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CO_2 Gasification of Biomass Chars. A Kinetic Study

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TITLE RUNNING HEAD: CO_2 Gasification of Biomass Chars

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ABSTRACT. The CO_2 gasification of pine and birch charcoals was studied by TGA at CO_2 partial pressures of 51 and 101 kPa. Linear and stepwise heating programs were employed to increase the information content of the experimental data sets. Low sample masses were used due to the high enthalpy change. Seven experiments with different experimental conditions were evaluated simultaneously for each sample. The method of least squares was employed. Three reactions appeared in the temperature domain evaluated (600 - 1000°C). The first and second reactions were due to the devolatilization and did not show a significant dependence on the CO_2 concentration. They were approximated by first order kinetics. The 3rd reaction corresponded to the gasification. Its modeling was based on an empirical approximation of the change of the reaction surface during the gasification and by a formal reaction order with respect to the CO_2 concentration. Very close results were obtained for the two charcoals. The dependence on the conversion could be well approximated by power law kinetics. In the next step of the evaluation, the experiments of the two samples (14 experiments combined) were evaluated together, assuming common activation energy values and a common reaction order with respect to the CO_2 concentration. This process led to nearly the same fit as the separate

evaluation of the two samples. The activation energy of the gasification step was 262 kJ/mol. The reaction order of CO_2 was 0.40.

KEYWORDS: Biomass, charcoal, char, kinetics, thermogravimetry.

1. Introduction

The Boudouard reaction plays a crucial role in several industrial processes. When biomass is gasified with CO_2, the first step is the devolatilization forming chars and volatiles (during the heat up of the biomass to the high temperatures needed CO_2 gasification). This step is followed by the reaction of the char with CO_2. The charcoal gasification may become a separate technological process in the future. The development of the charcoal production methods, especially the emerging of the high-yield charcoal technology[1] made charcoal an attractive form for the transportation and storage of renewable biomass energy. The gasification of the charcoal can be an advantageous way in the production of mechanical and electric energy. Compared to the direct biomass gasification, one of its advantages is the lack of the tar production. As contrasted with coals, renewable biocarbons (i.e. charcoal) have low ash, nitrogen and sulfur contents. Moreover, because of their pore structure and the presence of dangling bonds, biocarbons are much more reactive than fossil carbons.[2]

There are several papers dealing with the kinetics of the CO_2 gasification of biomass chars, as shown by a recent, extensive review.[3] When the experimental conditions allow the $C + CO_2 \rightleftharpoons 2\ CO$ reaction to proceed in both directions, the Langmuir-Hinshelwood kinetics is employed usually.[4-8] If the reaction is far from the equilibrium, then the kinetics usually can be well described by the following type of equations:[6,9-11]

$$d\alpha/dt \cong A_\nu \exp(-E/RT)\, f(\alpha)\, P_{CO_2}^{\nu} \qquad (1)$$

where α is the reacted fraction, function $f(\alpha)$ approximates the reactivity changes as the gasification proceeds, P_{CO_2} is the partial pressure of oxygen, and ν is a formal reaction order. (See also the *Nomenclature* at the end of the paper.) A_ν is the preexponential factor. We added ν as a subscript to indicate that the dimension of this quantity varies with ν: if P_{CO_2} is expressed in kPa then the dimension of A_ν is $s^{-1}\ kPa^{-\nu}$.[12] Equations of type 1 are also used for other char gasification reactions, replacing P_{CO_2} by the partial pressure of O_2 or H_2O.

There are theoretical models for the $f(\alpha)$ function in eq 1 which describes the change of the reactive surface area as the reaction proceeds.[13,14] The simple shrinking core model, $f(\alpha)=(1-\alpha)^{2/3}$, also falls into this category.[15] The theoretical $f(\alpha)$ models were deduced for pure, homogeneous carbons. The real charcoals, however, inherit chemical and structural inhomogeneities from their biomass feedstocks.[2,16]

Among others, mineral matter is known to catalyze the gasification and its distribution in the char is also uneven. Another approach is the use of empirical approximations for f(α). The *n*th order kinetics, $f(\alpha) \cong (1-\alpha)^n$ gives frequently good results, where *n* is an adjustable non-negative parameter.[10,11,17-19] Várhegyi et al. have used an empirical formula with three empirical parameters for the char + O_2 reaction that can have a wide variety of shapes, including shapes similar to those derived from the random pore models.[12,20,21] Recently Zhang et al. proposed a semi-empirical model for that purpose.[22]

The Arrhenius parameters can obviously be calculated without the determination of $f(\alpha)$ from data belonging to the same α values in different experiments. Nevertheless, we cannot use the kinetics for modeling if we do not have an $f(\alpha)$. Among others we cannot check the validity of the model by a comparison between the simulated and the experimental data without an $f(\alpha)$. One can obtain empirical $f(\alpha)$ functions by interpolating the experimental reactivity values in the case of isothermal experiments.[11] However, if the kinetics is based only on the isothermal sections of the experiments, we do not get information on the part of the reaction that takes place before reaching the isothermal conditions.

