COMBUSTION CHARACTERISTICS OF BIOMASS CHARCOAL PRODUCED AT DIFFERENT CARBONIZATION CONDITIONS

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ABSTRACT: The combustion properties of spruce chars and spruce forest residue chars were studied in the kinetic regime by a series of TGA experiments. The work aimed at establishing how the pressure of the char preparation affects the reactivity with oxygen. In the present phase of the work the pressure during char preparation was employed on a thin layer of biomass with ample ventilation. In this way only negligible pressure effects were observed during char combustion. The kinetics of the char burn-off was described by assuming a main reaction and a side reaction. 12 experiments at three different temperature programs were evaluated by the method of least squares to obtain a dependable kinetic model. A common activation energy of 137kJ/mol gave a reasonable description of both reactions in all the 12 experiments.
Keywords: char, forest residues, wood, combustion, model.

1 INTRODUCTION

Biomass charcoal has favorable properties for combustion applications. The combustion characteristics of biomass charcoal are influenced by the chemical and physical properties of the raw biomass and depend highly on the parameters of the carbonization process. There are charcoal fabrication methods employing elevated pressure that result in particularly high charcoal yields [1,2].

Concerning the raw materials, the forest residues are particularly interesting due to their low cost and high abundance. Forest residues are derived from the crown and branches of trees, including usually needles and foliage. In Norway alone, more than 1.5 million m^3 of forest residues are harvested and collected annually [3].

The present work aims at

- Studying the effect of pressure during the char preparation on the reactivity of the formed chars
- Establishing a dependable kinetic description of the char combustion in the kinetic regime
- Comparing the formation and properties of wood chars and forest residue chars.

This paper includes the first phase of the work, when the pressurized char formation is carried out in a thin sample layer of small particles, with good ventilation. In the next phase of the work the studied chars will be made from the same raw materials by a Flash Carbonization (FC) reactor, in the presence of the volatiles formed.

2 MATERIALS AND METHODS

2.1 Samples

The chars were prepared from Norway Spruce and its forest residue after a milling below 1mm. The raw materials were heated by 10°C/min till 500°C in an open sample pan to form char. A high-pressure thermogravimetric analyzer were employed (LINSEIS STA HP) which was operated either at atmospheric pressure or at 8-bar in the present study. The resulting samples will be referred in the paper as 1-atm and 8-bar chars, respectively.

2.2 Reactivity Studies

The chars were burned off in another TGA (Q5000 IR analyzer of TA instruments). Low sample masses (0.2 – 1mg) and a 100mL/min gas flow of 20% oxygen – 80% nitrogen were employed. Three different temperature programs were used: linear T(t) with a heating rate of 10°C/min; modulated experiments where a sine function with 5°C peak amplitude and 200 s wavelength was added to a 5°C/min linear T(t); and constant heating rate (CRR) T(t). In the latter case the equipment regulated the heating of the samples so that the reaction rate remained below a small preset limit. The employment of the different heating programs served to increase the information content of the experiments for the kinetic evaluation [4-6]. The low sample masses and slow heating programs are needed to maintain kinetic control and avoid excessive self-heating and possible self-ignition, as illustrated in the next section.

3 RESULTS AND DISCUSSION

3.1 Effect of the Transport Processes

The charcoal combustion has a huge exothermic reaction heat; the heating value of a typical charcoal is around 28-33 MJ/kg [7]. If the sample mass is not sufficiently low for the given heating rate, significant self-heating arises. The problem is illustrated in Figure 1, which compares the burn-off of 0.2 and 0.6 mg spruce chars at 10°C/min heating rate. In the latter case the self-heating of the sample resulted in an ignition at 436°C which consumed ca. half of the sample within a split second due to the resulting elevated sample temperatures, far from any kinetic and temperature control.

From this respect the CRR experiments are the safest. Their mass loss rate was kept below 0.2 µg/s at an initial sample mass of 1 mg, while the peak mass loss rate of the other experiments varied between 0.4 and 0.7 µg/s at initial sample masses of 0.2 – 0.5 mg. (The peak mass loss rate for the experiment with self-ignition in Figure 1 was found to be much higher, 68 µg/s.)

