Selectively production of levoglucosenone from cellulose via catalytic fast pyrolysis

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Abstract
Levoglucosenone (LGO) has a wide range of utilization in the field of organic synthesis. Magnetic solid acid (Fe\textsubscript{3}O\textsubscript{4}/C-SO\textsubscript{3}H\textsubscript{600}) was used in fast pyrolysis of cellulose to produce LGO. It was demonstrated that the catalyst could promote the pyrolysis of cellulose to produce LGO, but the yield was affected by the pyrolysis temperature and the relative amount of catalyst. The yield of LGO reached 20.0 wt% from catalytic fast pyrolysis of cellulose at 300 °C, which was significantly higher than that from cellulose (0.3 wt%). Furthermore, the kinetic analysis and recycling results showed that the catalyst could not only reduce the required temperature of cellulose in fast pyrolysis, but also still efficiently promote the production of LGO after recovery and activation.

Key words: Levoglucosenone, Magnetic solid acid, Catalytic fast pyrolysis, Cellulose.
Introduction

A great interest burgeons in renewable biomass as a source for fuel and chemicals production for the demands to replace alternatives to fossil fuels (Jiang et al., 2020a). Fast pyrolysis, one of the feasible and effective biomass utilization technology, can convert biomass into bio-oil (Sharifzadeh et al., 2019; Zhang et al., 2020). Bio-oil is a complex mixture of water and hundreds of organics including acids, ketones, aldehydes, esters, alcohols, furans, anhydrosugars, phenols and other macromolecular oligomers. Because of containing various compounds and the potential for wide range applications, it can be used as a liquid fuel or extracted valuable chemicals (Tshikesho et al., 2019). However, the concentration of most components in bio-oil obtained from the traditional pyrolysis process is relatively low, and it is currently uneconomical to separate special compounds from bio-oil. There is no doubt that bio-oil production with a high content of target products is essential (Meng et al., 2016). Recently, various selective pyrolysis methods have been investigated, such as pretreatment of raw material before pyrolysis, catalytic pyrolysis of biomass, and optimization of pyrolysis conditions (Zhang et al., 2021; Jiang et al., 2020b; Usino et al., 2020).

Levoglucosenone (LGO) is an anhydrosugar with a unique structure, which includes not only six different functionalized carbon atoms, but also two chiral centers, containing $\alpha,\beta$-unsaturated ketones and protected aldehyde functional groups. These unique properties make it a chiral synthon for the synthesis of a variety of new and valuable compounds, such as high-value drugs and bio-based polar aprotic solvent (Cao et al., 2015; Zhang et al., 2018; Liu et al., 2020). Although LGO has a considerable value for use, the content of LGO in bio-oil obtained by conventional pyrolysis of cellulose is extremely low, hindering its further utilizations. Therefore, it
is essential to develop a suitable catalyst for cellulosic fast pyrolysis to achieve LGO with high yields. It has been proposed that the catalysts currently used in the cellulosic pyrolysis to produce LGO include ionic liquids, liquid inorganic acids and solid acids (Doroshenko et al., 2019). Although ionic liquids can increase the yield of LGO significantly, high expenses make them unavailable in large-scale applications (Kudo et al., 2017). Cellulose impregnated with liquid inorganic acids (e.g. phosphoric acid, sulfuric acid) is also performed to promote LGO production (Dobele et al., 1999). However, this process shows several shortcomings: the impregnation of cellulose and acid requires a complicated pretreatment process; a large amount of waste acid is produced after the impregnation, which cannot be recycled and reused. In contrast, solid acid is thermally stable and can be readily recovered after pyrolysis. There is no need to go through a complicated impregnation process and only simple mechanical mixing with the cellulose is required. Therefore, solid acid is a better choice for catalytic fast pyrolysis of cellulose. Solid superacid SO$_4^{2-}$/ZrO$_2$ was subjected to catalytic pyrolysis, giving a LGO yield of 8.2 wt% (Wang et al., 2011). Lu et al. (2014a) developed a superacid SO$_4^{2-}$/TiO$_2$-Fe$_3$O$_4$ for catalytic pyrolysis of cellulose at 300 °C, obtaining a LGO yield up to 15.4 wt%. Phosphoric acid-activated carbon catalyzed pyrolysis of cellulose greatly improved the yield of LGO (Ye et al., 2017). The yield of LGO produced from cellulose catalyzed by solid acid still needs to be improved.