In the present work we studied a birch and a pine charcoal. We aimed finding reliable kinetics by a way that differed from the other studies of the field in the following points:

(i) Series of TGA experiments with linear and stepwise temperature programs were evaluated simultaneously by the method of least squares;

(ii) All parts of the experiments were used in the kinetic evaluation (contrary to the isothermal studies where the section before the stabilization of the experimental conditions is lost) ;

(iii) Care was taken to ensure true kinetic control by employing lower sample masses than it is usual in TGA studies of this field;

(iv) Two samples from different woods were evaluated by partly identical kinetic parameters to reveal the common features of their gasification behavior. In this way 14 experiments were fitted simultaneously by the model.

The employed experimental conditions helped to get reliable information on the char + CO_2 reaction alone. The results are hopped to inspire and assist further researches in this field.

2. Experimental

2.1. Samples. Two chars were prepared from bark-free birch (silver birch, *Betula Pendula*) and pine (Scots pine, *Pinus sylvestris*) grown in Norway. Cubic wood pieces of 10 mm were used for the charcoal preparation. After a drying of 24 hours at 105°C, they were dropped into a reactor preheated to 500°C and kept there for 150 minutes. The charcoals prepared in this way were ground and sieved to get particles of a size of 45-63 μm. The proximate analysis and the ash analysis of the samples are presented in Tables 1 and 2. As these data show, the mineral matter content of these chars is low,

around 1%. The potassium concentration in the ash is considerable lower than those in the agricultural products and wastes. The pine charcoal contains particularly high iron content, while the manganese and zinc contents of the birch charcoal are also worth mentioning. These type of metallic ions may have catalytic effects on the gasification.[9]

The BET specific surface areas of the charcoals were 7 and 6 m^2/g for the birch and pine charcoals, respectively. The amount of pores below 5 nm was negligible. The birch charcoal was found to be mesoporous; 58% of its volume was found to be in pores below 50 nm. This value was less, 26% in the pine charcoal. The specific surface areas of the samples were lower than the usual values for charcoals. This may be due to the fast heating during the preparation. Various studies on charcoals and chars with similar and lower specific surface areas have appeared in the literature. Among others, Várhegyi et al.[12] studied the combustion kinetics of a corncob charcoal produced by a modern, high-yield charcoal fabrication process. Its specific surface was 9 m^2/g and its internal surfaces affected markedly the combustion kinetics.[12]

Table 1. Proximate analysis of the charcoals and their raw materials

	Birch wood	Pine wood	Birch charcoal	Pine charcoal
Volatiles / % db	87.9	86.8	19.2	20.4
Fixed carbon / % db	11.8	13.0	79.9	78.6
Ash / % db	0.3	0.2	1.0	1.1

Table 2. Ash analysis of the charcoals [a]

	Birch charcoal (%, m/m)	Pine charcoal (%, m/m)
Na_2O	0.4	0.1
MgO	15.2	5.1
Al_2O_3	0.7	0.2
P_2O_5	7.4	0.8
SO_3	5.0	1.6
K_2O	14.7	6.2
CaO	30.2	18.3
TiO_2	0.1	0.0
Cr_2O_3	0.2	5.9
Mn_3O_4	7.5	3.7
Fe_2O_3	3.1	42.1
NiO	0.2	6.8
CuO	0.1	0.2
ZnO	2.7	0.1
SrO	0.3	0.0
MoO_3	0.0	1.3
BaO	0.9	0.3
Sum	*88.7*	*92.7*

[a] Atomic concentrations were obtained by XPS. The data were converted to the concentrations of the corresponding oxides. The components with concentrations ≥ 0.1 % (m/m) are shown in the Table.

