Solvolysis kinetics of three components of biomass using polyhydric alcohols as solvents

CrossMark

Yan Shi [a], Xueying Xia [a], Jingdan Li [a], Jing Wang [a], Tiantian Zhao [a], Hongmin Yang [a], Jianchun Jiang [b], Xiaoxiang Jiang [a,b,*]

[a] Engineering Laboratory for Energy System Process Conversion & Emission Control Technology of Jiangsu Province, School of Energy & Mechanical Engineering, Nanjing Normal University, Nanjing 210042, China
[b] Institute of Chemical Industry of Forest Products, China Academy of Forest, 210042, China

HIGHLIGHTS

- The solvolysis behaviors of three components of biomass were compared.
- The iso-conversional method was applied to estimate the apparent activation energies.
- The most probable mechanism functions were determined by the Malek method.
- The activated complex theory was applied to determine $\Delta S'$, $\Delta H'$ and $\Delta G'$.

ARTICLE INFO

ABSTRACT

The solvolysis behavior and reaction kinetics of the three components of biomass (cellulose, hemicelluloses and lignin) liquefied in polyhydric alcohols (PEG 400 or glycerol) were investigated in this paper. Three stages were observed during the solvolysis process and the main degradation stage could be further divided into two zones. The influences of solvents on the liquefaction process of three main components were compared. Based on Starink and Malek methods, kinetic parameters and mechanism functions were obtained. The derived average activation energy of cellulose, hemicellulose and lignin were 108.73, 95.66 and 94.13 kJ mol^{-1} in PEG 400, while the values were 102.16, 77.43 and 89.10 kJ mol^{-1} in glycerol, respectively. Higher efficiency was observed when using glycerol as solvent, which could be ascribed to the higher polarity value of glycerol. The conversion curves calculated with obtained mechanism models and kinetic parameters were in good agreement with the experimental data.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

As the only renewable carbon resource, biomass has received a great deal of attention recently for its striking characteristics of huge reserves, low sulfur and nitrogen content and carbon neutrality. The term biomass can generally be defined as all the organic matter containing energy from the sun acquired through photosynthesis (Sungsuk et al., 2016). It is one of the sustainable energy sources considered as an alternative for fossil fuels (Aysu and Kücük, 2013). Lignocellulosic biomass, mainly in form of abundant agricultural and forestry wastes, has the most potential applications. However, the lignocellulosic biomass is a complex compound mainly composed of cellulose, hemicellulose and lignin. Cellulose is a homogenous polysaccharide composed of linear chains of glucose monomers linked with β-1,4-glucosidic bonds (Bui et al., 2015). Hemicellulose is a heterogeneous, branched polymer of different monosaccharides (Cheng and Timilsina, 2011). Lignin exhibits a complex three dimensional (3D) structure through carbon–carbon linkages or ether bonds in the phenyl propane units (Zhao et al., 2014). Cellulose and hemicellulose fibers are tightly bonded to lignin by hydrogen and covalent bonds (Bui et al., 2015), which makes their degradation difficult.

In the past decades, many efforts have been made for fuel and chemical production from lignocellulosic biomass through thermo-chemical and biochemical conversion technologies. In comparison with biochemical technologies, thermo-chemical processes, typically including pyrolysis (Sharma and Rao, 1999) and direct liquefaction (Kurimoto et al., 1999; Yamada and Ono,

* Corresponding author at: Engineering Laboratory for Energy System Process Conversion & Emission Control Technology of Jiangsu Province, School of Energy & Mechanical Engineering, Nanjing Normal University, Nanjing 210042, China.
E-mail address: 62081@njnu.edu.cn (X. Jiang).

1999), were considered to be more promising methods, obtaining low molecular weight liquid products in high yields. During the pyrolysis process, organic materials degrade at elevated temperatures ranging between 400 °C and 1000 °C (Aysu and Kücük, 2013) in the absence of oxygen. However, the process of pyrolysis has certain disadvantages, such as the high operating temperature, which could lead to cross-linking reactions between hydrocarbons and aromatics, resulting in tar that reduces bio-oil production (Liu and Zhang, 2008). In comparison with pyrolysis, the reaction conditions of solvent liquefaction of biomass are milder. The presence of organic reagents will dilute the concentration of products to prevent the cross-linking and reverse reactions.

