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A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin

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ABSTRACT

The conversion of biomass by thermochemical means is very promising for the substitution of fossil materials in many energy applications. Given the complexity of biomass the main challenge in its use is to obtain products with high yield and purity. For a better understanding of biomass thermochemical conversion, many authors have studied in TG analyzer or at bed scale the individual pyrolysis of its main constituents (i.e. cellulose, hemicelluloses and lignin). Based on these studies, this original work synthesizes the main steps of conversion and the composition of the products obtained from each constituent. Pyrolysis conversion can be described as the superposition of three main pathways (char formation, depolymerization and fragmentation) and secondary reactions. Lignin, which is composed of many benzene rings, gives the highest char yield and its depolymerization leads to various phenols. The depolymerization of the polysaccharides is a source of anhydro-saccharides and furan compounds. The fragmentation of the different constituents and the secondary reactions produce CO, CO_2 and small chain compounds. For temperature higher than 500 °C, the residues obtained from the different constituents present a similar structure, which evolves towards a more condensed polyaromatic form by releasing CH_4, CO and H_2. As the aromatic rings and their substituent composition have a critical influence on the reactivity of pyrolysis products, a particular attention has been given to their formation. Some mechanisms are proposed to explain the formation of the main products. From the results of this study it is possible to predict the reactivity and energy content of the pyrolysis products and evaluate their potential use as biofuels in renewable applications.

Contents

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1. Introduction

A massive growth of fossil feedstock consumption accompanied the industrial revolution; but faced with the depletion of fossil resources and the impact of their use on the environment, alternative raw materials must be found. As the precursor of fossil feedstocks, biomass is also composed of carbon and appears to be one of the best renewable solutions for the substitution of fossil resources in many applications. Indeed, biomass can be used in energy applications for the production of heat, power and transportation fuels [1]. The production of chemicals (food additives, pharmaceuticals, surfactants, organic solvents, fertilizers) and biomaterials from biomass is also becoming more and more common [2]. The use of biomass for these applications generally requires multi-step conversions of the raw material. In order to develop more competitive processes, a valorization of the entire content of biomass in biorefineries inspired by the model of those exploited for petroleum products constitutes one of the key issues [3].

Among the processes of biomass valorization, its conversion by thermochemical means appears to be a promising alternative for many energy applications [1]. The most current thermochemical processes (which consist of a conversion of the biomass by the action of heat) are gasification, pyrolysis and combustion. However in some of these applications, further research is still needed to improve the purity of intermediate and final products. For instance, the development of the production of synthetic hydrocarbons by gasification and the Fischer–Tropsch process is hindered by overly high contaminant content in the gas produced by biomass gasification [4]. In the case of the production of bio-oil by flash pyrolysis, the oxygen content of the obtained product is generally too high for the substitution of conventional petroleum fuels [1,5]. As a consequence, additional upgrading steps, which dramatically affect the energy efficiency of the process, are frequently necessary to improve the purity of the products. That is why the development of the valorization of biomass by thermochemical means requires a better control of biomass conversion.

Pyrolysis is a capital step of biomass thermochemical conversion as it is the first step of all the processes. Pyrolysis consists in the conversion of biomass by the action of heat in an inert atmosphere into char, gas and a liquid composed of a mixture of hundreds of oxygenated organic compounds [6,7]. Depending on the operating conditions, an important variety of products and yields can be obtained [1,5]. Besides, the diversity in the composition of biomass which is constituted by three main polymers (i.e. cellulose, hemicelluloses and lignin) also contributes to the complexity of the final product. Many authors studied the influence of operating conditions on products yields [1,5,8]. For instance, it is widely accepted that a high heating rate favors the formation of volatile compounds whereas a low heating rate promotes the production of char [1,5]. However, owing to the complexity of biomass conversion, few authors tried to explain the influence of pyrolysis conditions on the chemical reactions involved at the molecular scale and sometimes different names are used for similar mechanisms [8,9]. From the literature, it appears that the pyrolysis of biomass is most frequently considered as the superposition of three main primary mechanisms (i.e. char formation,

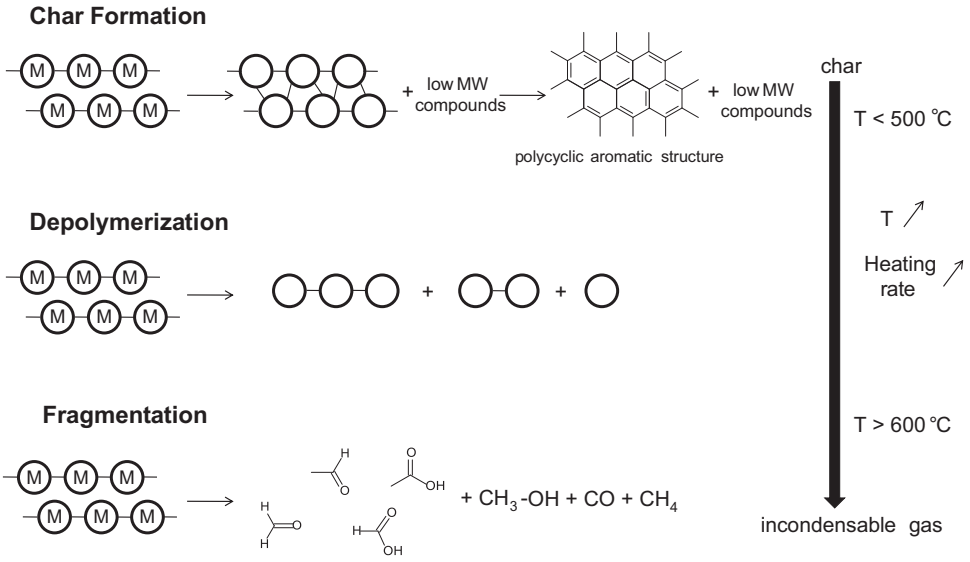

Fig. 1. Pathways involved in the primary mechanisms of the conversion of biomass constituents (M: monomer; MW: molecular weight).