2.2. Thermogravimetric experiments. A TA Instruments SDT 2960 TG-DTA apparatus has been employed for the thermogravimetric tests. This apparatus detects the mass loss with a resolution of 0.1μg and the temperature is measured in the sample holder. CO_2 and 1:1 mixture (v/v) of argon and CO_2 was used for the experiments with a flow rate of 160 ml/min. The reason of using argon in the ambient gas was connected to its atomic mass, 40, which is close to that of CO_2 (44). In this way its diffusion properties are also close to those of CO_2. Particular care was taken to avoid the presence of oxygen traces since the char + O_2 reaction would influence the TGA curves. The TGA furnace was

purged before the heating program by the reactant gas for 20 min. Each TGA experiment started with a 30 min drying section at 110°C which provided an additional purge by the reactant gas. The CO_2 gasification has a high endothermic reaction heat, 172.5 kJ/mol. Accordingly care was taken to exclude the usual heat transfer problems. For this reason, low sample masses (1 – 2 mg) and relatively slow heating rates (5 – 20°C/min) were employed.

Following our earlier work on the kinetics of the char + O_2 reaction,[12,20,21] we wished to base the work on constant heating rate experiments as well as on temperature programs containing isothermal sections. Such series of experiments contains more information for the determination of the unknown parameters and for the verification of the model.[23] As Figure 1 illustrates, the two charcoals have somewhat different reactivity. Accordingly, different stepwise heating programs were planned for the two samples. The temperature programs are shown in Figure 2. The isothermal sections were selected at 823 and 873°C for the birch charcoals and at 767 and 840°C for the pine charcoal. As the thin vertical lines indicate in Figure 1, the reaction rate was high enough for accurate measurements at the lower selected temperatures (823 and 767°C) and the reaction was still in the accelerating period at the higher selected temperatures (873 and 840°C).

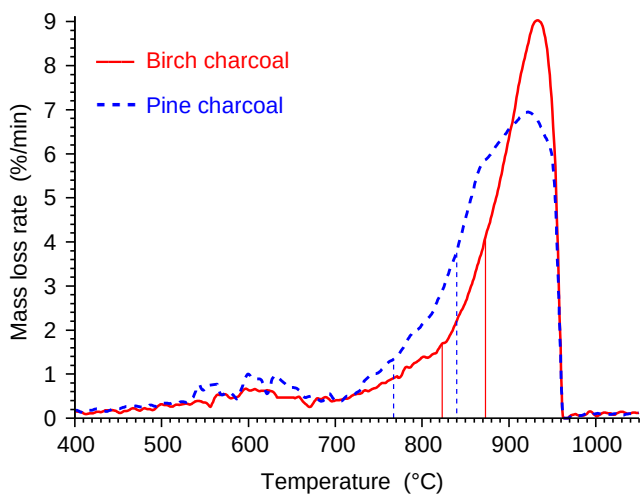

Figure 1. Comparison of the mass loss rate curves of the Birch and Pine charcoals in 50% CO_2 at 10°C/min. The thin vertical lines indicate the temperatures of the isothermal sections in the stepwise heating programs shown in Figure 2.

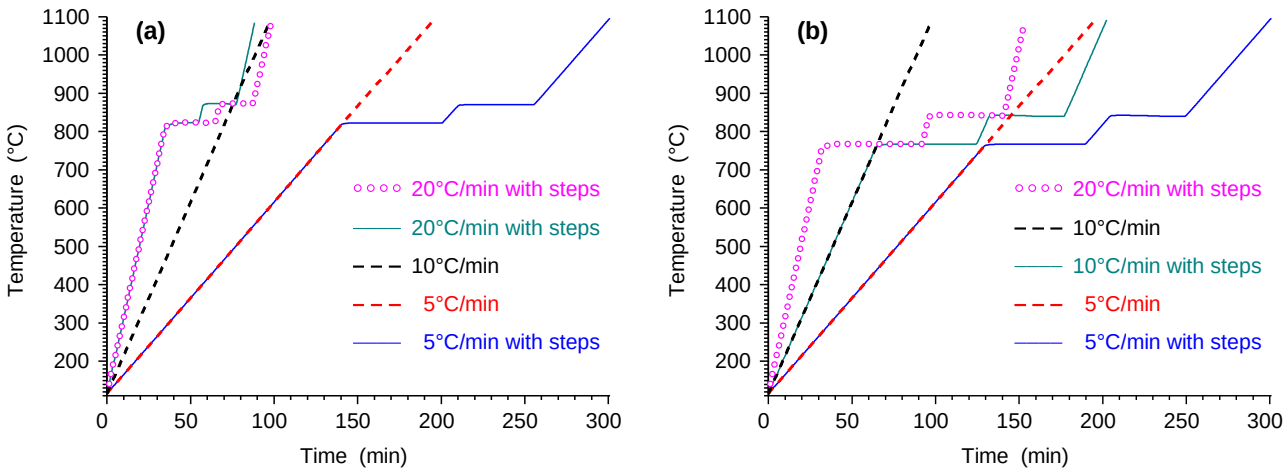

Figure 2. Temperature programs for the birch **(a)** and the pine **(b)** charcoals. The linear heating programs (- - -, - - -) were employed at both CO_2 concentrations. The stepwise programs denoted by circles (o o o) and solid lines (—, —) were used in the 50 and 100% CO_2 experiments, respectively.