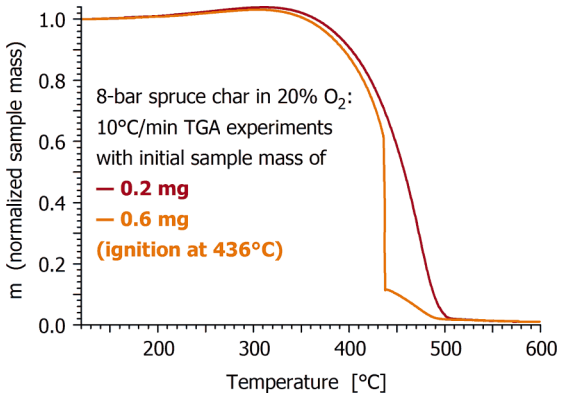


Figure 1: Comparison of the burn-off of 0.2 and 0.6 mg spruce chars in TGA exeriments at 10°C/min heating rate.

3.2 Effect of the Preparation Pressure on the Reactivity

The combustion reactivity of the 1 atm and 8 bar samples is compared in Figure 2 by the CRR experiments due to the reasons outlined above. The equipment had to use slightly different T(t) functions to achieve approximately the same mass loss curves for the samples prepared at 1 and 8 bar because the reactivity of the compared samples was not identical. To characterize the differences, the root mean square difference of the T(t) functions was calculated from 40 to 140 minutes, where most of the mass loss occurred in the CRR experiments. This value was found to be 3.1 and 3.3°C for Figures 2a and 2b, respectively.

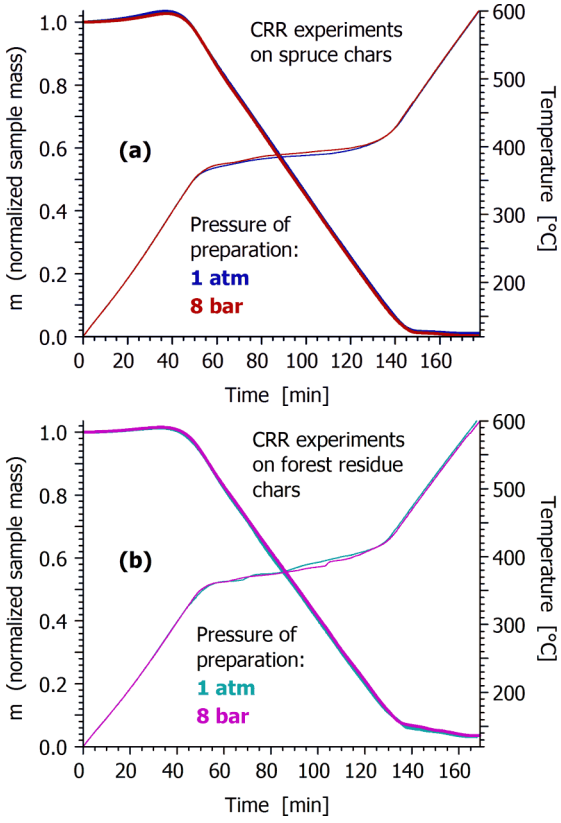
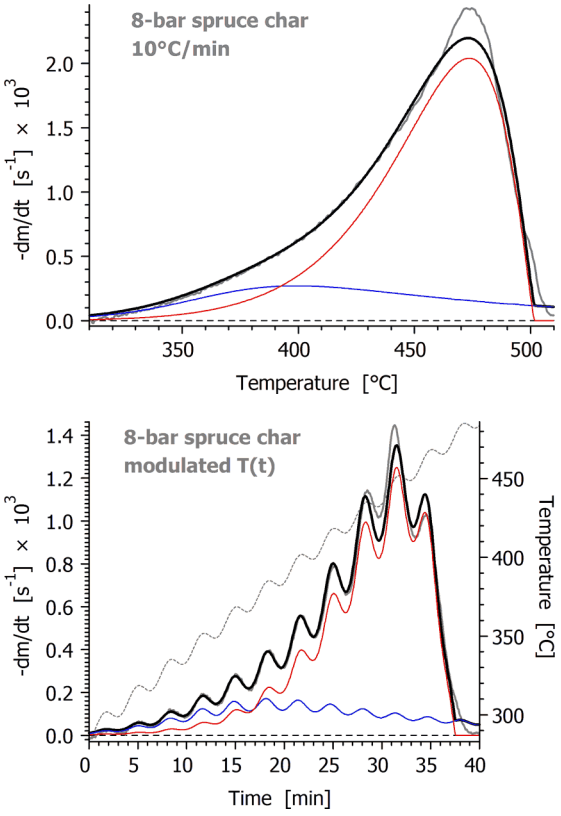