Based on previous research, an important and indispensable step for cellulose pyrolysis to generate LGO was the dehydration reaction (Zhang et al., 2017). Regarding this procedure, it has been reported that both Fe$_3$O$_4$ and acid catalyst could enhance the dehydration behavior and promote the yield of LGO in catalytic fast pyrolysis cellulose (Lu et al., 2014a; Halpern et al., 1973). In this study, magnetic
solid acid Fe$_3$O$_4$/C-SO$_3$H$_600$ was synthesized and applied in catalytic fast pyrolysis of cellulose to produce LGO. Different from previous reported investigations, this research could not only efficiently promote the conversion of cellulose to LGO, but also analyzed its kinetics and reaction mechanism in detail, and investigated the recovery and reuse performance of the catalyst.

**Materials and methods**

**Materials**

The microcrystalline cellulose, nano-Fe$_3$O$_4$ (≥99.5%, 20 nm) and glucose used in the experiment were purchased from Macklin biochemical Co., Ltd. (Shanghai). H$_2$SO$_4$ (99.8%) was purchased from Guangshi Agent Technology Co., Ltd. (Guangdong). Levoglucosan (LG) (>96%) and LGO (>96%) were purchased from Sigma-Aldrich (Shanghai).

**Catalyst preparation**

The preparation of the catalyst required two steps: carbonization and sulfonation. Firstly, the nano-Fe$_3$O$_4$ (2 g) and glucose (15 g) were mixed in deionized water (100 mL), and evaporated the water in an oil bath (100 °C) with vigorous stirring to ensure uniform dispersion of the nano-Fe$_3$O$_4$. After evaporation, the mixture was transferred to a crucible and heated to 500-700°C for a period of time in a tube furnace under N$_2$ atmosphere (240 mL/min) at a heating rate of 6 °C/min. The carbonized solid C/Fe$_3$O$_4$ therein was taken out and ground through a 200-mesh sieve, and then mixed with 98% H$_2$SO$_4$ at a ratio of 1 g/10 mL. After sulfonated in an oil bath for 20 h at a temperature of 150 °C, the sulfonated catalyst was washed with deionized water until neutral and dried at 105 °C for 24 h in an oven finally. The catalysts prepared at 500 °C, 600 °C and 700 °C were entitled Fe$_3$O$_4$/C-SO$_3$H$_{500}$, Fe$_3$O$_4$/C-SO$_3$H$_{600}$ and Fe$_3$O$_4$/C-SO$_3$H$_{700}$, respectively.
Catalyst characterization

The X-ray diffraction analysis of the catalyst was carried out in an X’Pert PRO MPD X-ray diffractometer using Cu Kα radiation source (λ=0.15418 nm). Fourier transform infrared spectroscopy (FTIR, Bruker TENSOR27, Optik Instruments, Brno, Czech Republic) was used to analyze the functional groups contained in the catalyst. Scanning electron microscope (SEM, ZEISS EVO LS10, Cambridge, UK) was used to scan the surface morphology of the catalyst. The acid sites of the catalyst were determined by NH₃ temperature programmed desorption (NH₃-TPD, Chemisorption analyzer, Quantachrome Instruments, Boynton Beach, FL). Thermogravimetric experiment was carried out in a TG analyzer (SDT650, TA, USA). Sample was put into alumina crucible, and heated from 50 °C to 650 °C at the rate of 10, 20 and 40 °C/min.

