Research paper

Detailed kinetic mechanism of gas-phase reactions of volatiles released from biomass pyrolysis

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A B S T R A C T

Comprehensive chemical models to describe the behavior of biomass pyrolysis, gasification and combustion are crucial for the simulation and design of thermochemical processes of ligno-cellulosic materials. Despite this importance, reliable and predictive models are still not well known. The original aspect of this work is to present a comprehensive and predictive model of pyrolysis, gasification, and combustion, starting from biomass characterization, through the description of released volatiles at the particle scale, until the effect of the secondary gas-phase reactions at the reactor scale. All these aspects can play a relevant role in the biomass thermo-valorization processes. Most of released species from biomass devolatilization are oxygenated hydrocarbons. This study aims at identifying some reference rate parameters, based on analogy and thermochemistry rules, for the different reaction classes. Once rate rules are defined, they allow an easy extension to analogous compounds. In this way, the kinetic mechanism already developed for jet and diesel fuels is extended to the new tar species released by biomasses. Despite unavoidable approximations when the interest is also at the reactor scale, this model is the only one, to our knowledge, able to describe the whole process from biomass to final products, in a predictive and satisfactory way.

1. Introduction

Biomass thermal conversion processes produce heat, electricity, and fuels. Fast pyrolysis is a promising process for the production of renewable bio-oils and chemicals [1]. Bio-oil is a complex mixture of anhydrous sugars, furan derivatives, oxygenated aromatics, and low molecular weight products [2,3]. Furthermore, the biomass integrated gasification/combined cycle system is amongst the most promising modern technologies, because of its higher energy efficiency compared to direct combustion [4]. One of the major issues in biomass gasification is to deal with tar formed during the process. Similar to bio-oil, tar is also a complex mixture of condensable hydrocarbons, which includes several oxygen-containing hydrocarbons, along with phenolic and multiple ring aromatic compounds. Tar produced from gasification process mainly contains compounds without oxygen (tertiary tar), as opposite to pyrolysis [5]. The composition of tar and bio-oil is a key factor in assessing pyrolysis and gasification processes. Indeed, it involves hundreds of organic compounds, and it depends on feedstock types, reactor temperature, residence time, and catalytic effects associated to ash. The approximation of tar as a narrow range of components leads to inaccurate predictions of dew point temperature and gasification efficiency. Aiming at improving the understanding of pyrolytic behavior of biomass, Shen et al. [6] recently reviewed biomass fast pyrolysis discussing the yields of liquid and gas products, focusing on the primary and secondary formation pathways of oxygenated compounds. Despite the outstanding importance of developing a reliable reaction model for the design and optimization of biomass pyrolysis and gasification, many difficulties lie behind its formulation. As already emphasized by Carstensen and Dean [7], the complexity and varieties of components found in biomass, together with involved reactions, are the main reasons of these difficulties. Even if the major components of biomass are only three macromolecules such as cellulose, hemicellulose and lignin, their relative compositions vary significantly [8], and only cellulose structure is well defined. A further difficulty in developing a detailed kinetic mechanism for biomass pyrolysis is that reactions proceed simultaneously in the condensed and gas phase, therefore their relative

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role is not well defined.

The kinetic modeling of pyrolysis, gasification, and combustion of biomasses is a very complex multi-component, multi-phase, and multi-scale problem. The strong interactions between chemical kinetics, heat and mass transfer processes involved in the thermal degradation of biomasses make the mathematical modeling difficult. These models require at least the following four features:

- Characterization of the biomass in terms of reference components;
- Kinetics of devolatilization of reference species in the solid/metaplastic phase;
- Kinetics of the gas-solid gasification and combustion of residual char;
- Secondary gas-phase reactions of gas and tar species released during devolatilization.

While biomass characterization, together with the corresponding multistep kinetic models of cellulose, hemicellulose, lignins, and extractives has been recently reviewed [8], secondary gas phase reactions of gas and tar released species are discussed in a greater detail in this work. Thus, Section 2 briefly summarizes the characterization method, along with the multistep kinetic scheme of biomass devolatilization. Section 3 analyzes and discusses the secondary reactions of gas and tar species released during biomass pyrolysis. Lastly, comparisons with experimental data highlight the advantages and reliability, as well as the limitations, of the overall kinetic model of pyrolysis, gasification, and combustion of biomasses.