3. Modeling and Evaluation

Branca and Di Blasi proposed a 3 parallel reactions to describe the combustion of wood chars in air.[19] The 1st and 2nd reactions referred to devolatilization steps while the 3rd reaction described the char burn-off. The devolatilization steps were assumed to be simple 1st order reactions independent of the oxygen concentration:

$$d\alpha_j/dt = A_j \exp(-E_j/RT)\,(1-\alpha_j) \qquad (j=1 \text{ and } 2) \qquad (2)$$

where α_j is the reacted fraction of the volatiles released in reaction *j*. The char burn-off reaction was described by a variant of eq 1:

$$d\alpha_3/dt = A'_3 \exp(-E_3/RT)\,(1-\alpha_3)^{n_3} \qquad (3)$$

where the A'_3 preexponential factor incorporates the dependence on the oxygen concentration. In the present work we shall follow this way of modeling with two modifications.

(i) For the present work an explicit formula was needed to describe the dependence of the gasification reaction on the CO_2 concentration. We used the dimensionless relative CO_2 concentration (V/V), C_{CO_2} to ensure a proper dimension for A_3 and employed the usual power law approximation:

$$d\alpha_3/dt = A_3 \exp(-E_3/RT)\,(1-\alpha_3)^{n_3}\, C_{CO_2}^{\nu} \qquad (4)$$

(ii) We cannot exclude the possibilities of growing internal surfaces as predicted by the models deduced for ideal carbons.[13,14] To check this possibility we carried out the evaluation with an empirical $f(\alpha)$ function that can mimic a wide variety of shapes:[12,20,21,24]

$$d\alpha_3/dt = A_3 \exp(-E_3/RT)\, f_3(\alpha_3)\, C_{CO_2}^{\nu} \qquad (5)$$

$$f_3(\alpha_3) = normfactor\ (\alpha_3 + z_3)^{a_3} (1-\alpha_3)^{n_3} \quad (6)$$

where a_3, z_3 and n_3 are adjustable parameters and *normfactor* is a normalizing factor ensuring that max $f_3(\alpha_3) = 1$. Equations 5 - 6 will be called "3-parameter $f(\alpha)$ function" in the treatment while eq 4 will be referred as power law $f(\alpha)$. Note that equations 5 - 6 are identical with eq 4 when a_3=0.

In this model, the overall reaction rate is a linear combination of the rates of the partial processes:

$$-dm/dt = \sum_{j=1}^{3} c_j d\alpha_j / dt \quad (7)$$

where m(t) is the sample mass divided by the initial sample mass. Since the reacted fractions α_j run from 0 to 1, c_j equals to the normalized mass loss of the *j*th partial reaction. The unknown parameters of the model are determined from a series of experiments by the method of least squares. The following sum is minimized:

$$S = \sum_{k=1}^{N_{exp}} \sum_{i=1}^{N_k} \left[\left(\frac{dm}{dt}\right)_k^{obs} (t_i) - \left(\frac{dm}{dt}\right)_k^{calc} (t_i) \right]^2 / N_k / h_k^2 \quad (8)$$

Here subscript *k* indicates the experiments differing in CO_2 partial pressure and/or heating program. N_{exp} is the number of experiments evaluated simultaneously, t_i denotes the time values in which the digitized $(dm/dt)^{obs}$ values were taken, and N_k is the number of the t_i points in a given experiment. h_k denotes the heights of the evaluated curves that strongly depend on the experimental conditions . The division by h_k^2 serves for normalization. The obtained fit was characterized by the following quantity:

$$fit\ (\%) = 100\ S^{0.5} \quad (9)$$

Eq 9 is also employed to express the fit of a subgroup within the evaluated experiments. In such cases S is written for the given subgroup. A subgroup may be a single experiment, too.

4. Results and discussion

4.1 Evaluation by 3-parameter and power law f(α) functions. We started the work by evaluating simultaneously a series of seven experiments on both charcoal by the method of least squares (eq 8) using the model defined by equations 2 and 5 - 7. Each series contained 4 linear *T(t)* and 3 stepwise *T(t)* experiments, as outlined in the *Experimental*. Parameter a_3 converged to 0 in the case of the pine charcoal, resulting in the power law kinetics of eq 4. For the birch charcoal a_3=0.07 and z_3=0.07 was obtained. The low a_3 value suggested that the power law kinetics is applicable for the birch charcoal, too. Accordingly the calculation was repeated with the a_3=0 constraint. This constraint has not changed much the rest of the parameters and the fit, as shown in Table 3.