Kinetic analysis

The kinetic parameters were obtained by distributed activation energy model (DAEM). It assumed that the thermal decomposition reaction consisted of many simple reactions that obeyed a normal distribution \( f(E) \).

\[
f(E) \sim N(E, \sigma)
\]  

(1)

Due to the existence of the kinetic compensation effect, the activation energy, the pre-reference factor, and the mechanism function were related to each other. Assuming that the pre-reference factor was a constant, the activation energy was only related to the mechanism function, as shown in formula (2).

\[
\alpha = 1 - \frac{A}{\beta} \int_{0}^{\infty} \Psi(E, T) f(E) dE
\]  

where \( \alpha \) is the conversion rate, %; \( \beta \) is the heating rate, °C/min; \( E \) is the activation energy, kJ/mol; \( A \) is the pre-exponential factor, \( s^{-1} \); \( \Psi(E, T) \) is the...
temperature integral:

\[
\Psi(E, T) = \int_0^T \exp\left(\frac{-E}{RT}\right) dT
\]  

(3)

**Fast pyrolysis**

The sample was subjected to fast pyrolysis in a semi-batch CDS reactor (CDS 5200, Oxford, PA, USA), and then the composition of the volatile products after pyrolysis was examined by Gas Chromatograph-Mass Spectrometer (GC-MS) (Agilent 7890A/5975C, Santa Clara, CA, USA). The sample was weighted and placed in the middle of the quartz tube, and both sides of the quartz tube were blocked with quartz wool. The sample was pyrolyzed at 250-500 °C for 20 s. The injector temperature was 280 °C, and the helium gas (1 mL/min) was used as carrier gas with a split ratio of 1:100. The capillary column used for chromatographic separation was Agilent HP- INNO (30 mm × 0.25 mm × 0.25 μm). The oven program was held at 40 °C for 3 min, then ramped to 280 °C at 5 °C/min and held at 280 °C for 8 min. The mass spectrometer operated at 70 eV in EI mode. After fast pyrolysis, the catalyst was recovered by the permanent magnet, and the recovered catalyst was subjected to Py-GC/MS experiment to verify its cyclic activity. The chromatographic peaks were identified by the NIST mass spectral data library. The quantification of products was performed by external standard method. Each experiment was performed in triplicate to ensure its repeatability. The yield and relative content of products were calculated as follows:

\[
\text{Compound yield (wt\%)} = \frac{\text{mass of compound}}{\text{mass of cellulose}} \times 100\%
\]  

(4)

\[
\text{Relative content of compound (%) = } \frac{\text{Area of a compound}}{\text{Area of all compounds}} \times 100\%
\]  

(5)
Results and discussion

Catalyst characterization

The SEM images of the catalysts are shown in Fig. 1. It could be seen that the surface of Fe₃O₄/C-SO₃H₅₀₀ and Fe₃O₄/C-SO₃H₆₀₀ contained countless pores. This facilitated the contact of the catalysts with cellulose. Although there were many pores on the surface of Fe₃O₄/C-SO₃H₇₀₀, it was very messy, probably due to the excessive temperature destroying the pore structure on the surface of Fe₃O₄/C-SO₃H₇₀₀. Among the three catalysts, the surface area of Fe₃O₄/C-SO₃H₅₀₀ (1.8 m²/g) was larger than that of Fe₃O₄/C-SO₃H₆₀₀ (0.7 m²/g) and Fe₃O₄/C-SO₃H₇₀₀ (0.6 m²/g) (Table 1). This might be caused by the higher calcination temperature causing Fe₃O₄ to be embedded in the pores.

The XRD peaks of the three catalysts were all identified as the crystalline phase of Fe₃O₄ (Fig. 2), which indicated that Fe₃O₄ remained stable after calcination and sulfonation during the preparation of catalysts. In FTIR analysis, the absorption peak at 598 cm⁻¹ was the Fe-O bond vibration in Fe₃O₄ (Fig. 3) (Guo et al., 2013). The absorption peaks at 1600-1800 cm⁻¹ were C=C, C=O and COO⁻ stretching vibrations and 3463 cm⁻¹ was -OH stretching vibration (Alvaro et al., 2005). The absorption peaks at 1061 cm⁻¹ (-SO₃⁻ stretching) and the 1223 cm⁻¹ (O=S=O stretching in -SO₃H) were important signs of the presence of -SO₃H functional groups (Fukuhara et al., 2011). All peak strengths of Fe₃O₄/C-SO₃H₅₀₀ were weak. The difference between Fe₃O₄/C-SO₃H₆₀₀ and Fe₃O₄/C-SO₃H₇₀₀ was that catalyst Fe₃O₄/C-SO₃H₆₀₀ appeared-SO₃⁻ stretching and O=S=O stretching in -SO₃H at bands 1061 cm⁻¹ and 1223 cm⁻¹, respectively. This showed the presence of -SO₃H functional group in Fe₃O₄/C-SO₃H₆₀₀. NH₃-TPD characterization also indicated that the acid sites of Fe₃O₄/C-SO₃H₆₀₀ (0.7 mmol/g) were higher than that of Fe₃O₄/C-SO₃H₅₀₀ (0.1 mmol/g) and
Fe$_3$O$_4$/C-SO$_3$H$_{700}$ (0.5 mmol/g) (Table 1).