2. Biomass characterization and multistep kinetic model of devolatilization

Pyrolysis is the first common step during gasification and combustion processes. Therefore, the characterization of pyrolysis products has attracted great analytical interests [9]. One and two-dimensional gas chromatography with flame ionization detector or time-of-flight mass spectrometry techniques allow qualitative and quantitative analysis of biofuels composition, thus describing a large portion of bio-oil [10,11]. Similarly, the application of tunable synchrotron vacuum ultraviolet photoionization mass spectrometry allows to improve the knowledge of this reaction system [12]. As biomass feedstocks are complex mixtures of several compounds, it is very essential to characterize them in terms of specific number of reference species. While usual characterization methods are limited to the study of cellulose, hemicellulose and lignin components [13–15], detailed characterization was recently extended to triglyceride and tannin species, representatives of extractives [8].

2.1. Biomass characterization

For this modeling work, the reference components of biomasses are cellulose, hemicellulose, lignin, and extractives, which constitute the largest portion of the biomass, often with ash. Biomass pyrolysis products are assumed as a linear combination of the pyrolysis products of these reference compounds, neglecting their possible interactions. When direct information on biochemical composition is not available, cellulose, hemicellulose, lignin, and extractive content is derived through the ultimate biomass composition in terms of H/C/O [8,15]. As reference species, together with cellulose and hemicellulose, three different types of lignins, rich in carbon, hydrogen and oxygen, are considered [16]. Finally, triglycerides and condensed tannins are two lumped reference species accounting for hydrophobic and hydrophilic extractives, respectively. Table 1 reports the seven reference species described

above. The biomass composition in terms of the seven reference components is calculated from biomass elemental composition by solving the system of atomic mass balances for carbon, hydrogen and oxygen, together with a constraint that defines all fractions to be positive. The following system of linear equations expresses the three atomic balances:

$$C_{BM} = \alpha \cdot C_{RM_1} + \beta \cdot C_{RM_2} + \gamma \cdot C_{RM_3}$$

$$H_{BM} = \alpha \cdot H_{RM_1} + \beta \cdot H_{RM_2} + \gamma \cdot H_{RM_3}$$

$$O_{BM} = \alpha \cdot O_{RM_1} + \beta \cdot O_{RM_2} + \gamma \cdot O_{RM_3}$$

where RM_1, RM_2 and RM_3 are the reference mixtures and α, β and γ their corresponding fractions. Reference mixtures are different combinations of the seven reference species. RM-1 is a mixture of cellulose and hemicellulose, while RM-2 is a mixture of lignins with triglycerides and finally RM-3 is again a mixture of lignins with some content of tannins. Further details on this characterization method are reported in Debiagi et al. [8].

2.2. Multistep pyrolysis model

Although the biomass composition and the thermal treatment conditions can significantly change the product distribution, a similar set of products is always obtained on a qualitative basis. A peculiarity of this model is the detailed characterization of pyrolysis products, which not only includes water vapor and permanent gases (H_2, CO, CO_2, CH_4, and C_2H_4), several alcohols, aldehydes, and carbonyl compounds, but also different sugars, phenolics and heterocyclic species. At high temperatures, several chemisorbed species contribute to char devolatilization progressively releasing CO_2, CO and H_2.

Each reference component decomposes independently through a multistep, branched mechanism of first-order reactions. Table S1 of the Supplemental Material reports the overall multicomponent and multistep kinetic mechanism of primary biomass pyrolysis. This kinetic mechanism models the formation of intermediate solid and chemisorbed species, together with char, gas, and tar species.

Both cellulose and hemicellulose are polymeric sugar chains releasing, together with permanent gases, a wide number of hydrocarbon and oxygenated species, including methanol, acetic acid, hydroxy-acetaldehyde, acetone, acetol, furfural, 5-hydroxymethyl-furfural, levoglucosan and anydro-sugars [6]. The multistep lignin decomposition mechanism is a simplification of the detailed scheme of Faravelli et al. [16]. These reactions are active in a broad temperature range and release phenolic components. Phenol, anisole (metoxy-benzene), 2,6-dimethoxy-phenol, 4-(3-hydroxy-1-propenyl)phenol, and 3-(4-hydroxy-3,5-dimethoxy-phenyl) acryl-aldehyde are a few lumped and representative species of these compounds. Phenol is also released by the first decomposition step of tannins, while triglycerides (TGL) quickly decompose to a lumped species representative of free fatty acid.

The rates and stoichiometries of these lumped reactions were originally derived from experimental findings [15]. The kinetic model is continuously updated, based on new experimental data and comparisons across a wider range of experimental conditions. Recently, experimental data showed the overshooting of temperature at the center of thick biomass particles, and allowed a better evaluation of the endothermic release of tars and the exothermic charring process [17].

While several detailed kinetic mechanisms are discussed in the literature [18–20], the lumped kinetic scheme discussed and applied in this work is very simplified, aiming at an effective use not