Table 3. The obtained kinetic parameters [a]

Evaluation	7 experiments of a sample			14 experiments on both samples	
Sample	Birch	Birch	Pine [c]	Birch	Pine
Model [b]	3-parameter f(α)	Power law f(α)	3-parameter f(α)	Power law f(α)	
Fit (%)	5.01	5.06	5.56	5.11	5.66
E_1 / kJ mol^{-1}	125	130	100	118	118
E_2 / kJ mol^{-1}	166	170	143	149	149
E_3 / kJ mol^{-1}	262	262	263	262	262
$\log_{10} A_1/s^{-1}$	4.99	5.30	3.38	4.62	4.47
$\log_{10} A_2/s^{-1}$	5.77	6.06	4.47	5.00	4.82
$\log_{10} A_3/s^{-1}$	8.94	8.99	9.28	9.02	9.25
n_3	0.47	0.44	0.74	0.44	0.75
a_3	0.07	0	0	0	0
z_3	0.07	-	-	-	-
ν_3	0.37	0.36	0.49	0.40	0.40
c_1	0.08	0.08	0.09	0.08	0.08
c_2	0.10	0.09	0.13	0.10	0.13
c_3	0.82	0.83	0.78	0.83	0.78

[a] The partial reactions are visualized in Figures 3 and 4 where line styles •••, — and - - - belong to partial reactions 1, 2 and 3, respectively.

[b] "3-parameter *f(α)*" and "Power law *f(α)*" refer to equations 5 - 6 and 4, respectively.

[c] The evaluation of the pine experiment by equations 5-6 resulted in the power law model (a_3=0). Note that z_3 is undefined if a_3=0.

The shapes of the obtained $f_3(\alpha_3)$ functions are presented in Fig 3. One can see that the $f_3(\alpha_3)$ of birch charcoal has higher curvature while that of the pine charcoal is closer to the shrinking core model. This may be due to the higher pore volume in the birch charcoal, as outlined in the *Experimental*.

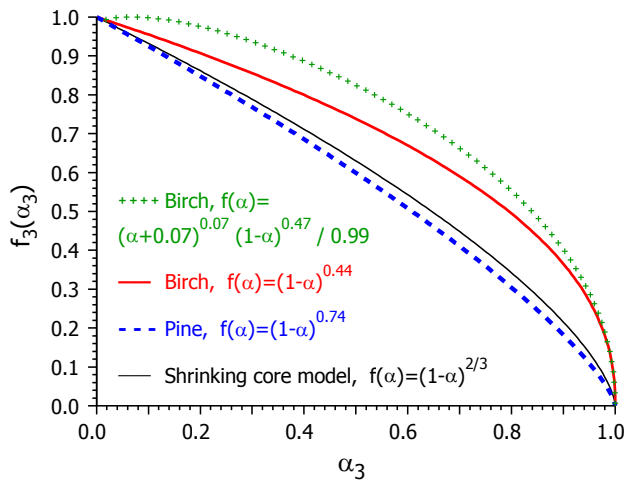

Figure 3. The obtained empirical $f(\alpha)$ functions for the 3rd reaction (gasification). The shrinking core model, $f(\alpha)=(1-\alpha)^{2/3}$ is indicated for comparison.

4.2 Evaluation of both charcoals assuming common activation energies and ν. As Table 3 shows, we obtained practically the same activation energies for the gasification step of the two charcoals. The activation energies of the devolatilization steps, E_1 and E_2 were different. However, these reactions belong to low, flat peaks with a high degree of overlap, as it will be shown later, in Figures 4 and 5. Test calculations revealed that the least squares sum is not sensitive on the values of E_1 and E_2: if their values are altered, the remaining parameters can compensate the change. Accordingly, one can find common values for E_1 and E_2 without a noticeable worsening of the fit. In another test calculation we checked the variance of the least squares sum on ν, and found that the assumption of a common ν for both charcoals only slightly changes the fit. In this way we obtained a model in which E_1, E_2, E_3 and ν was common for both charcoals. Parameters A_1, A_2 and A_3 expressed the reactivity differences between the charcoals, since the rate constants are proportional to the corresponding preexponential factors. Parameter n_3 determines the shape of the corresponding $f_3(\alpha_3)$ that may be different in the two charcoals due to the differences in their pore distribution while c_1, c_2 and c_3 can describe the compositional differences between the charcoals. Accordingly the 14 experiments of the two charcoals were evaluated together with these assumptions. In this evaluation 18 unknown parameters were determined from the 14 experiments by the method of least squares: common values for E_j and ν (4 parameters) and charcoal-dependent values for A_j (6 parameters), n_3 (2 parameters) and c_j (6 parameters). We aimed at revealing the common features in the gasification of the two charcoals in this way. The fit of the experimental mass loss rate curves by their simulated counterparts is shown in Figures 4 and 5. The partial curves are also presented there. The resulting parameters are listed in Table 3. The fit was separately calculated for the birch and pine charcoal experiments so that one could compare them with the corresponding values of the separate evaluations of the two series. These data show that the

