Journal of Analytical and Applied Pyrolysis 105 (2014) 363–368

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Modeling the physiochemistry of levoglucosan during cellulose pyrolysis

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ARTICLE INFO

Article history:
Received 14 April 2013
Accepted 29 November 2013
Available online 11 December 2013

Keywords:
Levoglucosan
Evaporation
Polymerization
Cellulose
Anhydro-oligosaccharides

ABSTRACT

Levoglucosan is the main product of cellulose pyrolysis and also a potential platform chemical for biobased products. Previously we reported that during cellulose pyrolysis, levoglucosan is initially a liquid that is subject to the competing processes of evaporation and polymerization. While levoglucosan that evaporates can be transported out of the pyrolysis reactor and recovered, the non-volatile anhydro-oligosaccharides are trapped within the reactor where they dehydrate to char and low molecular weight compounds. We propose a physiochemical model for pyrolysis of levoglucosan using experimentally determined kinetic parameters for evaporation and polymerization of levoglucosan. After verifying the accuracy of the model, we used it to simulate behavior of levoglucosan under fast pyrolysis conditions. The simulation results showed that increasing the sample mass and applying higher heating rates promote polymerization of levoglucosan at the expense of evaporation. The detrimental effects of heating rate on levoglucosan evaporation suggest that although increased amounts of levoglucosan form during cellulose pyrolysis when higher heating rates are applied, much of the levoglucosan cannot be recovered as vapor because it turns into oligosaccharides that subsequently dehydrate to light oxygenates and char. Adopting experimental conditions that enhance the evaporation of levoglucosan, such as higher sweep-gas rates or reduced system pressures in combination with higher heating rates, is highly recommended for increasing levoglucosan recovery.

1. Introduction

Cellulosic biomass is an important feedstock for the production of biofuels via fast pyrolysis. Under appropriate pyrolysis conditions, cellulose can substantially depolymerize to the anhydrosugar levoglucosan as the major product [1,2]. The yield of levoglucosan during fast pyrolysis of pure cellulose can be as high as 58%. High yields are desirable since levoglucosan is a valuable platform chemical for production of biofuels or biobased products. However, even under conditions that promote the depolymerization of cellulose to anhydrosugar over the decomposition of the pyranose rings into light oxygenates [3], levoglucosan may react further to form char and light oxygenates [4].

Pyrolysis of cellulose has been extensively studied [5–9]. The commonly accepted Broido-Shafizadeh model [10] proposes that upon heating cellulose converts to a poorly characterized reaction intermediate known as active cellulose, which subsequently decomposes to tar, char, or gas via competitive processes. Slow pyrolysis promotes the formation of char and gas whereas fast pyrolysis promotes the formation of tar, including levoglucosan and other condensable products. High heating rates and short retention times are usually considered the key factors for increasing levoglucosan yields from cellulosic materials [3]. However, contradictory findings have been reported for flash pyrolysis of cellulose when the heating rate is extremely high. For example, Funazukuri et al. [11] conducted a flash pyrolysis of cellulose using a microfluidizedbed reactor in which the heating rates were above 10,000 °C/s. Surprisingly, they found that the maximum yield of levoglucosan in tar products was only about 10%, which decreased with increasing temperatures above 300 °C. They claimed that levoglucosan is the major product of slow pyrolysis of cellulose, but it is not a primary product under flash pyrolysis conditions. Lédé et al. [12] also found that under very high heat fluxes, levoglucosan was not the major product in either the vapor phase or the water-soluble fraction of the condensate. These phenomena cannot be explained by the mechanism of cellulose pyrolysis previously suggested.

On the other hand, it has also been reported that cellulose appears to melt into liquid intermediate products prior to rapid devolatilizing [12–14]. The condensed solid products obtained from flash pyrolysis of cellulose are found to be partly watersoluble and to contain levoglucosan and anhydro-oligosaccharides [15–17].

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http://dx.doi.org/10.1016/j.jaap.2013.11.026

Nomenclature

M_L	mass of levoglucosan in residue at time t (kg)
t	time (s)
k_p	polymerization rate constant (kg/s)
R	gas constant (J/mol K)
A_p	pre-exponential factor for polymerization
E_{ap}	activation energy for polymerization (J/mol)
k_e	evaporation rate constant (kg/s m^2)
S	surface area (m^2)
A_e	pre-exponential factor for evaporation
E_{ae}	activation energy for evaporation (J/mol)
M_{L0}	initial mass of levoglucosan (kg)
ΔM	mass changes of reacting mixture (kg)
M_T	mass of reaction residue (kg)
M_0	initial mass of reacting mixture (kg)
d	diameter of inner-cross area of sample cup (m)
T	temperature at t (°C)
T_0	temperature at $t=0$ (°C)
r	heating rate (°C/s)
M_{oligo}	mass of anhydro-oligosaccharide (kg)

Since significant amounts of anhydro-oligosaccharides with varied degrees of polymerization (DP) have been found in the water-soluble fraction of the condensate, some of the previous studies suggested that anhydro-oligosaccharides are primary pyrolysis products and that the formation of anhydro-oligosaccharides may precede the appearance of levoglucosan [12,17].