Figure 2: Comparison the burn-off of char samples prepared at 1 and 8 bar from spruce **(a)** and its forest residue **(b)**. The T(t) functions and the normalized sample masses are denoted by thin and thick lines, respectively.

3.3 Kinetic Modelling of the Experiments

Contrary to the ideal cases, the real chars are not homogeneous. The simplest model for the description of an inhomogeneity is to assume that the sample is composed of more than one pseudo-component. Here we assumed two pseudo-components which represent two parts with different reactivity in a given char. This means the assumption of two partial reactions. Both reactions were described by n-order kinetics. The unknown parameters were determined by the method of least squares. As Figure 2 shows, the burn-off is preceded by a mass-gain due to chemisorption and is followed by a small additional mass loss. This latter that was attributed to carbonate decomposition reactions in the ash forming in the combustion. The domains of these processes were excluded from the kinetic evaluation.

The aim was to find a common activation energy that described both partial reactions in all the 12 experiments on the four chars, while allowing different reaction orders and pre-exponential factors. The best fit of the model to all the experiments was achieved at E=137kJ/mol. The results are illustrated by the chars prepared at 8 bar in Figures 3 and 4.



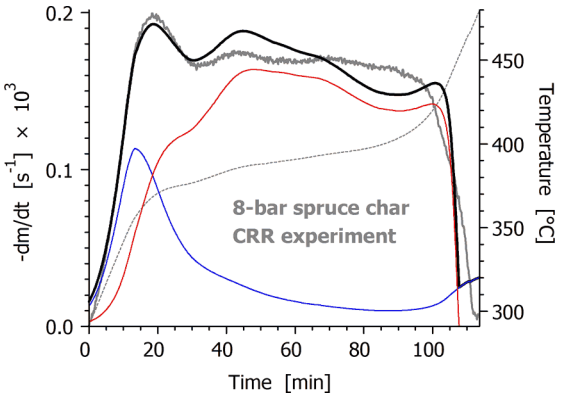


Figure 3: Kinetic evaluation of the experiments on 8-bar spruce chars. Notation: Experimental mass loss rate curves normalized by the initial sample mass (gray —); their calculated counterpart (black —); modulated and CRR temperature programs (gray ---). The curves of the main and side reactions are represented by red and blue colors, respectively.