assumptions of common E_1, E_2, E_3 and ν only slightly changed the fit between the experimental and simulated data.

4.3 Notes on the obtained parameters. In this section a brief discussion is given on the parameters obtained from the simultaneous evaluation of the two charcoals. The differences between the $\log_{10} A_j$ values in the corresponding rows of Table 3 (0.16 – 0.24 s^{-1}) indicates that the devolatilization reactions are 1.4 – 1.5 times faster in the birch charcoal while the rate constant of the gasification reaction is higher in the pine charcoal by a factor of 1.7. The obtained n_3 parameters are very near to the ones resulted from the separate evaluation of the charcoals. The plot of the corresponding $f_3(\alpha_3)$ functions were close to the solid and dashed lines of Figure 3; the differences were hardly visible. Accordingly there was no need for an additional figure; the differences between the $f_3(\alpha_3)$ of the birch and pine charcoals can be suitably illustrated by Figure 3. As shown in Table 3, the activation energy of the gasification step, E_3, proved to be a well defined quantity: all evaluations and test calculations in the present study resulted in values 262 – 263 kJ/mol.

According to Ollero et al.[6] the literature values for the gasification of biomass chars varies between 99 to 318 kJ/mol. Struis et al.[25] listed several references showing that the usual activation energies for this reaction are around 200 kJ/mol. Their own results were 212 ± 8 kJ/mol. DeGroot and Shafizadeh[9] presented activation energies between 171 and 234 kJ/mol. Marquez-Montesinos et al.[17] determined conversion-dependent activation energies for a charcoal with high mineral content. At low conversion both the original charcoal and its acid washed counterpart had around 248 kJ/mol values. It is difficult to analyze why the activation energies scatter highly in the literature. We think it may be connected to differences in the experimental methods and the evaluation procedure.

We obtained 0.40 for the reaction order with respect to CO_2 during the evaluation of all experiments together. Similar values appeared in several earlier works.[5,6,11]

