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# Impact of organically bonded potassium on torrefaction: Part 2. Modeling

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## HIGHLIGHTS

- Mass losses of different biomasses are modeled by two-step reaction in series.
- The model includes *K*, hemicellulose and cellulose contents.
- The pre-exponential factors are given as a function of *K* content for spruce.
- The model is validated for aspen, straw, miscanthus and bark.

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## ABSTRACT

In torrefaction, the mass yield depends on the biomass type, size of the biomass, torrefaction temperature, and residence time. Mass yield curves vs. residence time are usually modeled based on biomass type at different torrefaction temperature. This work is the second part of a study on the effect of alkali metals on torrefaction in which the *K* content affects the degradation of biomass during torrefaction.

In this part of the study, the mass loss of spruce wood with different content of *K* was modeled using a two-step reaction model based on four kinetic rate constants. The results show that it is possible to model the mass loss of spruce wood doped with different levels of *K* using the same activation energies but different pre-exponential factors for the rate constants. Three of the pre-exponential factors increased linearly with increasing *K* content, while one of the pre-exponential factors decreased with increasing *K* content. Therefore, a new torrefaction model was formulated using the hemicellulose and cellulose content and *K* content. The new torrefaction model was validated against the mass loss during the torrefaction of aspen, miscanthus, straw and bark. There was good agreement between the model and the experimental data for the other biomasses, except bark. For bark, the mass loss of acetone extractable material was also needed to be taken into account. The new model can describe the kinetics of mass loss during torrefaction of different types of biomass. This is important for considering fuel flexibility in torrefaction plants.

## 1. Introduction

Torrefaction of biomass can help increase the use of biomass to produce energy in conventional power plants and to produce syngas in gasifiers. Torrefaction can result in a less hydrophilic solid product with a higher heating value which is more easily grindable than the parent material. Better grindability is generally beneficial in pellet and powder productions in industrial gasification and combustion processes [1].

In order to predict the mass yield and its required residence time in course of torrefaction, modeling the reaction rate is a crucial tool [2–4]. It has been shown that the most important components undergoing devolatilization during biomass torrefaction are hemicellulose, cellulose and extractives [5]. Hemicellulose starts to degrade significantly at about 240 °C whereas cellulose degradation begins at about 255 °C, but becomes more significant at 270–280 °C. For the extractives, the picture is less clear. Lower molecular weight extractives volatilize [6] and some other degrades [7,8] during torrefaction, but new acetone extractible compounds are also formed during torrefaction [5].

Pyrolysis of xylan has been modeled using a two-step reaction in series [9]. In the model, first, the xylan forms volatiles and an intermediate solid product. In the second step, the intermediate product produces volatiles and char [9,10]. The model has been applied to modeling the heat treatment of wheat straw and corn

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stalks in the temperature range 127–375 °C [11]; beech wood [12] in the temperature range 255–311 °C; and, the torrefaction of willow, wheat straw and pine wood chips [2,4,13]. In the study of beech wood [12], the extractives and reactive hemicellulose degraded in the first step and a fraction of cellulose and some more hemicellulose degraded in the second step. In contrast to the previous studies, the last models [4,13] included non-isothermal part from 200 °C to torrefaction temperature as well as isothermal reaction at torrefaction temperature.

Rousset et al. [14] assumed three separate parallel reactions for hemicellulose, cellulose and lignin degradation during torrefaction. And then they concluded that half of the hemicellulose degrades whereas cellulose and lignin do not degrade significantly during torrefaction at 210 and 250 °C. Chen and Kuo [15] modeled separately the degradation of wood components during torrefaction. Similar to the previously mentioned studies, they found that hemicellulose degradation is the most significant in the temperature range 200–300 °C; while lignin degradation could hardly be observed.

Repellin et al. [3] proposed a global one step reaction model to predict the mass yield of the wood chips during torrefaction. In their study, it was concluded that hemicellulose was the most reactive component while cellulose and lignin rarely decompose in the temperatures range 220–260 °C. They compared their global one step model with Di Blasi-Lanzetta and Rousset models. A good correlation between experimental and calculated values was observed and they concluded that the models can be employed to optimize the industrial reactions; however they believed that it is not easy to understand the physical meaning of the complex models.

Recently, it has been observed that some of the mineral matters influence the thermal degradation of biomass during torrefaction [16,17]. However, in the mentioned modeling studies [2–4,14] the influence of the mineral matters on the thermal degradation was not taken into account.

