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Experimental study on the liquefaction of cellulose in supercritical ethanol

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Abstract. Cellulose is the major composition of solid waste for producing biofuel; cellulose liquefaction is helpful for realizing biomass supercritical liquefaction process. This paper is taking supercritical ethanol as the medium, liquefied cellulose with the intermittence installation of high press cauldron. Experiments have studied technical condition and the technology parameter of cellulose liquefaction in supercritical ethanol，and the pyrolysis mechanism was analysed based on the pyrolysis product. Results show that cellulose can be liquefied, can get good effect through appropriate technology condition. Under not catalyst, highest liquefaction rate of cellulose can reach 73.5%. The composition of the pyrolysis product was determined by GC-MS.

1. Introduction

Energy and environment issues are the focus of today's world development, and also important support and key content of the realization of the Chinese dream. The problem of energy depletion is becoming increasingly severe, while optimistic estimates of oil reserves are available only for 30~40 years [1], a very scarce resource in energy. In 2014, China's oil imports amounted to 310 million tons, with an apparent consumption of 518 million tons, net imports of 308 million tons, and foreign dependence as high as 59.5%. Bio fuel (Bio-Oil or Biofuel) is one of the important ways to alleviate this problem. As solid waste for preparing bio fuels, the main components of biomass include cellulose, hemicellulose and lignin. Through the study of the cellulose component contributes to the analysis of biomass liquefaction, liquefaction process and inference mechanism of liquefaction of biomass. Therefore, in this paper, more than 98% of the cellulose content of medical cotton as raw materials.

With the rapid development of green chemical technology, supercritical fluid technology (SCF) has become more and more widely used in the field of environmental and energy chemistry[2-3]. The supercritical fluid is a fluid whose temperature and pressure are both above the critical point. The supercritical fluid has strong dissolving ability of solute, but also has the sensitivity of pressure and temperature, mean by changing the control conditions of tiny, dissolving ability will have a greater change, thus more easy separation of fluid and solute; supercritical fluid with low viscosity and high diffusion coefficient characteristics is more conducive to heat and mass transfer. Therefore, the supercritical fluid is an excellent solvent and heat transfer medium. At present, there are many substances which can be used as supercritical fluid, such as alcohols[4], phenol[5], acetone[6], carbon dioxide[6], water[6], etc.. In view of the acidity of biomass pyrolysis liquid, the advantage of esterification between organic acid and alcohol is easy. Ethanol can be through biomass production by fermentation, to reduce the dependence on traditional fossil industry, do the pyrolysis supercritical medium of cellulosic ethanol is selected in this paper.

2. Experimental

2.1. System for supercritical pyrolysis

The main experimental equipment of supercritical pyrolysis system include GCF series permanent magnet rotating stirred tank reactor, 101A-1E drying box, and cyclone separator. The experimental raw materials were obtained by using medical absorbent cotton.

In the experiments of GCF series permanent magnetic stirring reactor, by heating, the cooling tube, exhaust valve, the volume is 1 L the reaction kettle body and stirring speed 0-1000 r/min stirring paddle, pressure gauge, temperature control device, stirring control device, motor, and transmission system components. The kettle cover and the kettle body are all made of stainless steel (1Cr18Ni9Ti). The sealing form of the reaction kettle is sealed by the circular arc and round arc surface without the gasket, and the frequency contact between the cambered surface and the frequency line. Through the contact surface high smoothness and high accuracy, to achieve a very good sealing effect. The maximum working pressure of the equipment can reach 20 MPa, and the maximum operating temperature can reach 350℃.

2.2. Methods

First of all, 20 g medical absorbent cotton is fed into the kettle body, and then 300 ml ethanol (0.795 g/ml) is sent into the kettle to mix the defatted cotton and alcohol evenly. Then, the kettle lid and the kettle body are sealed to carry out heating and heating. After reaching the reaction temperature, the maintenance time is more than 3 hours. The total mass of the solid and the liquid is then weighed, and the remaining solid and liquid are separated, and the remaining solids are dried at 105 ℃ to a constant weight. The liquid is then fed into a cyclone for separation. Then the liquid into the centrifuge was separated, filtered through the membrane of 0.2 m finally, samples were obtained by GC/MS analysis. The instrument used is the chromatograph mass spectrometer of British Finnigan company. The manufacturers are Thermo Quest Trace GC 2000/Trace MS. GC/ MS spectrometer parameters: column: HP-5MS; column temperature: 30~270 ℃ (heating rate of 10 ℃ /min), pyrolysis products of ethanol medium to maintain 7min.

3. Results and analysis

3.1. Pyrolysis rate and liquefaction rate analysis

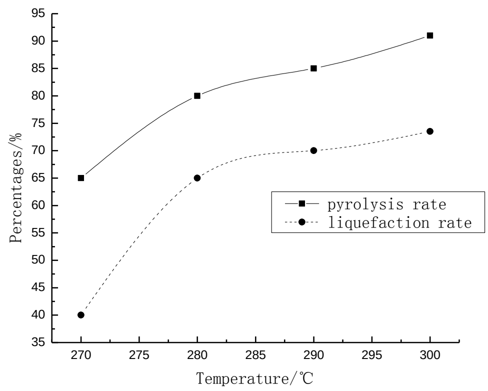

Figure 1. Cellulose's liquefaction rate and pyrolysis rate in supercritical ethanol

As shown in Figure 1, the reaction temperature range is 270-300 ℃, the reaction pressure range is 10-14MPa, and the liquefaction rate of cellulose under supercritical ethanol is varied. The experimental results show that the liquefaction rate of cellulose increases with the increase of temperature, but the increase decreases with the increase of temperature, and the liquefaction rate of cellulose reaches 73.5% at the reaction temperature of 300℃. The liquefaction rate decreases as the temperature increases. As the liquid product is cracked two times or more times, the formation of noncondensable gas leads to a decrease in the liquefaction rate. As shown in Figure 1, the pyrolysis rate of cellulose increases with the increase of temperature, and decreases first and then increases. The pyrolysis rate of cellulose reached 91% at the reaction temperature of 300 ℃.