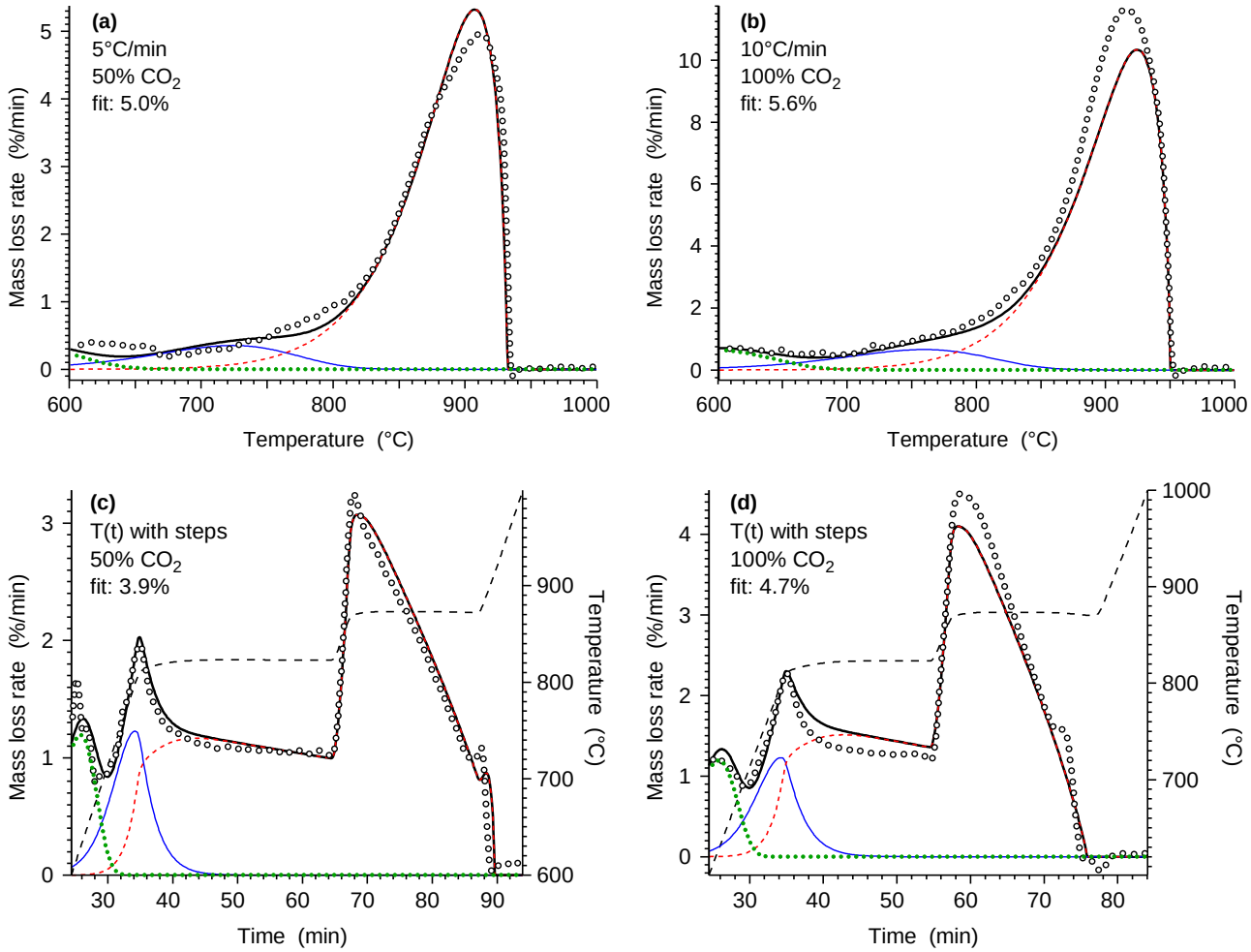

Figure 4. Four experiments with the birch charcoal from a series of 14 experiments evaluated simultaneously, as described in the text. Experimental curves (o o o), simulated curves (**—**), and the partial curves (•••, —, - - -) are shown. The temperature is also shown (– – –) in panels **(c)** and **(d)**.

