Fuel 109 (2013) 476–483

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Kinetics study on thermal dissociation of levoglucosan during cellulose pyrolysis

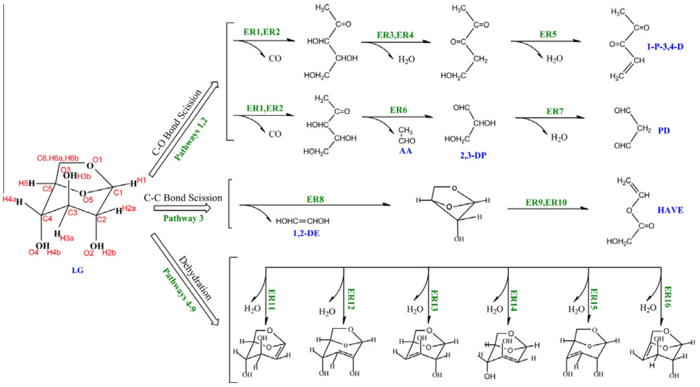
Xiaolei Zhang *, Weihong Yang, Wlodzimierz Blasiak

Division of Energy and Furnace Technology, Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

HIGHLIGHTS

- Kinetics study on levoglucosan primary decomposition in cellulose pyrolysis.
- Including C–O bond scission, C–C bond scission, and levoglucosan dehydration.
- Transition state calculation without tunneling correction is suitable method.
- Arrhenius equation for every elementary reaction and every pathway are obtained.
- One dehydration pathway is a preferred pathway for levoglucosan decomposition.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 July 2012
Received in revised form 13 March 2013
Accepted 15 March 2013
Available online 30 March 2013

Keywords:
Rate constant
Cellulose pyrolysis
Levoglucosan decomposition
Dehydration

ABSTRACT

The mechanisms and kinetics studies of the levoglucosan (LG) primary decomposition during cellulose pyrolysis have been carried out theoretically in this paper. Three decomposition mechanisms (C–O bond scission, C–C bond scission, and LG dehydration) including nine pathways and 16 elementary reactions were studied at the B3LYP/6-31 + G(D,P) level based on quantum mechanics. The variational transition-state rate constants for every elementary reaction and every pathway were calculated within 298–1550 K. The first-order Arrhenius expressions for these 16 elementary reactions and nine pathways were suggested. It was concluded that computational method using transition state theory (TST) without tunneling correction gives good description for LG decomposition by comparing with the experimental result. With the temperature range of 667–1327 K, one dehydration pathway, with one water molecule composed of a hydrogen atom from C3 and a hydroxyl group from C2, is a preferred LG decomposition pathway by fitting well with the experimental results. The calculated Arrhenius plot of C–O bond scission mechanism is better agreed with the experimental Arrhenius plot than that of C–C bond scission. This C–O bond scission mechanism starts with breaking of C1–O5 and C6–O1 bonds with formation of CO molecule (C1–O1) simultaneously. C–C bond scission mechanism is the highest energetic barrier pathway for LG decomposition.

1. Introduction

Thermal biomass conversion processes including pyrolysis, gasification, and combustion have been extensively studied by identifying selected products, varied feedstock and operating conditions. Biomass pyrolysis is the primary step for all these thermal biomass conversion processes. Pyrolysis process has been studied by variable experimental approaches, such as TGA [1,2], isothermal reactor [3–5], tube furnace [6], and so on. However, little has been published on the mechanism and kinetics of the molecular/atomic level.

---

* Corresponding author. Tel.: +46 8 790 85 31.
E-mail address: zhxl@kth.se (X. Zhang).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.03.035

Modeling chemical and physical processes of wood and biomass pyrolysis are well summarized by Di Blasi [7], there are primary and secondary decomposition for chemical kinetics of biomass pyrolysis. LG is one typical primary product for biomass pyrolysis. LG acts either as a product of cellulose pyrolysis or as an intermediate for the formation of other products [8], which mainly include dianhydro-β-d-glucopyranose, levoglucosenone, 1,6-anhydro-β-d-glucofuranose, furfural, and furfural derivatives [9]. Kawamoto et al. [10–12] studied the cellulose pyrolysis mechanism in earlier studies and concluded that LG is the primary direct product of cellulose decomposition, and it is subsequently degraded to lower-molecular-weight (LMW) products or polymerized into polysaccharides, which will be carbonized to form char; there is competition between the formation of LMW products and solid char. In the cellulose pyrolysis reaction scheme proposed by Banyasz et al. [13,14], it was concluded that cellulose can either be transferred into LG (tar), char, or gases (hydroxyacetaldehyde, formaldehyde, and CO) via an intermediate, namely depolymerizing cellulose. A molecular mechanism of detailed formation and decomposition of levoglucosan has been studied by previous work [15–19]. The decomposition of LG into low-molecular-species has higher activation energy than the formation of LG from cellulose, which indicated that the cellulose decomposition into intermediate is the rate-determining step for the whole cellulose pyrolysis process.

