

Liquefaction of Rice Straw with Ethylene Carbonate

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Abstract: In this study, rice straw (RS) was liquefied by ethylene carbonate (EC) using H_2SO_4 as a catalyst. The effects of various process conditions on the liquefaction characteristics were investigated by FT-IR and residue content analysis. The results show that cellulose and lignin are degraded during the liquefaction process and large amounts of groups are generated. In addition, it is difficult to effectively liquefy RS by using EC alone as the liquefying agent without other additives. Compared to water addition on liquefaction, the residue content can be significantly reduced up to 30% by adding H_2O_2 . It has also been proved that the liquor ratio (RS/EC, w/v) of 1:5 with H_2O_2 as an additive at 145°C for liquefaction time of 60 min in the presence of H_2SO_4 can accelerate the liquefaction process and high liquefaction yield can be obtained.

Keywords: rice straw; liquefaction; residue content; ethylene carbonate

1 Introduction

Nowadays, most polymeric materials are derived from non-renewable petroleum based products. However, the consumption of fossil fuel resources can not only lead to environmental issues, but also increase the shortage of fossil fuel resources. From this point of view, renewable resources have been considered as potential replacements for fossil fuel resources. While straw is one of the most naturally abundant renewable resources in the world, it is usually burned or discarded without recycling in the countryside. Therefore, the reuse of straw as a biodegradable polymeric material has become a hot research topic in recent years^[1].

Liquefaction of biomass has many potential applications such as in the preparation of



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foams, moldings, and adhesives^[2-4]. Ethylene carbonate (EC)^[5], polyhydric alcohols^[6], phenol^[7], and dioxane^[8] have been used as liquefying agents in the acid-catalyzed liquefaction process. Although EC can liquefy wood chips with high efficiency, it can't liquefy straw adequately and leaves behind a product with high residue content^[9]. Therefore, in the present study, liquefaction conditions of EC such as the liquor ratio, H₂O₂ dosage, H₂O dosage, H₂SO₄ dosage, liquefaction temperature, and time have been studied for achieving optimum technological conditions.

2 Experimental

2.1 Materials

Rice straw (RS) was cut into 40 ~ 80 mesh size pieces and dried in an oven at 105°C for 24 h. The pieces were then stored in a desiccator. H₂O₂ (30%) and H₂SO₄ (98%) were used without pretreatment. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2 Liquefaction

RS and EC were added into a reactor with a reflux condenser. After heating and stirring in an oil bath, the product was collected using methanol.

2.3 Measurement of residue content

After washing, the reaction solution was vacuum-filtered through a quantitative filter paper, and the residue was dried to constant weight in an oven at 105°C. The residue content was calculated using the following equation^[10]:

$$\text{Residue content}(\%) = (\text{weight of residue} / \text{weight of RS}) \times 100\%$$

2.4 FT-IR spectra

The FT-IR spectra of RS and the liquefied product were obtained using the KBr pellets method with an FT-IR spectrometer (Nicolet Nexus, Thermoelectron Corporation). The scanning range was 500 ~ 4000 cm⁻¹.

3 Results and discussion

3.1 FT-IR spectra

The FT-IR spectra of RS and the liquefied product are shown in Fig. 1. Strong IR absorption peaks are observed at 3340 cm⁻¹ and 1737 cm⁻¹ for the liquefied product. These peaks are assigned to hydroxyl and carbonyl groups, respectively, which arise from the breakdown of the original lignin^[11]. In addition, three new characteristic absorption peaks are observed at 2851 cm⁻¹, 1262 cm⁻¹, and 896 cm⁻¹, which indicate that new methylene and ester groups are generated during the liquefaction reaction, suggesting excellent decomposition of cellulose and lignin^[12].