The types of solvents have remarkable influence on biomass liquefaction. The liquefaction process has been achieved in numerous solvents such as cyclic carbonates (Yip et al., 2009), phenol (Alma et al., 2001; Zhang et al., 2006), ionic liquids (Li et al., 2010; Du and Qian, 2011), hydrogen-donor solvents (Murnieks et al., 2014; Wang et al., 2007) and polyhydric alcohols (Yona et al., 2014; Yan et al., 2010; Zhang et al., 2012; Kima et al., 2015). Through liquefaction in different kinds of solvents, lignocellulosic components are brought to low molecular weight compounds with high reactivity that can be used as fuel and chemical raw materials. The liquefaction of lignocelluloses in high-polarity solvents will have higher efficiency. Most of the polyhydric alcohols have a high dipole moment. Free radical reactions and the ionic reactions including nucleophilic, electrophilic and elimination reactions that occur in the liquefaction process are relevant to the polarity of the reaction system. Therefore, higher conversion rates and bio-oil yield were usually obtained in the polyhydric alcohols with higher polarity (Huang and Yuan, 2015).

An intensive understanding of the liquefaction reaction kinetics is required for the full utilization of lignocellulosic biomass as sources of energy and chemicals. Yan et al. (2010) investigated the kinetics of cornstalk liquefied in polyhydric alcohols by kinetic models under different reaction temperatures. The results indicated that the liquefaction process of cornstalk was multilevel. The apparent reaction rate constants increased with the increase of reaction temperatures. The apparent activation energy and frequency factor were also obtained. The liquefaction process of wood and its three cell wall components were studied by Zhang et al. (2013) using polyethylene glycol (PEG 400)/glycerol as solvents. Kinetics of liquefaction of wood and its major cell wall components were presented, and the kinetic parameters were estimated. Grilc et al. (2015) investigated the solvolysis of wood, cellulose, hemicellulose and lignin in glycerol in the presence of homogeneous imidazolium-based ionic liquid (IL) catalysts. 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. Different depolymerisation reactivity of three components of wood was also taken into consideration. However, the internal liquefaction mechanism of lignocellulosic biomass in polyhydric alcohols was still unclear with a handful of researches, which set a great limitation on further utilization of biomass. In addition, kinetic parameters obtained only from several data may lead to unreliable results. Therefore, more efforts should be made to study the kinetics of biomass liquefaction in polyhydric alcohols.

In this paper, using cellulose, hemicelluloses and lignin as raw material, the liquefaction behavior and reaction kinetics in polyhydric alcohols (PEG 400 or glycerol) were studied. Apparent activation entropy ($\Delta S'$), activation enthalpy ($\Delta H'$), activation free enthalpy ($\Delta G'$) and steric effect (P) of the formation of active complex were calculated. On the basis of kinetic characteristics and reaction mechanisms, solvolysis kinetics of lignocellulosic components was also compared.

2. Materials and methods

2.1. Materials

Pure biomass components, including cellulose (α-cellulose, CAS: 9004-34-6), hemicellulose (xylan from corn cob, CAS: 9014-63-5) and lignin (sodium lignosulfonate, CAS: 8061-51-6), were commercial products purchased from Aladdin Industrial Corporation, Shanghai, China. Polyethylene glycol (PEG 400) and glycerol were used as liquefaction solvents in the alcoholysis of applied feedstocks. The ratio of lignocellulosic components to solvents was selected as 1:6. All these chemicals obtained from commercial sources were of analytical reagent grades, which were used without further purification.

2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (NETZSCH STA 409PC). To eliminate the influences generated by inner heat and mass transfer, the lignocellulosic components to solvents samples, with the mass of 15 mg, were spread evenly at the bottom of the alumina crucible of the thermal analyzer. The analysis provides for simultaneous measurement of weight changes from room temperature (about 25 °C) to 600 °C under pure nitrogen atmosphere with different heating rates of 10, 20 and 40 K/min. The flow rate of nitrogen was maintained at 30 ml/min to maintain the inner gas environment and to sweep away the volatiles released. The data of thermogravimetry (TG) and derivative thermogravimetry (DTG) were obtained using the software of the analyzer. To ensure reproducibility, all experiments were replicated at least twice.

2.3. Kinetic modelling of solvolysis

The liquefaction of lignocellulosic components in polyhydric alcohols was a solvolysis process and the solvents played important roles in the decomposition process. On the other hand, the concentration of liquefaction solvent (polyhydric alcohol) could be assumed as a constant due to relatively superfluous of solvent in the liquefaction system (Zhang et al., 2014). The temperature dependence of the rate constant can be described by the Arrhenius equation $(k(T) = A \exp(-E/RT))$. Thus the kinetic equation of solvolysis following the famous Arrhenius equation and the conversion rate could be expressed as follows:

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

In this equation, α is the fractional conversion, t is the time, $k(T)$ is the temperature-dependent rate constant, $f(\alpha)$ is the liquefaction reaction model, A is the pre-exponential factor, E is the apparent activation energy, T is the Kelvin temperature, R is the universal gas constant (8.314 J/mol K).

The fractional conversion α is defined as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{2}$$

where m_0 (%), m_t (%) and m_f (%) are the initial, actual, and the final mass of the sample, respectively.

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

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{3}$$