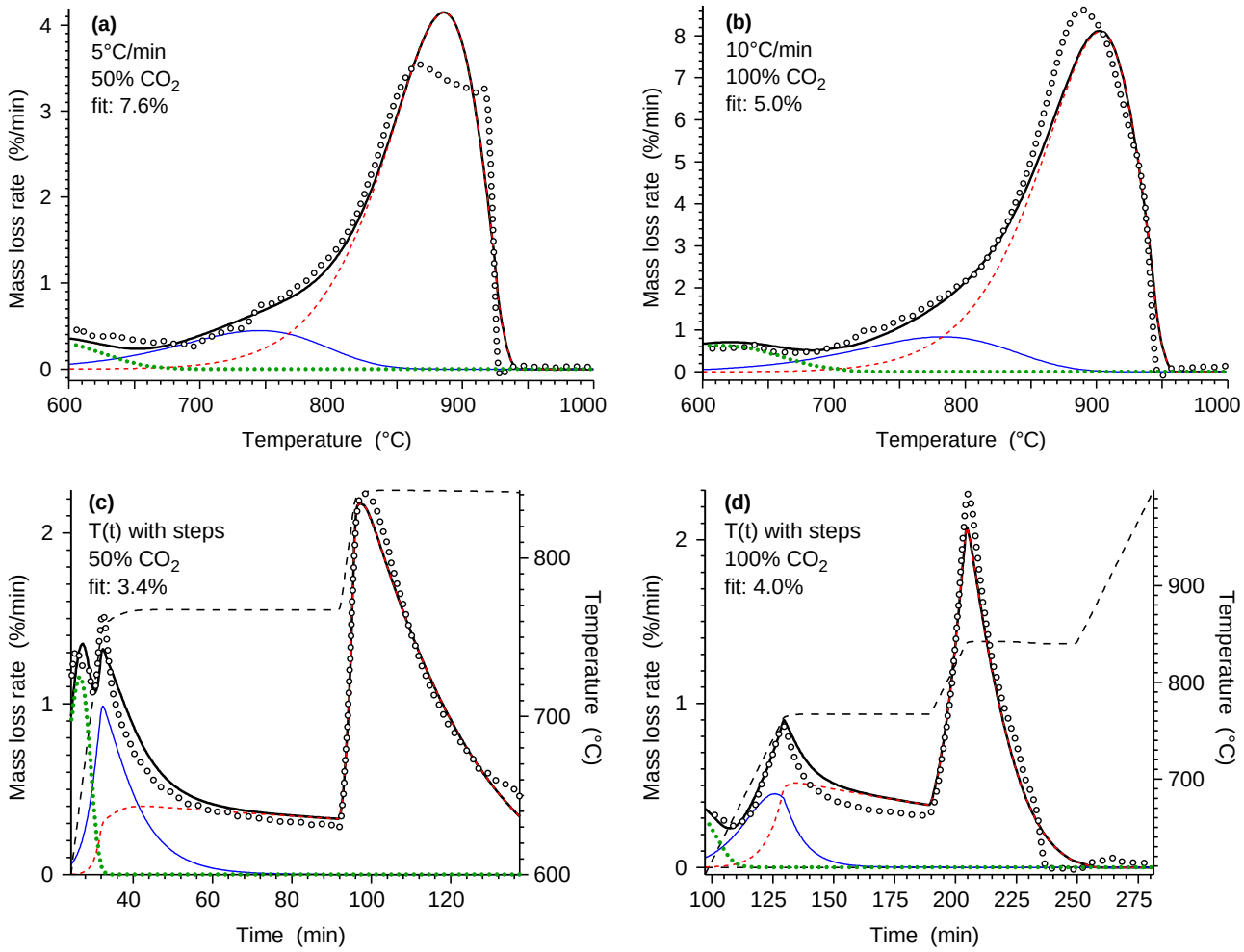

Figure 5. Four experiments with pine charcoals from a series of 14 experiments evaluated simultaneously, as described in the text. (See the notation at Figure 3.)

5. Conclusions

The gasification kinetics of two charcoals were determined using TGA experiments with linear and stepwise T(t) programs. The method of least squares was used. Contrary to the isothermal studies when one has to wait for the stabilization of the experimental conditions, we studied the whole gasification process. A particular care was given to ensure a true kinetic control by employing much lower sample masses than it is usual in the TGA studies on the gasification of biomass chars. The results were justified by the fit between the experimental and calculated data in series of 7 and 14 experiments.

The devolatilization of the charcoal was described by the way proposed earlier by Branca and Di Blasi[19] for charcoal combustion. The dependence of the gasification on the conversion was examined by a versatile, 3-parameter empirical $f(\alpha)$ formula. The results were identical or close to the power law (nth order) kinetics.

Despite the differences between the feedstock, ash composition and pore structure of the two chars, their decomposition kinetics revealed considerable similarities. This made possible to describe all the

14 experiments on the two samples together assuming common activation energies and common reaction order of the CO_2 concentration on both charcoals. In this model the dependence of the reaction rate on the conversion was approximated by power law kinetics. Altogether 18 adjustable parameters were determined from 14 TGA experiments. The reactivity differences between the two charcoals were expressed by different preexponential factors while the structural differences were described by different reaction orders with respect to the conversion.

The activation energy of the gasification step, E_3, proved to be a well defined quantity: all evaluations and test calculations in the present study resulted in values 262 – 263 kJ/mol.

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NOMENCLATURE

α reacted fraction of a pseudocomponent

a parameter of $f(\alpha)$ in eq 6

A pre-exponential factor (s^{-1})

A_ν the pre-exponential factor of eq 1 which is not used in the present paper due to its variable dimension, s^{-1} $MPa^{-\nu}$

c_j normalized mass loss belonging to a given partial reaction

C_{CO_2} relative concentration (V/V) of the carbon dioxide in the ambient gas flow

E activation energy (kJ/mol)

$f(\alpha)$ a function expressing the dependence of the reaction rate on the conversion

fit $100\ S^{0.5}$ (%)

h height of a $-dm^{obs}/dt$ curve

m normalized sample mass (dimensionless)

$m^{calc}(t)$ normalized sample mass calculated from a model

$m^{obs}(t)$ mass of the sample divided by the initial sample mass

ν formal reaction order with respect to P_{CO_2} or C_{CO_2} in equations 1, 4, 5

n formal reaction order with respect to $(1-\alpha)$ in equations 3, 4, 6.

N_{exp} number of experiments evaluated simultaneously

N_k number of evaluated data on the kth experimental curve

P_{CO_2} partial pressure of CO_2 (kPa)

R gas constant (8.3143×10^{-3} kJ mol^{-1} K^{-1})

S least squares sum

t time (s)

T temperature (°C, K)

z parameter of $f(\alpha)$ in eq 6

Subscripts:

i digitized point on an experimental curve

j pseudocomponent

k experiment

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