysis rate is 90.82%, and total sugar yield is 95.16%, respectively. Design Expert software analysis results show that the main factors affecting the acid pre-treatment effect are the pre-treatment time and temperature, while the influence of acid concentration is relatively small. The degradation and dissolution of hemicellulose and the decrease of crystallinity of some cellulose are very important for improving the subsequent enzymatic conversion.

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