This study is the second part of a study on the role of alkali metals on the thermal degradation of biomass during torrefaction. In this study the objective is to model the mass loss during torrefaction of biomass, taking into account the influence of potassium on the mass loss during torrefaction. Potassium was added to demineralized spruce at different levels and torrefied for 30 min at temperatures between 240 and 280 °C. The kinetic parameters for the two-step model were determined from this data. A new torrefaction model was developed based on these kinetic parameters. The model was validated and compared to experimental data of other biomasses including straw, miscanthus, aspen and bark.

In the model, the components which could decompose were hemicellulose and cellulose. This model does not take into account the volatilization of extractives, which does not hinder its application to wood or herbaceous biomass with low levels of acetone extractible material, but does limit the application to bark.

A two-step model was chosen over other modeling approaches such as modeling each component separately because it is robust enough to accurately model the kinetics of mass loss in different biomasses, while being simpler than having separate expressions for each component. Since we focused on biomass samples, modeling decomposition of the individual components would have required analyzing the components, particularly hemicellulose and cellulose in the torrefied wood samples, which was beyond the scope of this work.

## 2. Material and methods

The biomasses used in this work were three woody biomasses including spruce, aspen and spruce bark, plus two herbaceous biomasses including miscanthus and straw. All the samples were ground and sieved to the particle size of 125–250 μm.

The carbohydrate analyses of the biomasses were conducted to determine the hemicellulose and cellulose contents. Acid methanolysis followed by GC was applied to determine the sugar contents and composition of hemicellulose [18]; and acid hydrolysis followed by GC was used to quantify the cellulose content [19]. The details of the carbohydrate analysis are available elsewhere [18,19]. The results of carbohydrate analysis are presented in Table 1. There is some variation in the hemicellulose and cellulose contents with spruce bark having much lower cellulose content than the other biomass samples.

Some of the samples were used raw but the others were demineralized by acid-washing and then loaded with $K$ cations. The contents of the elements were analyzed by ICP, and the results are shown in Table 3 of part I of this work.

The samples used to calculate the rate constants for the model in this work were acid-washed spruce, $K$-low, medium and high loaded spruce with 0.12%, 0.6% and 1.2% $K$ contents and impregnated spruce which contains 0.33% $K$. The samples were dried at 105 °C overnight after loading and then stored in sealed containers in the laboratory.

The mass yield curve of the samples during torrefaction was obtained using a thermo gravimetric analyzer (TGA). The heating rate was 20 °C/min with an isothermal step of 30 min at 240, 250, 260, 270 or 280 °C. The details of the torrefaction in TGA have been explained in the part I of this work [17].

The rate constants obtained from the spruce runs were used to model torrefaction of raw aspen, $K$-high aspen (0.82% $K$), raw miscanthus, $K$-high miscanthus ($K = 0.64\%$), raw straw, and raw bark. All the biomasses were torrefied at 240 and 280 °C, except $K$-high miscanthus which was torrefied at 240, 250, 260, 270 and 280 °C and $K$-high aspen which was torrefied at 240, 260 and 280 °C.

## 3. Calculation

A model for a two-step reaction in series is used to describe the mass loss rate of biomass under torrefaction conditions:

$$B \xrightarrow{k_C} C \qquad \text{(Reaction 1.a)}$$

$$B \xrightarrow{k_{V1}} V_1 \qquad \text{(Reaction 1.b)}$$

$$C \xrightarrow{k_D} D \qquad \text{(Reaction 1.c)}$$

$$C \xrightarrow{k_{V2}} V_2 \qquad \text{(Reaction 1.d)}$$

In steps (1.a) and (1.b) the reactive biomass is denoted ‘$B$’ which is converted to an intermediate solid $C$ with a reduced degree of polymerization. The intermediate solid $C$ reacts to form the final solid residue $D$. In reactions (1.b) and (1.d), ‘$V1$’ and ‘$V2$’ are volatiles.

The reaction rates are given by:

$$r_B = -(k_C + k_{v1}) \times [B] \qquad (1)$$

**Table 1**
Carbohydrate analysis of the biomasses.

| Components (wt.% dry) | Hemicellulose | Cellulose |
|---|---|---|
| Straw | 34 | 30 |
| Miscanthus | 26 | 45 |
| Spruce | 25 | 35 |
| Aspen | 27 | 42 |
| Spruce bark | 27 | 18 |