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A sectional approach for biomass: Modelling the pyrolysis of cellulose

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ABSTRACT

We present the adaptation of the sectional model approach to the pyrolysis of cellulose, $(C_6H_{10}O_5)_n$. Cellulose is the major component of lignocellulosic biomass. Due to its longitudinal structure, cellulose is characterised by one-dimensional chains composed of a varying number of cellobiose molecules, $C_{12}H_{22}O_{11}$. Fragments of those chains with similar mass are grouped into size classes (BINs) determined by characteristic numbers of cellobiose units. During the pyrolysis of cellulose, reaction temperatures of more than 500 K (depending on the heating rate) initiate bond dissociation between cellobiose units. We have developed a new reaction scheme for the pyrolysis of cellulose based on literature models. However, we present the sectional approach as a new concept for modelling the degradation of cellulose. We propose a kinetic data set of $A = 2.2 \cdot 10^{13}\ s^{-1}$ and $E_A = 225.9$ kJ/mol for the dissociation of a single glycosidic bond. Additionally, our model includes the cellobiose devolatilisation to glucose or tars (levoglucosan) including primary gaseous products, the formation of char and water, and secondary gas-phase reactions. Our reactor simulations of cellulose pyrolysis at constant heating rates of 1, 10, 15, and 150 K/min show good agreement with two different experimental data sets.

1. Introduction

One likely candidate as a renewable alternative to fossil fuels is lignocellulosic biomass. The dry material of plants and trees consists primarily of three major components: cellulose, hemicellulose (also known as polyose), and lignin. Depending on the type of feedstock (hardwood, softwood, or agricultural), the constituent fractions can vary strongly, but characteristic trends can be observed [1–4]. Generally, dry mass of lignocellulosic biomass roughly comprise 40–50% cellulose, 20–30% hemicellulose, and 20–35% lignin. Several other components (starch, ash, pectins, lipids, and other trace species) can exist in negligible quantities in hard- and softwoods, whereas the quantities in agricultural plants, e.g. switchgrass, can be significant. Compositions of various lignocellulosic biomass feedstocks were widely investigated and can be found in e.g. [1,5,6]. However, their actual composition has a significant impact on biomass pyrolysis and its product distribution. Good overviews of wood and biomass pyrolysis can be found in [7,8]. Worasuwannarak and co-workers [3,4] investigated the pyrolysis of three different types of lignocellulosic biomass (rice straw, rice husk, and corncob) and they found that water is the main product for all the samples. This is due to the high oxygen content in lignocellulosic biomass. Further products during pyrolysis include CO, CO_2, CH_4, tars (e.g. levoglucosan $C_6H_{10}O_5$), and solid residues (char). However, the pyrolysis of pure cellulose produces mostly tars.

1.1. Cellulose

The focus of this paper is on cellulose. It is the major, and by far the most investigated, component of lignocellulosic biomass. Cellulose is a polysaccharide produced by plants during photosynthesis. Cellulose covers approximately one third of all plant matter making it the most abundant organic compound on earth. The bundles of cellulose fibres serve as the structural component of the primary cell walls of plants and trees. Its potential as an alternative fuel source over lignocellulosic biomass is increased by the fact that it is indigestible by human beings. Hence, unlike starch (a main constituent of many agricultural plants), it does not interfere directly with the human food chain. In practice, the conversion of cellulose to biofuels, e.g. cellulosic ethanol, is under investigation [5,7,9–11]. However, it must be considered that inedible energy plants still require agricultural area and water resources and compete, therefore, with food production.

Cellulose has the molecular formula $(C_6H_{10}O_5)_n$ and its chemical composition corresponds to a polymer of typically between several hundred to over ten thousand D-glucopyranose monomers. These are linked by 1,4′-β-glycosidic bonds with an alternate rotation of 180° forming linear chains (see Fig. 1). Depending on chain length, i.e. number of monomers or degree of polymerisation, the properties of cellulose can vary immensely. Unlike in the structure of the polysaccharide starch, which has the same molecular formula but its glucopyranose

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Nomenclature

A	pre-exponential Arrhenius factor
b	temperature exponent
C	proportionality constant
E_A	activation energy
k	reaction rate coefficient
l	characteristic length
M	molar mass
N	number
R	universal gas constant
T	temperature
t	time
x	index
β	heating rate

units are linked with α-glycosidic bonds, no branches or coils occur. The numerous intra- and intermolecular hydrogen bonds of this structure help to create a robust, rigid crystalline structure [9,12]. Four general types of cellulose can be distinguished, namely cellulose I, II, III, and IV. Cellulose I is the one occurring in nature and consists of two crystalline forms Iα (e.g. dominant in some algae and bacteria) and Iβ (e.g. dominant in wood or cotton) [13,14]. Up to temperatures of 300–400 K its crystalline structure is dominated by intrachain hydrogen bonds. However, at 450–550 K it transforms to an amorphous and more reactive structure characterised by (weaker) interchain hydrogen bonds [12,15]. After this initial conversion step the degradation of (amorphous) cellulose chains occurs by bond dissociation between the monomer linkages. In order to consider this phenomenon, we composed cellulose out of cellobiose units ($C_{12}H_{22}O_{11}$) in our model which is based on the early works of Haworth et al. [16,17] and the recent work of Assary and Curtiss [18] (see Fig. 1).