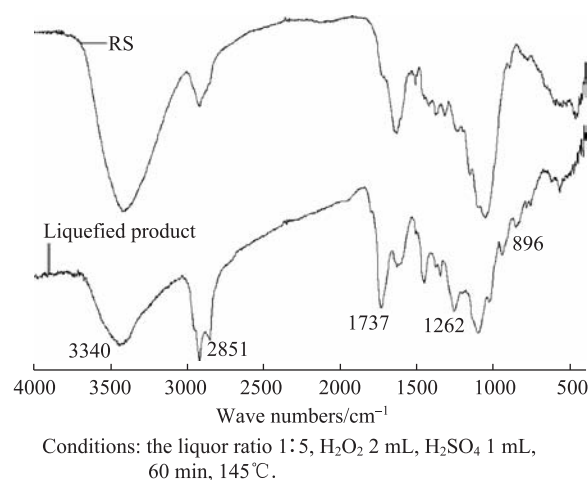


Fig. 1 FT-IR spectra of RS and the liquefied product

3.2 Effect of the liquor ratio and H₂SO₄ dosage

Fig. 2 shows the effect of the liquor ratio (RS/EC, w/v) on the residue content. The residue content can be dramatically reduced by increasing the amount of EC. This reduction is probably related to solubility and glycolysis effects during liquefaction. However, considering the cost of liquefaction, a residue content of 20.5% at the liquor ratio of 1:5 may be more economical than a residue content of 17.3% at the liquor ratio of 1:6.

The function of the H₂SO₄ is mainly to decrease the liquefaction time and temperature. Fig. 3 shows the effect of H₂SO₄ dosage on the residue content. When the dosage of H₂SO₄ is increased from 0.5 mL to 1.25 mL, the residue content decreases from 33.4% to 18.3%. However, when the dosage of H₂SO₄ is increased further to 1.75 mL, the residue content is slightly increased to 19.3% instead. With less than 1.25 mL of H₂SO₄, alcoholysis and catalysis effects of H₂SO₄ play an impor-

tant role in reducing the residue content. However, with 1.75 mL of H_2SO_4 , recondensation of the degraded products is more significant than alcoholysis and catalysis.

3.3 Effects of water and H_2O_2 dosage

The effects of water and H_2O_2 dosage on the EC liquefaction of RS are shown in Fig. 4. With 1 or 2 mL of water, the residue content noticeably decreases from 46.3% to 38.5% or 33.2%. This decrease in the residue content is mainly attributed to the hydrolysis effect in H_2SO_4 catalyzed liquefaction. However, with 3 or 4 mL of water, the residue content is increased slightly compared to the cases with 1 or 2 mL of water. This is mainly because the temperature of the liquefaction system decreases when excess water is added. On the other hand, adding 1 ~ 3 mL of H_2O_2 reduces the residue content to 33.4% ~ 18.3%. However, the residue content does not decrease further with more addition of H_2O_2 . In

this liquefaction system, the residue content is affected by hydrolysis and oxidation. A small amount of H_2O_2 can lead to the oxidation of RS, which significantly accelerates the liquefaction process. The residue content obtained after liquefaction with 1 mL H_2O_2 is similar to that with 2 mL water. It is assumed that the oxidation effect of 1 mL H_2O_2 is almost equivalent to the hydrolysis effect of 1 mL water. However, there would be a negative effect on the liquefaction yield of RS if the liquefaction temperature is decreased significantly by the addition of H_2O to the the liquefaction process.

3.4 Effects of liquefaction time and temperature

The effect of liquefaction time on the residue content of RS is shown in Fig. 5. When H_2O_2 is used for EC liquefaction at 145°C for less than 60 min, the liquefaction reaction proceeds rapidly and the residue content is reduced to 20.5%. After 60 min, liquefaction proceeds slowly. RS is perfectly liquefied after 75 min, with a residue content of only 16.3%.

This relationship between residue content and liquefaction time suggests that the liquefaction process follows pseudo-first-order kinetics.

Fig. 6 shows the effect of liquefaction temperature on the RS liquefaction process. Under the condition 1[#], EC is not very effective in decreasing the residue content, since the residue content is always higher than 45%. The residue content slightly decreases from 59.0% to 46.4% with increase in the liquefaction temperature from 120°C to 145°C . This is because the degradation of the crystalline portions of cellulose to the amorphous form can be accelerated by increasing the liquefaction temperature. However, when the liquefaction temperature is increased to 170°C , the residue content increases to 57.3%, which may be due to