Figure 1. SEM images of catalysts.

Figure 2. XRD patterns of catalysts.

Figure 3. FTIR analysis of catalysts.
Table 1. The total acid sites and textural properties of the catalysts

| Catalysts                  | Acid sites (mmol/g) | BET surface area (m²/g) | Pore volume (cm³/g) |
|----------------------------|---------------------|-------------------------|---------------------|
| Fe₃O₄/C-SO₃H₅₀₀            | 0.1                 | 1.8                     | 0.006               |
| Fe₃O₄/C-SO₃H₆₀₀            | 0.7                 | 0.7                     | 0.006               |
| Fe₃O₄/C-SO₃H₇₀₀            | 0.5                 | 0.6                     | 0.002               |

**TG and kinetic analysis**

The TG analysis of pure cellulose and cellulose mixed with the solid acid catalyst is shown in Fig. 4 and Table 2. The main weight loss area of cellulose was 300-400 °C, and after mixing with the solid acid, the main weight loss area shifted to 200-400 °C. Considering the heating rate was 40 °C/min, the initial weight loss temperature of cellulose was 335 °C, which was higher than that of cellulose mixed with catalysts (199-263 °C). $D_{max}$ was the maximum weight loss rate in the decomposition reaction process, which indicated the degree of the decomposition reaction. The greater the $D_{max}$ was, the more intense the decomposition reaction revealed. The $D_{max}$ of cellulose (2.0-2.8%/°C) was also higher than that of cellulose mixed with the solid acid catalysts (0.2-0.7%/°C). The reason was that the thermal stability of cellulose was high, the thermal decomposition was carried out at a higher temperature and the reaction was concentrated, while the thermal stability of cellulose mixed with the catalyst was reduced, resulting in the dispersed decomposition reaction, and the wide main weight loss area.

The DAEM is currently the most accurate thermal analysis kinetic model, which can accurately simulate the experimental curve, as shown in Fig. 5. The kinetic parameters calculated according to DAEM are shown in Table 3. $E$ referred to the global activation energy, that was, the energy that needed to be absorbed when the sample was decomposed. The larger the $E$, the more energy needed to be absorbed
during the decomposition, and the more difficult it was to decompose. $\sigma$ refers to the deviation of activation energy, which indicates the concentration of decomposition reaction. Consider the heating rate was 40 °C/min, compared with the cellulose mixed with the catalyst (168.1-175.5 kJ/mol), the cellulose had the highest activation energy (187.4 kJ/mol). After mixed with the catalyst, activation energy for cellulose decomposition was reduced, thereby reducing the initial decomposition temperature. In addition, the $\sigma$ of cellulose (0.1 kJ/mol) was the smallest and the reaction was the most concentrated, while the cellulose mixed with catalyst had larger $\sigma$, and the reaction was dispersed. It could be seen that the thermal stability of cellulose could be destroyed after adding the catalyst, and the cellulose could be decomposed at a lower temperature.
Figure 4. TG and DTG curves of cellulose and cellulose mixed with catalyst.
| Samples                        | Heating rates (°C/min) | \(T_i\) (°C) | \(T_t\) (°C) | \(T_{\text{max}}\) (°C) | \(D_{\text{max}}\) (%/°C) |
|-------------------------------|------------------------|---------------|---------------|--------------------------|---------------------------|
| Cellulose                     | 10                     | 308           | 368           | 346                      | -2.8                      |
|                               | 20                     | 322           | 383           | 363                      | -2.4                      |
|                               | 40                     | 335           | 403           | 381                      | -2.0                      |
| Cellulose + Fe\(_3\)O\(_4\)/C-SO\(_3\)H\(_500\) | 10                     | 250           | 413           | 317                      | -0.7                      |
|                               | 20                     | 257           | 419           | 323                      | -0.7                      |
|                               | 40                     | 263           | 425           | 329                      | -0.6                      |
| Cellulose + Fe\(_3\)O\(_4\)/C-SO\(_3\)H\(_600\) | 10                     | 218           | 424           | 300                      | -0.4                      |
|                               | 20                     | 225           | 430           | 304                      | -0.4                      |
|                               | 40                     | 227           | 434           | 307                      | -0.3                      |
| Cellulose + Fe\(_3\)O\(_4\)/C-SO\(_3\)H\(_700\) | 10                     | 193           | 437           | 267                      | -0.3                      |
|                               | 20                     | 197           | 440           | 275                      | -0.3                      |
|                               | 40                     | 199           | 441           | 286                      | -0.2                      |

