



Kinetic and product composition study on the cellulose liquefaction in polyhydric alcohols



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HIGHLIGHTS

- The solvolysis behaviors of cellulose in PEG 400 and glycerol were compared.
- The main liquefaction stage could be divided into two zones.
- The iso-conversional method was applied to estimate the apparent E.
- The most probable mechanism functions were determined by the Master-plots method.
- The functional groups of volatiles and product distributions were also evaluated.

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ABSTRACT

The liquefaction process of cellulose in polyhydric alcohols (PEG 400 and glycerol) was studied by TG-FTIR. Three stages were observed during the solvolysis process and the main liquefaction stage could be further divided into two zones. The differences of liquefaction behavior of cellulose in the two solvents were compared, and the functional groups of volatiles produced by solvolysis were also evaluated. A step-wise procedure based on iso-conversional and Master-plots methods was used for the kinetic and mechanism analysis of the main liquefaction stage. The calculation results based on the kinetic model were in agreement with the experimental data of the conversion rate. The kinetic parameters and mechanism functions between cellulose liquefaction in PEG400 and in glycerol were quite different, which verified that solvolysis behavior and reaction process were seriously influenced by solvent species. Finally, the detailed types of volatiles and product distribution were measured by Py-GC-MS.

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1. Introduction

As the fossil fuel energy dries up, and environmental pollution becomes more serious, human beings have been inspired to pursue novel types of energy instead of petroleum-based energy. Biomass is such a potential renewable alternative energy source, and has attracted a great deal of attention in recent decades.

Generally, there are several methods for utilization of lignocellulosic biomass including gasification, pyrolysis and liquefaction (McKendry, 2002; Rezzoug, 2002). The former two methods provide a simple and cost-effective way to convert lignocellulosic biomass into syngas and bio-oil, but these methods have some

drawbacks, such as higher reaction temperature (600–900 °C) or pressure (Zhang et al., 2014), which will lead to a cross-linking reaction between hydrocarbons and aromatics resulting in tar that is difficult to further decompose (Liu and Zhang, 2008). In addition, the indirect route by gasification implies the Fischer–Tropsch synthesis as a second step to transform the syngas into liquid fuels (Ngoc et al., 2015). The most studied way to directly produce liquids from biomass is fast pyrolysis, and it is the only technology performed in demonstration plants and used at the industrial level for bio-oil production to date (Xu and Etchevery, 2008). But the high equipment requirements and harsh reaction conditions lead to the limitation of its practical application. On the contrary, the reaction conditions of solvent liquefaction (solvolysis) are milder, and it is considered to be the most promising method for the production of low molecular weight liquid fuels (Wang et al., 2013). The liquefaction process has certain advantages, such as the presence of solvent which prevents the cross-linking and reverse

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reactions by diluting the concentration of the products, and relatively lower temperatures when compared with pyrolysis (Liu and Zhang, 2008; Liu et al., 2012).

Biomass has been successfully liquefied by using numerous reactive solvents, the potentially suitable solvents applied including phenolic compounds (Alma et al., 2001), polyhydric alcohols (Seljak et al., 2012; Kunaver et al., 2012), hydrogen-donor solvents (Wang et al., 2007; Araya et al., 1986) and ionic liquids (Mäki-Arvela et al., 2010; Du and Qian, 2011). Polyhydric alcohols used in biomass liquefaction include glycerol, ethylene glycol (EG), diethylene glycol (DEG), polyethylene glycol (PEG) and their mixture. The types of solvents have remarkable effects on the liquefaction process. Wang and co-workers (Wang et al., 2013) demonstrated the liquefaction of pinewood sawdust in the presence of various solvents (carbon dioxide, water, ethanol and acetone), and that the liquefaction process can be most significantly improved by increasing the yield of liquid oil and suppressing the formation of solid residue when ethanol was employed as the solvent. Additionally, solvents can also strongly affect the distribution of liquid products. In biomass liquefaction, the solvent to biomass ratio has a great influence on the liquefaction behavior. When the concentration of biomass is too high, the liquefaction residue content increases. The further increase in biomass concentration leads to re-condensation reactions of the decomposed components which would break the liquefaction process (Zhang et al., 2012). On the other hand, polyhydric alcohols can be effectively not only dissolved and dispersed the liquefied components but also retarded re-condensation of free-radical fragment (Mishra and Saka, 2011).