It is known that liquid levoglucosan polymerizes at elevated temperatures to produce anhydro-oligosaccharides [18–21]. Previously, we reported that liquid levoglucosan formed during cellulose depolymerization and is subject to two competing processes: evaporation and polymerization [4]. While levoglucosan that evaporates can be recovered as the final product, the anhydro-oligosaccharides formed by polymerization of levoglucosan are non-volatile and cannot escape from the reactor. Instead, the oligomers eventually dehydrate to char and light oxygenates. We further found that reaction conditions strongly influence the competing processes of evaporation and polymerization, therefore influence the ultimate yield of levoglucosan [22]. These findings suggest that the anhydro-oligosaccharides found in condensed solid products of cellulose pyrolysis could be the result of levoglucosan polymerization.

Modeling of evaporation and polymerization of levoglucosan during pyrolysis would be helpful in elucidating the mechanism of cellulose pyrolysis as well as allowing the quantitative prediction of levoglucosan yield as a function of reaction conditions. Few previous attempts have been made to model these physiochemical phenomena. Houminer and Patai [23] pyrolyzed levoglucosan inside a sealed reactor and used the results to develop an empirical model of levoglucosan polymerization. Since the sealed reactor did not allow vapors to escape, evaporation of levoglucosan was not considered in their model. Oja and Suuberg [24] measured the vapor pressure of levoglucosan at low temperatures (up to 183 °C) to investigate its volatility, but the rate of evaporation of levoglucosan was not quantified in their study.

The purpose of the present study was to build a theoretical model of levoglucosan physiochemistry to quantify the recovery of levoglucosan during pyrolysis.

A theoretical model of levoglucosan pyrolysis was developed. The kinetic parameters of the model were determined by experimental data of levoglucosan pyrolysis in isothermal conditions. The model was validated by comparing simulations of slow pyrolysis of levoglucosan in non-isothermal conditions to experimental results in the same conditions. The model was then used to simulate fast pyrolysis of levoglucosan and to explore the effects of operating conditions on the recovery of levoglucosan.

2. Methods

2.1. Modeling of levoglucosan evaporation and polymerization

The model assumes that liquid levoglucosan upon heating is transformed into either liquid oligosaccharide or vaporized levoglucosan. Designating the mass of liquid levoglucosan as M_L, the rate of levoglucosan mass loss is given by:

$$\frac{dM_L}{dt} = \left[\frac{dM_L}{dt}\right]_{poly} + \left[\frac{dM_L}{dt}\right]_{evap} \tag{1}$$

where t is the time and the subscripts on the rate terms refer to polymerization and evaporation of levoglucosan.

Polymerization of levoglucosan was modeled as a first-order reaction with respect to the mass of liquid levoglucosan:

$$\left[\frac{dM_L}{dt}\right]_{poly} = -k_p M_L \tag{2}$$

The polymerization rate constant, k_p is a function of temperature:

$$k_p = A_p e^{-(E_{ap}/(R(T+273.15)))} \tag{3}$$

where A_p and E_{ap} are, respectively, the pre-exponential factor and activation energy for polymerization rate coefficient, R is the gas constant, and T is the reaction temperature (°C).

Evaporation is proportional to the surface area, S, of liquid levoglucosan in the reaction mixture; thus, the rate of liquid levoglucosan loss via evaporation is given as:

$$\left[\frac{dM_L}{dt}\right]_{evap} = -k_e S \tag{4}$$

The evaporation rate constant, k_e, is a function of temperature:

$$k_e = A_e e^{-(E_{ae}/(R(T+273.15)))} \tag{5}$$

where A_e and E_{ae} are, respectively, the pre-exponential factor and activation energy for the evaporation rate coefficient.

Substituting Eqs. (2) and (4) in Eq. (1) gives:

$$\frac{dM_L}{dt} = -k_p M_L - k_e S \tag{6}$$

Under isothermal conditions for constant surface area, the following equation can be solved numerically for the amount of levoglucosan remaining as a function of time if the rate coefficients and surface areas are known:

$$\ln(k_p M_L + k_e S) - \ln(k_p M_{L0} + k_e S) = -k_p t \tag{7}$$

where M_{L0} is the initial mass of liquid levoglucosan and t is the reaction time.

The evaporation coefficient at constant temperature can be estimated by heating levoglucosan in a thermogravimetric analyzer (TGA) and observing the weight change of the sample. Since loss of levoglucosan via polymerization does not change the weight of the sample (the resulting oligosaccharide is non-volatile), the weight change of the sample, ΔM, represents only the levoglucosan evaporation. This is obtained by integrating Eq. (4) as below:

$$\Delta M = -\int_0^t \left[\frac{dM_L}{dt}\right]_{evap} dt = \int_0^t k_e S \ dt \tag{8}$$

Thus the total amount of reacting mixture, M_T, is:

$$M_T = M_0 - \Delta M = M_0 - \int_0^t k_e S \ dt \tag{9}$$