\(T_i\) is the temperature of pyrolysis at which the main weightless zone begins, 5%.

\(T_t\) is the temperature of pyrolysis at which the main weightless zone finishes, 95%.

\(T_{\text{max}}\) is the temperature corresponding to the highest point of the DTG peak.

\(D_{\text{max}}\) is the weight loss rate corresponding to the highest point of the DTG peak.
Figure 5. The experimental curve and curve fitted by DAEM model.
Table 3. Kinetic parameters on the basis of the distributed activation energy model

| Samples                  | $\lg A$ (s$^{-1}$) | $E$ (kJ/mol) | $\sigma$ (kJ/mol) | $R^2$    | Compensation effect         |
|--------------------------|--------------------|---------------|-------------------|----------|-----------------------------|
| Cellulose                | 15                 | 187.4         | 0.1               | 0.9992   |                             |
|                          | 20                 | 246.9         | 3.6               | 0.9996   | $E=5.1915\ln A+8.0246$     |
|                          | 25                 | 307.0         | 6.1               | 0.9994   | $R^2=1$                     |
| Cellulose + Fe$3O_4$/C-SO$_3$H$_{500}$ | 15                 | 175.5         | 11.3              | 0.9963   |                             |
|                          | 20                 | 231.1         | 15.5              | 0.9964   | $E=4.8464\ln A+8.0474$     |
|                          | 25                 | 287.1         | 19.6              | 0.9964   | $R^2=1$                     |
| Cellulose + Fe$3O_4$/C-SO$_3$H$_{600}$ | 15                 | 171.1         | 17.6              | 0.9967   |                             |
|                          | 20                 | 225.3         | 23.5              | 0.9967   | $E=4.7249\ln A+7.8654$     |
|                          | 25                 | 279.9         | 29.4              | 0.9967   | $R^2=1$                     |
| Cellulose + Fe$3O_4$/C-SO$_3$H$_{700}$ | 15                 | 168.1         | 22.0              | 0.9975   |                             |
|                          | 20                 | 221.3         | 29.2              | 0.9975   | $E=4.6415\ln A+7.6873$     |
|                          | 25                 | 275.0         | 36.3              | 0.9974   | $R^2=1$                     |
Effect of different catalysts on the yield of LGO