Several kinetic models have been reported in the literature for the liquefaction of biomass. Grilc et al. (2015) carried out solvolysis of wood, cellulose, hemicellulose and lignin in glycerol in the presence of homogeneous imidazolium-based ionic liquid (IL) catalysts, and a novel kinetic model for the solvolysis of biomass and its components was developed by following the mass of solid particles and their specific surface area (BET method) as a function of time and temperature. The solvolysis of wood dowels of various diameters in acidified phenol is described by Ammar et al. (1994), and a simple mathematical model based on a dual diffusion reaction was proposed. Grilc et al. (2016) studied the one-step solvolysis and hydro-treatment of oak, fir, and beech sawdust in a slurry reactor using tetralin, phenol and glycerol as solvents. A new lumped kinetic model was developed according to the reaction mechanisms. Mishra and Saka (2011) investigated the kinetics of Japanese beech wood liquefaction in subcritical phenol using a batch-type reaction vessel, and the kinetics for liquefaction was modeled using first-order reaction rate law. The different kinetic mechanisms were found to exist for lignin and cellulose at two different temperature ranges: a lower range of 160–290 °C and a higher range of 310–350 °C, whereas for hemicellulose, it was only liquefied in the lower temperature range. Zhang et al. (2014) subjected wood and its three cell wall components to a liquefaction condition using glycerol/polyethylene glycol (PEG 400). Kinetics of liquefaction of wood and its major cell wall components was presented, and the kinetic parameters were estimated. However, the results of these studies obtained from a small amount of data, which may have led to inaccurate results.

Cellulose solvolysis is of great importance in the thermochemical conversion of biomass to sources of energy due to its high proportion (more than 50%) in biomass (Wu et al., 2013). Thus, in the present work, the kinetic behavior and proper mechanism functions of cellulose liquefaction in polyhydric alcohols (PEG400 and glycerol) were examined. In addition, the types of volatiles and product distribution were also obtained. The effects of different solvents on liquefaction process were analysed as well.

2. Materials and methods

2.1. Materials

Cellulose (CAS number: 9004-34-6) tested in the experiment is the commercial product from Aladdin Industrial Corporation, Shanghai, China. The grain diameter of cellulose is under 90 μm. In this paper, polyethylene glycol 400 (PEG 400) and glycerol were used as the liquefaction reagents. They were reagent grade and used without further purification. The ratio of polyhydric alcohols to cellulose applied in this study was 6:1.

2.2. TG-FTIR analysis

The thermogravimetric analyzer was coupled to the FTIR spectrophotometer (409PC-iS10) to investigate the mass loss of samples under the liquefaction of polyhydric alcohols and on-line formation of typical volatiles. In the TGA experiment, the samples were heated from ambient temperature to 600 °C at the heating rate of 10, 20, 40 °C min⁻¹ under a nitrogen flow of 30 ml min⁻¹ to maintain an inert atmosphere for the liquefaction. The mass of the samples were about 10 mg to avoid the possible temperature gradient inside samples and ensure the kinetic control of the process. The FTIR was connected to TG by a Teflon tube and a flow cell, which were preheated to 453 K to prevent condensation of the evolved gases. The volatiles were carried into an infrared detector with high pure nitrogen once produced. The scanning range was set to be 4000–400 cm⁻¹.

2.3. Liquefaction kinetics

The liquefaction of lignocellulosic biomass in solvents was a solvolysis process and the solvents played important roles in the decomposition of biomass in accordance with the previous studies of liquefaction reaction mechanisms (Alma and Acemioglu, 2004; Acemioglu and Alma, 2002; Yan et al., 2010). On the other hand, the solvent in the liquefaction system was superfluous, thus the concentration of liquefaction solvent (polyhydric alcohols) could be considered as constant. Therefore, the following assumptions were made in the development of the reaction kinetics of cellulose liquefaction (Alma and Acemioglu, 2004; Yan et al., 2010): (1) the concentration of polyhydric alcohols remained constant in the whole liquefaction process; (2) the liquefaction process of cellulose in the presence of polyhydric alcohol is identified as an irreversible reaction; (3) the temperature dependence of the rate constant could be described by the Arrhenius equation.

Thus, the conversion rate of liquefaction was considered as the following equation (Zou et al., 2010):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where α is the fractional conversion, t is the time, T is the Kelvin temperature, $k(T)$ is the rate constant, A is the pre-exponential factor, E is the activation energy, R is the universal gas constant and $f(\alpha)$ is the temperature-independent function of conversion related to the decomposition mechanism.

For a linear heating rate, $\beta = dT/dt$, Eq. (1) is transformed to

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (2)$$

The integration function of Eq. (2) is generally expressed as:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right)dT \quad (3)$$

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