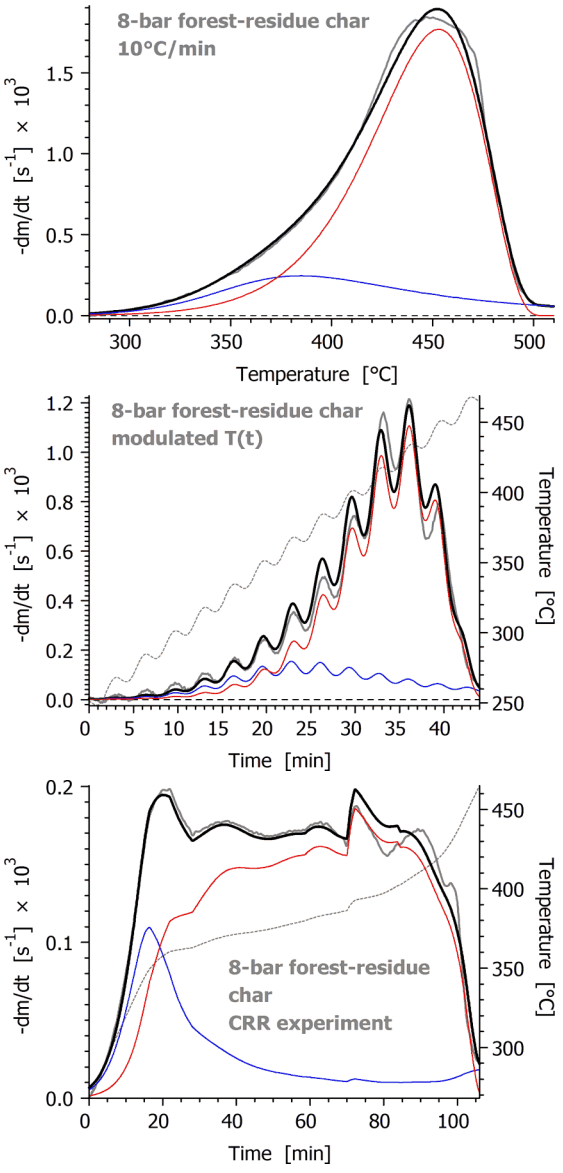


Figure 4: Kinetic evaluation of the experiments on 8-bar forest residue chars. Notations: same as in Figure 3.

3.4 Kinetic Parameters

As Figures 3 and 4 illustrates, the burn-off is described by a main peak and a smaller side peak, which were represented by red and blue colors.

The experiments themselves are not completely free from self-heating problems, as outlined in Section 3.1. Accordingly the temperature of the peak tops has some uncertainties that have to be described in the kinetic modelling. For this purpose the pre-exponential factor of the main peak, A_{main}, was used: a higher pre-exponential factor results in a simulated peak at lower temperature at a given set of kinetic parameters. Hence the pre-exponential factor of the main peak was allowed to vary also from experiment to experiment for the chars produced from both spruce and its forest residue. In this way the following parameters were determined by the method of least squares:

(1) A common activation energy value (as outlined in the previous section)

(2) A pre-exponential factor for the main reaction, A_{main}, that was allowed to vary from experiment to experiment due to the heat transfer (temperature control) uncertainties

(3) The rest of the parameters (A_{side}, n_{main}, n_{side}, and the areas of the partial peaks) which depended on the type of the char, i.e. spruce char or its forest residue char

The obtained kinetic parameters are shown in Table I. Here the A_{main} values belonging to the CRR experiments are listed because the CRR experiments were less influenced by the heat transfer problems than the others.

Table I: The obtained kinetic parameters[a]

Raw material	Spruce		Spruce forest residue	
Pressure of preparation	1 atm	8 bar	1 atm	8 bar
$\log_{10} A_{main}$	7.31	7.25	7.42	7.49
n_{main}	0.61	0.56	0.78	0.80
$\log_{10} A_{side}$	8.48	8.33	8.37	8.61
n_{side}	4.21	4.70	3.07	3.60

[a] *Remarks to Table I:* The activation energy is 137kJ/mol for each reaction, as outlined in Section 3.3. The dimension of the pre-exponential factors is s^{-1}. The listed A_{main} values belong to the CRR experiments.

3.5 Effect of the Feedstock on the Reactivity

As the similar kinetic description, similar kinetic parameters and similar curves in Figures 3 and 4 indicate, the burn-off kinetics of the spruce and its forest residue chars are rather similar. Nevertheless, the spruce forest residue chars are more reactive because the middle points of their mass loss curves occurred at roughly 15°C lower temperatures than those of the spruce chars in the experiments with linear and modulated T(t). This difference may be caused by the catalytic effects of the much higher ash content of the forest residue chars [6].

4 CONCLUSIONS

The combustion properties of spruce chars and its forest residue chars were studied in the kinetic regime by a series of TGA experiments. The chars were prepared in a thin layer of biomass, with ample ventilation under

atmospheric and 8-bar pressures, respectively.

Due to the high combustion heats of the charcoals, an extreme care was needed to avoid excessive self-heating and ensure a nearly kinetic control. This included slow heating rate, special temperature programs, and small initial sample masses of 0.2 - 1 mg.

The difference between the combustion reactivity of the 1-atm and 8-bar chars was found to be negligible.

A kinetic model was established that took into account the experimental uncertainties and described the inhomogeneity of the chars formed from inhomogeneous raw materials.

The burn-off kinetics of the chars formed from spruce forest residues was similar to that of the spruce chars, though the former exhibited higher reactivity, which may be caused by the catalytic effects of its much higher ash content.

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7 PROJECT LOGO