The yield of LGO prepared by fast pyrolysis of pure cellulose and fast pyrolysis of cellulose catalyzed by different catalysts was shown in Fig. 6. The yield and relative content of LG were also analyzed as it was the main product in non-catalytic pyrolysis of cellulose. During the non-catalytic pyrolysis of pure cellulose, the yield and relative content of LG were as high as 38.6 wt% and 84.3%, respectively, while the yield (0.3 wt%) and relative content (0.9%) of LGO in the pyrolysis products were very low. In catalytic pyrolysis of cellulose, both the yield and relative content of LG decreased significantly. It could be seen from the different cellulose pyrolysis results that there was a significant negative correlation between the production of LG and LGO, which should be further analyzed. The higher the yield and relative content of LGO was, the more obvious the decrease in the yield and relative content of LG obtained. Fe$_3$O$_4$ and acidic sites -SO$_3$H enhanced the dehydration behavior in the cellulose pyrolysis process, which was the main reason for the improvement in LGO yield. The yield of LGO (20.0 wt%) in the pyrolysis product was obtained from cellulose catalyzed by Fe$_3$O$_4$/C-SO$_3$H$_{600}$, which was higher than that from cellulose catalyzed by Fe$_3$O$_4$/C-SO$_3$H$_{500}$ (4.2 wt%) and Fe$_3$O$_4$/C-SO$_3$H$_{700}$ (13.5 wt%). The functional groups and acidic sites in the catalyst were the keys to promoting the formation of LGO. Fe$_3$O$_4$/C-SO$_3$H$_{500}$ had fewer functional groups and acidic sites, causing the poor catalytic effect. Fe$_3$O$_4$/C-SO$_3$H$_{600}$ exhibited more -SO$_3$H functional groups than Fe$_3$O$_4$/C-SO$_3$H$_{700}$. Furthermore, Fe$_3$O$_4$/C-SO$_3$H$_{600}$ had the highest acidic site, which might also an important factor to promote the formation of LGO. Fe$_3$O$_4$/C-SO$_3$H$_{600}$ had the best catalytic effect, and its reaction condition was further optimized.
Figure 6. The effect of three catalysts to pyrolyze cellulose on the yield and relative content of LG and LGO.

Effects of the catalytic pyrolysis temperature on the yield of LGO

The distribution of pyrolysis products could vary with temperature as the dominant reaction pathways shifted in rate and overall extent (Maduskar et al., 2018).

Fig. 7 shows the yield and relative content of LG and LGO at different temperatures during non-catalytic and catalytic pyrolysis. As the temperature increased, the cellulose was fully depolymerized and accompanied by a series of competitive reactions. The yield of LG increased from 38.6 wt% to 60.1 wt% as the temperature increased from 300 °C to 500 °C, while the yield of LGO (0.2 wt%-0.3 wt%) was very low. As depicted in Fig. 8a, LG and 1,6-anhydro-beta-D-glucofuranose (AGF) were the main products obtained by non-catalytic fast pyrolysis of cellulose at 300 °C, with relative content of 79% and 8%, respectively. As the temperature rose from 300 °C to 500 °C under non-catalytic pyrolysis conditions, the main products of cellulose pyrolysis were still LG and AGF, but hydroxyacetaldehyde (HAA), furfural (FF), 5-hydromethyl-furfural (5-HMF) and other compounds were also produced. Although the increase in temperature was accompanied by a series of competitive reactions that led to a decrease in the relative content of LG, the increase in
temperature also made the cellulose fully depolymerized resulting in the increasing yield of LG.

The catalytic pyrolysis of cellulose with Fe\textsubscript{3}O\textsubscript{4}/C-SO\textsubscript{3}H\textsubscript{600} could promote the formation of LGO and inhibit the formation of LG and AGF. The increase in the yield of LGO might be caused by the catalytic dehydration of LG. The promotion on LGO production was more obvious at 300 °C. According to Fig. 8b, it could be seen that the primary pyrolysis product of catalytic fast pyrolysis of cellulose at 300 °C was transformed from LG to LGO, accompanied by a certain amount of 1,4:3,6-dianhydro-\(\alpha\)-d-glucopyranose (DGP). During catalytic pyrolysis, the LGO yield tended to increase at 250-300 °C and then decrease at 300-500 °C. The highest yield of LGO (20.0 wt%) was obtained at 300 °C and the lowest LGO yield was got at 500 °C (4.9 wt%). The relative content of LGO also increased at 250-300 °C, and then decreased at 300-500 °C. The low yield and relative content of LGO at 250 °C could be attributed to the incomplete decomposition of cellulose and the difficulty in providing enough heat to enable the Fe\textsubscript{3}O\textsubscript{4}/C-SO\textsubscript{3}H\textsubscript{600} to catalyze the dehydration of cellulose. Catalytic fast pyrolysis could effectively reduce the competitive reaction in the cellulose pyrolysis process at 500 °C, and make the product distribution concentrate on the anhydrosugars LG, LGO, and DGP (Fig. 8d). The formation of LGO was mainly through glycosidic bond cleavage reactions in which cellulose was depolymerized and then exposed on dehydration reactions of the pyran ring. The dehydration process was the main reactions that affected the formation of LGO, mainly occurred at low temperatures, and the cleavage of glycosidic bonds mainly occurred in the medium temperature. As the pyrolysis temperature increased, the rate of cellulose glycosidic bond cleavage reaction was accelerated. When it was faster than the dehydration rate, only a small part of the glycosidic bond cleavage product
could be dehydrated, which limited the production of LGO, resulting in the reduction of LGO production at 300-500 °C in catalytic pyrolysis. These results also demonstrated that Fe$_3$O$_4$/C-SO$_3$H$_{600}$ could not only promote the formation of LGO, but also reduced the pyrolysis temperature of cellulose.