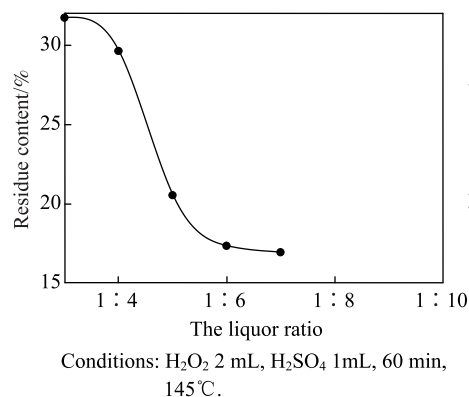


Fig. 2 Effect of the liquor ratio on the residue content

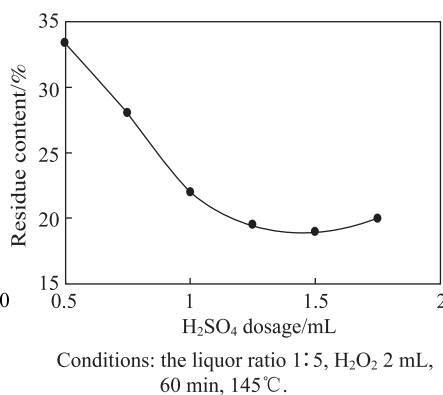


Fig. 3 Effect of H_2SO_4 dosage on the residue content

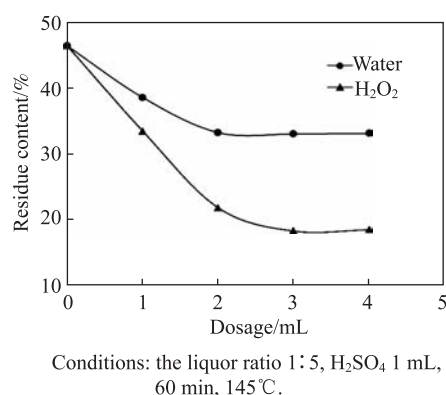


Fig. 4 Effect of the amount of water and H_2O_2 on the residue content in EC liquefaction

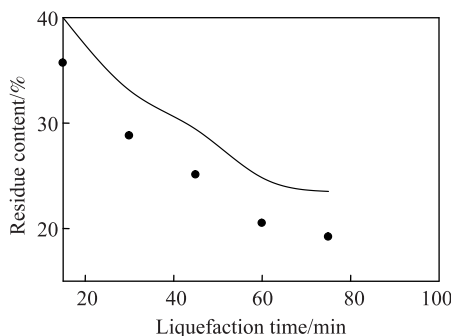
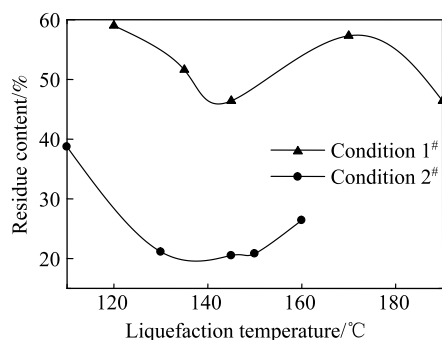


Fig. 5 Effect of liquefaction time on the residue content

the recondensation reaction during the delignification process. On the other hand, as shown in the curve corresponding to condition 2[#], adding H₂O₂ can dramatically decrease the residue content. When H₂O₂ is added in the EC liquefaction process, the residue content is only 20.5% at 130°C. This may be attributed to the fact that the degradation and liquefaction of RS is accelerated by H₂O₂ oxidation and strong hydrolysis. Adding H₂O₂ can effectively liquefy RS with high liquefaction yield.



Condition 1[#]: the liquor ratio 1:5, H₂SO₄ 1mL, 60 min;
condition 2[#]: the liquor ratio 1:5, H₂O₂ 2 mL, H₂SO₄ 1 mL, 60 min.

Fig.6 Effect of liquefaction temperature on the residue content

3 Conclusions

Cellulose, hemicellulose, and lignin are degraded during the liquefaction of rice straw (RS) and large amounts of ester and methylene groups are produced as a result of alcoholysis, oxidation, and hydrolysis reactions. In addition, RS can be liquefied using ethbonate carbonate (EC) along with H₂SO₄ and H₂O₂. Based on the residue content and economic efficiency, the optimum conditions for EC liquefaction are the liquor ratio (RS/EC, w/v) 1:5, H₂O₂ dosage 2 mL, H₂SO₄ dosage 2 mL, liquefaction time 60 min, and liquefaction temperature of 145°C.

Acknowledgments

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