Progress in Energy and Combustion Science 53 (2016) 41–79

Contents lists available at ScienceDirect

Progress in Energy and Combustion Science

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

Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis

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ARTICLE INFO

Article history:
Received 31 July 2015
Accepted 14 October 2015
Available online 15 December 2015

Keywords:
Cellulose
Lignin
Pyrolysis
Biomass
Scheme
Multi-scale

ABSTRACT

In this work about pyrolysis of lignocellulosic biomass, the individual reaction mechanisms of cellulose, hemicellulose and lignin are initially described. The recent advances in the understanding of the fundamental reaction pathways are described, including quantum-mechanical calculations, and the description of pyrolysis as a two-step process, i.e., primary pyrolysis and secondary charring, the effect of the presence of an intermediate liquid compound, and the influence of inorganic species are discussed.

The need to describe biomass pyrolysis as the sum of the contributions of its individual components is then emphasised. The process of determining biomass mass loss kinetics is analysed, and the product composition and heat of reaction that are experimentally obtained during pyrolysis are presented, along with detailed schemes that can be used to predict them.

Finally, it is demonstrated that a multi-scale consideration of pyrolysis on multiple levels – specifically, on molecular, particle and reaction levels – is required to accurately describe biomass pyrolysis. Intra-particle phenomena and particle models are discussed and the reactor level is analysed with a focus placed on fixed bed and fluidised bed pyrolysis. In summary, a list of 10 research focal points that will be important in the future is presented.

Contents

Abbreviations: AAEM, alkali and alkaline earth metallic; AC, active cellulose; BFC, bio flashchain; BTX, benzene, toluene, xylene; CELL, cellulose; CFD, computational fluid dynamics; CPD, chemical percolation devolatilisation; DAEM, distributed activation energy model; DGM, dusty gas model; DP, degree of polymerisation; DPM, discrete particle model; DSC, differential scanning calorimetry; DVC, depolymerisation, vapourisation and cross-linking; FC, fixed carbon; FG, functional group; FTIR, Fourier transform infrared spectroscopy; FWO, Flynn–Wall–Ozawa; GC, gas chromatography; HAA, hydroxyacetaldehyde; HMF, hydroxymethylfurfural; HPLC, high-performance liquid chromatography; HTC, hydrothermal carbonisation; HTL, hydrothermal liquefaction; ILC, intermediate liquid compound; KAS, Kissinger–Akahira–Sunose; LGA, levoglucosan; LIF, laser induced fluorescence; LIG, lignin; LMWC, low molecular weight compounds; NMR, nuclear magnetic resonance; NR, non-reducing; PAH, polyaromatic hydrocarbons; PM, particulate matter; RAC, Ranzi–Anca-Couce; RPM, representative particle model; SY, solid yield; TGA, thermo-gravimetric analysis.

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http://dx.doi.org/10.1016/j.pecs.2015.10.002
0360-1285/

1. Introduction

The energetic and chemical utilisation of biomass has become a prominent topic during recent years, and it is expected to play a more important role in the future due to its benefits. Biomass is a renewable energy source, is available worldwide, allows the production of heat and power on demand, and, if its collection is performed in a sustainable way, is CO_2-neutral. The main types of biomass are [1,2]:

- wood and woody biomass;
- herbaceous and agricultural biomass;
- aquatic biomass;
- animal and human biomass wastes.

Biomass conversion can occur through either biochemical, physico-chemical or thermochemical processes [3,4]. During biochemical conversion, molecules of biomass are broken down into smaller molecules by bacteria or enzymes. This process is much slower than thermochemical conversion, but does not require an input of much external energy. The principal routes for biochemical conversion are digestion (anaerobic and aerobic) and fermentation. During aerobic digestion, or composting, different types of microorganisms that have access to oxygen from the air produce carbon dioxide, heat, and a solid digestate. In anaerobic digestion, the main products are methane and carbon dioxide in addition to a solid residue. During fermentation, part of the biomass is converted into sugars by acid or enzymes. The sugar is then converted into ethanol or other chemicals with the help of yeasts. During physico-chemical processes, vegetable oil is generated from some types of biomass like seeds from sunflower or rape seeds by pressing. During thermo-chemical processes, biomass is converted at high temperatures. The main thermo-chemical processes are pyrolysis, combustion, gasification, hydrothermal liquefaction and hydrothermal carbonisation [5–8].

- Pyrolysis: thermal degradation of carbonaceous material in the absence of an externally supplied oxidising agent, usually at temperatures in the range of 300–600 °C. The products of pyrolysis are char (solid), permanent gases and a pyrolytic liquid (liquid at room temperature), which is often referred to as bio-oil or pyrolysis-oil. Char can be employed as a domestic cooking fuel, for barbecuing or other energy purposes, upgraded to activated carbon, or used in the metallurgical industry, as well as many other applications [9]. When the obtained char, also called in this application biochar, is redirected to the soil, the properties of the former are highly improved over the mid- and long-terms, also representing a strong CO_2 sink [10–13]. The obtained bio-oil can be upgraded to liquid fuel for combustion engines (e.g., transportation) [14,15], or directly employed for power or heat generation. Catalytic hydrotreating, with the addition of hydrogen [16], and catalytic cracking [17] of the bio-oil can be conducted for the upgrading, which is required in order to reduce the oxygen content of the liquid fuel. Moreover, catalytic pyrolysis profoundly alters the pyrolytic product distribution. Therefore, catalysts such as zeolites are also commonly employed in the pyrolysis process to directly produce pyrolyis liquids with a reduced oxygen content [15]. Bio-oil is also a promising source for chemicals in a biorefinery concept [18,19] and for biological pesticides [20]. Pyrolysis gases can be also used for heat and power generation.
- Gasification: thermal degradation of carbonaceous material in the presence of an externally supplied oxidising agent (air, pure oxygen or steam). The main product of gasification is a mixture of gases (producer gas), the main components of which are CO, CO_2, H_2, H_2O, CH_4, N_2 (just when air is used as oxidising agent), tar and small particles of ash or char. The producer gas can be used as fuel gas in internal combustion engines for power and heat production. It could also be used to fuel gas turbines or fuel cells. Liquid fuels can also be obtained from the producer gas through methanol or Fischer–Tropsch synthesis [5,21–23].
- Combustion: complete oxidation of the biomass feedstock. In contrast to pyrolysis and gasification, which represent fuel conversion processes, combustion can provide heat. The hot gases are used for direct heating purposes, for power generation producing steam by means of subsequent steam turbine processes, and as an