Figure 7. Effect of the temperature on the relative content and yield of LG and LGO.
**Figure 8.** Typical ion chromatograms of cellulose pyrolysis: (a) cellulose in noncatalytic pyrolysis at 300 °C, (b) cellulose in catalytic pyrolysis at 300 °C, (c) cellulose in noncatalytic pyrolysis at 500 °C, (d) cellulose in catalytic pyrolysis at 500 °C, (1) LG, (2) AGF, (3) LGO, (4) DGP, (5) HAA, (6) FF, (7) 5-HMF.

**Effect of the Fe₃O₄/C-SO₃H₆₀₀ to cellulose ratio**

The ratio of Fe₃O₄/C-SO₃H₆₀₀ to cellulose is also an important factor affecting the distribution of pyrolysis products. With the increase in the amount of catalyst, the yield and relative content of LGO showed a trend of initially increasing followed by a decrease, while the yield and relative content of LG continued to decrease as the amount of catalyst increased (Fig. 9). This showed that when the amount of catalyst was increased, the conversion of LG to LGO was promoted. The best ratio of Fe₃O₄/C-SO₃H₆₀₀ to cellulose was 1:1, in which the yield and relative content of LGO were 20.0 wt% and 50.7%, respectively. When the ratio of Fe₃O₄/C-SO₃H₆₀₀ to cellulose rose from 1:3 to 1:1, the acidic sites of the catalyst gradually increased, and the cellulose was able to completely contact the catalyst, so the yield of LGO continued to rise. When the ratio of Fe₃O₄/C-SO₃H₆₀₀ to cellulose increased from 1:1 to 3:1, the relative content of LGO changed a little, but the yield of LGO decreased to 12.6 wt%, which indicated that the excess catalyst exhibited a negative effect on the yield of LGO. The conclusion could be depicted as: first, an excessive amount of
catalyst would increase the heat transfer resistance of the sample, making it difficult for heat energy to accurately act on the catalytic reaction, thereby weakening the catalytic effect (Mullen and Boateng, 2010). Second, dehydration and charring reactions of cellulose were boosted by excessive catalyst, resulting in the reduction of organic volatile products (Branca et al., 2011). In addition, excess catalyst might also catalyze further reactions of LGO, leading to reduction in LGO yield (Bai et al., 2019).

**Figure 9.** Effect of Fe\textsubscript{3}O\textsubscript{4}/C-SO\textsubscript{3}H\textsubscript{600}-to-cellulose ratio on the relative content and yield of LG and LGO at 300 °C.

**Recycling of the catalyst**

In order to evaluate the stability of the catalyst, the reuse of Fe\textsubscript{3}O\textsubscript{4}/C-SO\textsubscript{3}H\textsubscript{600} for LGO production was repeatedly conducted under the optimum conditions of 300 °C and the ratio of cellulose to catalyst of 1:1. As shown in Fig. 10, the yields of LGO in the three cycle experiments were 14.1 wt%, 11.6 wt%, and 8.3 wt%, respectively. This showed that the catalyst could still effectively increase the yield of LGO in the cellulose pyrolysis product after undergoing the cycle experiment, but the acid sites in the catalyst might fall off during multiple cycles, so the catalyst effect of catalyst was significantly reduced. To improve the circulated feasibility the catalyst, the three-cycled catalyst was mixed with H\textsubscript{2}SO\textsubscript{4} and sulfonated at 150 °C for 20 h for regeneration. The results of fast pyrolysis showed that the catalytic activity of the
regenerated catalyst was completely restored, and the yield of LGO reached 20.6 wt%.