3.2. Analysis of liquefied products

Gas chromatography – mass spectrometry was applied to separate and identify the products. Identification of the GC/MS peaks was based in most cases on comparison with spectra of the spectrum library. As shown in Table 1, the reaction temperature is 290 ℃, without adding catalyst in supercritical ethanol as the medium, cellulose pyrolysis products to remove the main product of ethanol and relative content, the relative content by the peak area normalization method is obtained.

Table 1. The main component of liquid product from cellulose in supercritical ethanol

Classes	Compound	Area/%
esters		29.63
	ethyl hydroxyl acetate	3.68
	diethyl pentanoate	3.47
	ethyl ethoxyacetate	2.30
	ethyl 2-ethylhexanoate	2.25
	ethyl 4-oxopentanoate	2.18
	diethyl hexanedioate	2.07
	ethyl 2-(hydroxymethyl)butanoate	1.89
	diethyl butanedioate	1.79
	diethyl 2-methylbutanedioate	1.72
	ethyl (2E)-pent-2-enoate	1.66
	ethyl 2-hydroxy-3-methylbutanoate	1.55
	ethyl butanoate	1.12
	ethyl 2-methyl-5-oxohexanoate	1.05
	ethyl (2E)-but-2-enoate	0.96
	ethyl penta-2,3-dienoate	0.96
	triethyl ethane-1,1,2-tricarboxylate	0.67
	ethyl hexadecanoate	0.31
the five membered heterocyclic element containing oxygen		22.7
	2-methyltetrahydrofuran-2-ol	9.98
	2-ethoxytetrahydrofuran	4.12
	furan-2-ylmethanol	3.51
	2-(1-methylethyl)-1,3-dioxolane	2.83
	tetrahydrofuran-2-ylmethanol	2.26
cyclopentyl ketones		13.81
	2-methylcyclopent-2-en-1-one	5.38
	2,3-dimethylcyclopent-2-en-1-one	3.91
	3-methylcyclopentane-1,2-dione	1.85
	3-ethyl-2-hydroxycyclopent-2-en-1-one	1.57
	cyclopent-2-en-1-one	1.10

In summary, the amount of carbon in the pyrolysis products of cellulose in supercritical ethanol is below 10. The pyrolysis products of cellulose in supercritical ethanol has three main categories: the first category is about 30% relative content of esters, these compounds are ethyl, including ethyl hydroxyacetate, diethyl pentanedioate, ethyl ethoxyacetate, ethyl 2-ethylhexanoate, ethyl 4-oxopentanoate, diethyl hexanedioate, ethyl 2-(hydroxymethyl) butanoate, diethyl butanedioate, diethyl 2-methylbutanedioate, and so on. It is inferred that cellulose is produced by pyrolysis of cellulose, followed by esterification with ethanol. These compounds can be used as components of bio gasoline, as well as in flavors, spices, cosmetics, pharmaceuticals, and soap.

The second is the five-membered heterocyclic element containing oxygen, with a relative content of about 22.7%. This substance is flammable and toxic. Including 2-methyltetrahydrofuran-2-ol, 2-ethoxytetrahydrofuran, furan-2-ylmethanol, 2-(1-methylethyl)-1,3-dioxolane, tetrahydrofuran-2-ylmethanol and so on.

The third category is cyclopentyl ketones relative content of about 13.8%, including 2-methylcyclopent-2-en-1-one, 2,3-dimethylcyclopent-2-en-1-one, 3-methylcyclopentane-1,2- dione, 3-ethyl-2-hydroxycyclopent-2-en-1-one, cyclopent-2-en-1-one. Among them, 2,3-dimethylcyclopent-2-en-1-one used for baking food, Boudin, frozen dairy products. In addition to the three compounds, there are a few ethers and aromatic compounds containing benzene rings, aromatic compounds containing benzene rings, derived from pyrolysis of other impurities.

4. Conclusion

The experimental results show that the supercritical liquefaction can be achieved by cellulose, and good results can be obtained by controlling proper technological conditions. And draw the following preliminary conclusions:

(1) The pyrolysis and liquefaction of cellulose in supercritical ethanol medium are related to the reaction temperature. The high temperature will lead to two pyrolyses, which will reduce the liquefaction rate. The reaction temperature is the most important factor affecting pyrolysis and liquefaction of cellulose, so it is important to find suitable temperature. The optimum temperature range of cellulose in supercritical ethanol is 290~300 ℃.

(2) Analysis of the products of pyrolysis in supercritical ethanol cellulose by GC-MS results showed that the pyrolysis of cellulose in supercritical ethanol, carbon number 10 overall, but the products tend to ethyl and the five-membered ring.

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