LG not only plays an important role during cellulose pyrolysis, it has also been considered as a model compound for tar [20–23]. The decomposition of LG becomes one important part of tar cracking [24–28]. Kinetics constant for the reactions of tar cracking has been studied extensively. First order kinetics for both primary and secondary pyrolysis of almond shells with a fluidized bed reactor was studied by Font et al. [24], it was proposed that the pre-exponential factor and activation energy for the secondary tar cracking are 4.5×10^6 and 110.0 kJ/mol. Lédé [25] reported the kinetic constants of the fast pyrolysis of wood sawdust performed in two different cyclone reactors. It was shown that the vapor-phase cracking reactions mainly occur inside a very thin and hot boundary layer close to the heated surface of the cyclone. The influence of the gas-phase secondary tar-cracking reactions on final gas composition for refuse-derived fuel (RDF) pyrolysis was investigated by Cozzani et al. [26]. Overall kinetic parameters obtained by a simple kinetic model were also suggested by Cozzani with pre-exponential 4.1×10^4 and activation energy 102.3 kJ/mol. Graham et al. [27] suggested the key kinetic parameters (rate constants, pre-exponential constant and activation energy) for the vapor-phase cracking reactions which occur during cellulose pyrolysis using a continuous ultra-pyrolysis reactor. For cellulose, the apparent activation energy for cracking reaction calculated by Antal [28] is 204 kJ/mol. Despite these numerous kinetics studies for tar cracking, however, the results calculated for tar cracking cannot describe the LG decomposition exactly due to the complexity of tar components. Shin et al. [29] studied the general kinetics of LG decomposition between 625 and 700 °C, it was proposed that two sequential reactions are needed for describing primary and secondary decomposition of LG. The primary and secondary Arrhenius equations are $k_1 = 3.5 \times 10^{10}\ \exp(-185/RT)$; $k_2 = 7.0 \times 10^{12}\ \exp(-228/RT)$. Detailed kinetics description about primary and secondary products is still needed for LG decomposition.

Based on the detailed formation mechanisms of some products and related intermediates from LG decomposition from our previous work [15], the kinetics of these mechanisms will be studied in this paper, which will be a big improvement for Shin et al's. [29] kinetics. The individual Arrhenius equations for all the elementary reactions are obtained, including rate constants, pre-exponential factors, and activation energies. Based on these individual rate constants, the global Arrhenius equations for the nine pathways are also obtained, by comparing with the experimental results, the appropriate calculation methods will be obtained, and first-order Arrhenius expressions for every elementary reactions and every pathways can be suggested, all the Arrhenius equations, rate constants, pre-exponential factors, and activation energies can be used in future experimental or theoretical studies.

2. Computational details

For LG decomposition mechanism, the optimized geometries and the lowest electronic energies for all the reactants, intermediates,

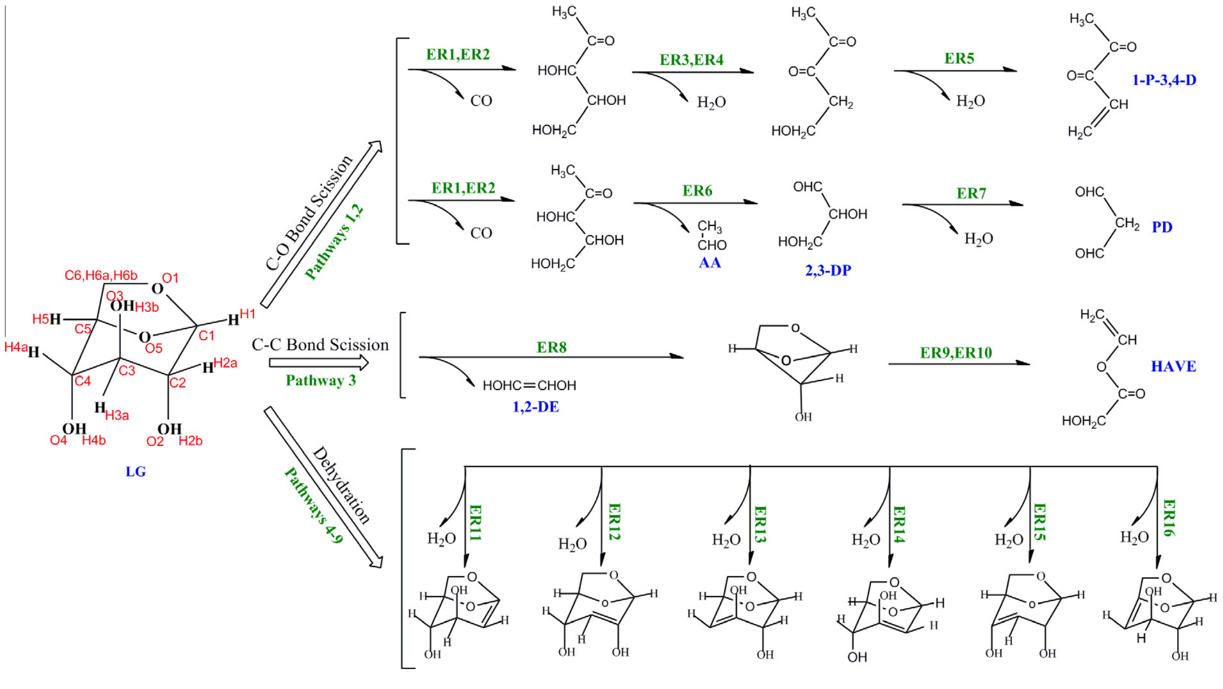


Fig. 1. Mechanism description for the LG decomposition, including the C–O bond scission, the C–C bond scission, and the LG dehydration.