Compared with catalysts such as liquid acids and ionic liquids, Fe$_3$O$_4$/C-SO$_3$H$_{600}$ could not only efficiently catalyze the production of LGO from cellulose, but also could be recycled and reused, which was more economical and practical.

![Figure 10. Effect of catalyst cycle on LGO yield at 300 °C.](image)

The mechanism of fast pyrolysis of cellulose to LGO

According to currently proposed views, there were two main ways to produce LGO. First, cellulose was pyrolyzed and depolymerized to produce LG, and LG was further dehydrated to produce LGO. Second, cellulose was first dehydrated during pyrolysis, and then the glycoside bonds at both ends were broken to form LGO (Zhang et al., 2017; Lu et al., 2011). The latter process did not produce LG. In this experiment, since the increase in LGO yield was consistent with the decrease in LG yield, it was speculated that Fe$_3$O$_4$/C-SO$_3$H$_{600}$ could promote further dehydration of LG to produce LGO. To verify it, pure LG was mixed with Fe$_3$O$_4$/C-SO$_3$H$_{600}$ for fast pyrolysis at 300 °C. The typical ion chromatogram was shown in Fig. 11. The results showed that the presence of Fe$_3$O$_4$/C-SO$_3$H$_{600}$ could indeed catalyze the dehydration of LG to produce LGO and DGP. It is noticeable that although LGO and DGP were both products of LG's further dehydration, the increase in the yield of LGO was
significantly more than that of DGP. This showed that the catalytic effect of Fe$_3$O$_4$/C-SO$_3$H$_{600}$ was also selective. After observing the chemical structure of the three anhydrosugars, it could be found that LG and LGO had similar bicyclic structures (1,5- and 1,6-acetal rings). The conversion of LG to LGO only required dehydration to form C$_2$ carbonyl and C$_3$=C$_4$ bonds. The conversion from LG to DGP initially requires intramolecular transglycosylation to form 1,4-anhydride, and then etherification to form 3,6-anhydride (Shafizadeh et al., 1978). The latter was more complicated. This explained that Fe$_3$O$_4$/C-SO$_3$H$_{600}$ selectively catalyzed the dehydration of LG to LGO instead of DGP during the pyrolysis of cellulose. A possible pathway for the production of LGO by catalytic pyrolysis of cellulose was presented in Fig. 12. First, cellulose broke the glycosidic bonds on both sides by thermal pyrolysis to produce LG. Then LG was further dehydrated under acid catalysis to generate LGO. In this procedure, S1 with the carbon-carbon double bonds was produced through 3-OH obtained H (Lu et al., 2014b). Acid catalysis caused this reaction and promoted its dehydration. Then a keto-enol tautomerism reaction occurred to form a carbon-oxygen double bonds (S2). After these conversions were completed, acid catalysis caused S2 to lose another molecule of H$_2$O to produce LGO.
Figure 11. Typical ion chromatograms of LG in noncatalytic and catalytic pyrolysis: (1) LG, (2) LGO, (3) DGP.

Figure 12. Possible reaction mechanism of catalytic fast pyrolysis of cellulose for LG and LGO production.
Conclusions

Magnetic solid acid $\text{Fe}_3\text{O}_4/\text{C-SO}_3\text{H}_{600}$ was prepared to catalyze fast pyrolysis of cellulose for the selective production of LGO. The yield of LGO was increased from 0.3 wt% to 20.0 wt% at a pyrolysis temperature of 300 °C. The catalytic pyrolysis of cellulose could not only reduce the reaction-required temperature and promote the LGO production, but also could be reused for recycling in an economical and practical approach. In addition, this study explored the mechanism ofcellulosic pyrolysis to produce LGO, indicating that LGO could be produced via further dehydration of LG.

Declarations

Not applicable.

Funding

This work was funded by the National Natural Science Foundation of China (No. 51606204), the Science and Technology Planning Project of Guangzhou city and Guangdong province (No. 2017A020216007, 201707010236).

Conflict of Interest

The authors declare that they have no conflict of interest.

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