1.2. Pyrolysis

There are three ways of thermally converting biomass into technically more usable forms of energy: combustion, gasification, and pyrolysis. Combustion, however, is not considered as a promising alternative because of environmental issues. Biological conversion such as fermentation or digestion is also widely field-tested, especially in rural areas. These processes mostly yield single products (ethanol, biogas with a very high methane content). However, their relatively long process times, usually days or weeks, make them economically inferior to thermal conversion [10].

The main goal of gasification is the production of fuel gases (yields in the order of magnitude of 80%), mainly of synthesis gas (syngas), a mixture of CO and H_2. Hence, the process takes place under relatively high temperatures, i.e. above 1000 K, in order to increase the gas yield. A proportion of the required energy is provided internally by exothermic reactions of parts of the feedstock, which contains an oxygen component itself. Gasification, as well as combustion, is always initiated by pyrolysis and requires total or partial oxidation as a following step.

During pyrolysis, the feedstock is thermally decomposed under the exclusion of external oxygen. These conditions and moderate process temperatures require an external thermal source often achieved by constantly heating the feedstock to a designated temperature of approximately 1000 K. As an example, Worasuwannarak et al. [3] report that the pyrolysis of cellulose starts at a temperature of around 450 K and is completed at around 875 K.

Pyrolysis can be in general characterised by three main physical parameters: process temperature, residence time, and heating rate. Process temperatures of approximately 500–900 K favour the production of liquids (yields in the order of magnitude of 75%), i.e. bio-oil in case of biomass pyrolysis. However, gaseous and solid product yields are not negligible, i.e. at around 10%. Pyrolysis at approximately 675 K and below is known as slow pyrolysis, as opposed to fast pyrolysis at approximately 775 K. The long residence times of slow pyrolysis (in order of hours) compared to those of fast pyrolysis (in order of seconds) favour the production of carbonaceous residues (char). The heating rate is known to play an important role in influencing the product distribution. High heating rates, as used in fast pyrolysis, also minimise the production of solid residues. The process of fast pyrolysis is characterised by several essential steps. First, the solid feedstock is dried to a matter which contains less than 10% water. In order to heat up the dry material very rapidly, it needs to be rather finely grinded, typically to a particle size of less than 3 mm. Hence, the feedstock is decomposed very quickly to produce mainly vapours and aerosols. Finally, these primary products are rapidly cooled to generate high amounts of bio-oil [10]. Since this liquid product facilitates transportation and storage, fast pyrolysis is of particular interest as an option to convert biomass into higher energy content materials. For commercial use, the resulting bio-oil can be converted to biofuels, e.g. via Fischer–Tropsch processes to BtL-fuel (Biomass to Liquid), heat, electricity or chemicals.

2. Modelling

2.1. The sectional model approach

The sectional model approach is a concept originally developed for modelling the formation and degradation of aerosols [19]. Over the last decades, it has become an effective tool in modelling the formation of soot particles in combustion processes, e.g. [20–23]. The sectional approach distinguishes the species of interest in subsequent size and/or mass classes, so-called BINs. This classification takes into account that molecules of the same species class with different size and/or mass have different properties. The smallest BIN consists of one basic molecule, whereas the other subsequent pseudo species are composed of multiple numbers of this building block.

To the authors' knowledge the sectional approach has so far not been adapted to thermal decomposition of lignocellulosic biomass, and cellulose respectively. In models from literature, cellulose is characterised as a lumped species. However, it is known that the properties of cellulose depend on chain length, i.e. number of monomers. By

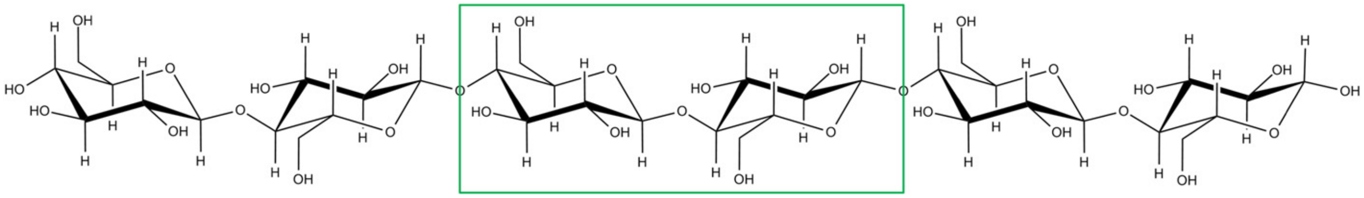

Fig. 1. Chemical structure of cellulose $(C_6H_{10}O_5)_n$ and cellobiose building block $C_{12}H_{22}O_{11}$ (box).

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