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Steam gasification of wood char and the effect of hydrogen inhibition on the chemical kinetics.

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ABSTRACT: Gasification kinetics parameters have been derived for birch and beech char samples (45µm<d<60µm) pyrolysed under identical conditions. Reactivity experiments were made in steam-hydrogen-nitrogen mixtures at atmospheric pressure. Reactivity profiles have been obtained in the temperature range from 750 °C to 950 °C, for H_2O partial pressures of 0.05, 0.1, 0.2, 0.5 and 1.0 bar and H_2 partial pressures of 0.1, 0.2 and 0.3 bar. Assuming n^{th} order kinetics for pure steam experiments, the activation energy and the reaction order are E=211 kJ/mol and n=0.51 for beech and E=237 kJ/mol and n=0.57 for birch. A kinetic expression based on Langmuir-Hinshelwood kinetics fairly describes the observed hydrogen inhibition effect on the steam-carbon reaction. The differences between the kinetics determined for the two fuels are relatively small and partly due to the origin and quality of the raw wood. The kinetic parameters obtained are presented using a kinetic compensation diagram; they are compared with literature data and discussed. The influence of the calculation procedure on the results is also discussed. It is found that the data evaluation procedure mostly influences the pre-exponential factor and less the activation energy and reaction order.

INTRODUCTION

The gasification process requires an oxidising agent that provides oxygen for the formation of CO from solid fuel. The oxidising, or gasifying, agents are air, oxygen, steam and CO_2. CO_2 is produced during the pyrolysis and early oxidation processes and generally not externally added. The most common agent is air because of its availability at zero cost. Air, though cheap, is not a perfect agent because of its nitrogen content. The product gas from air gasification has generally a low heating value of 4-7 MJ/Nm^3. Oxygen gasification produces a higher heating value (10-18 MJ/Nm^3) but has a drawback due to the high production cost of oxygen.

Steam is another alternative. It also generates a medium calorific value gas (10-14 MJ/Nm^3) and moreover increases the hydrogen content of the product gas. The presence of steam is important in case of further catalytic upgrading of the product gas[1]. Steam gasification is however a highly endothermic reaction and requires a temperature above 800 °C to take place[2] if no catalyst is present[3,4]. The heat required for the reaction has to be transferred either by partial char combustion in the same reactor –mixing H_2O with oxygen/air[1,5]- or by indirect heating[6,7].

Because of biomass moisture, and steam from pyrolysis in downdraft gasification, steam will always be present in gasification whether it is used or not as a gasification agent. Hydrogen is one of the products of steam gasification and its effect on the reaction is also relevant. Some kinetic data for steam gasification of biomass have been published[2,8,9,10,11,12,13,14,15,16,17,18], but very few considering the effect of H_2 inhibition[19,20,21,41].

The diversity in evaluation of the results from char reactivity experiments is large. The definition of gasification rate varies among researchers and so does the criteria to select the reactivity values from the experiments. Few authors[16,22] have concerns regarding this.

This study presents the kinetic parameters and reactivity profiles for steam gasification of birch and beech char. The inhibition effect of hydrogen is also studied using Langmuir-Hinshelwood kinetics. In addition, the influence of the treatment of the experimental results is analysed by comparing the kinetic parameters differently obtained from the same experiments.

The same birch char has been used for CO_2/CO gasification[23]. The kinetic study of char gasification in $H_2O/H_2/CO_2/CO$ mixtures will be a continuation of the work presented.

THEORETICAL BACKGROUND

H_2O/H_2 REACTION MECHANISMS

The overall steam gasification reaction can be represented by:

$$C_f + H_2O \rightleftharpoons CO + H_2 \qquad (1)$$

However, the reaction is much more complex and involves several steps. Numerous studies have been conducted in order to understand the mechanisms of the steam gasification reaction. The catalytic activity of the ash plays an important role in this discussion[24,19,25]. H_2O gasification is more complex than CO_2 gasification because not only H_2O is involved but also H_2, CO_2 and CO due to the equilibrium of the water gas shift reaction[19,25].

Hüttinger and Merdes[26] give a comprehensive description of the models proposed in the literature for the carbon-steam reaction. Basically, there are two models of the reaction mechanism: the oxygen exchange model and the hydrogen inhibition model. The equations involved are:

$$C_f + H_2O \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} C(O) + H_2 \qquad (2)$$

$$C(O) \overset{k_3}{\longrightarrow} CO + C_f \qquad (3)$$

$$C_f + H_2 \underset{k_{4b}}{\overset{k_{4f}}{\rightleftharpoons}} C(H)_2 \qquad (4)$$

$$C_f + \frac{1}{2}H_2 \underset{k_{5b}}{\overset{k_{5f}}{\rightleftharpoons}} C(H) \qquad (5)$$

The oxygen exchange model is based on equations 2 (reversible -k_{1f} and k_{1b}-) and 3, the traditional hydrogen inhibition model is based on equations 2 (irreversible -only k_{1f}-), 3

and 4 and a different version of the hydrogen inhibition model substitutes equation 4 by equation 5. Each model has a different explanation of the inhibition effect of hydrogen. According to the oxygen exchange model, it is due to the equilibrium of the dissociation reaction (Eq. 2). For the traditional hydrogen inhibition model, the formation of the $C(H)_2$ complex is the reason for inhibition. Finally, the second version of the hydrogen inhibition model involves a dissociative chemisorption of hydrogen on the active sites[27,28], blocking them for the oxygen transfer reaction with steam.

The reaction rate for the models presented is similar, with the exception of dependency on hydrogen partial pressure:

$$r_c = \frac{k_{1f}\, p_{H2O}}{1 + \dfrac{k_{1f}}{k_3} p_{H2O} + f(p_{H2})} \tag{6}$$

where

$$f(p_{H2}) = \frac{k_{1b}}{k_3} p_{H2} \quad \text{, oxygen exchange model} \tag{6.1.}$$

$$f(p_{H2}) = \frac{k_{4f}}{k_{4b}} p_{H2} \quad \text{, hydrogen inhibition model (traditional)} \tag{6.2.}$$

$$f(p_{H2}) = \frac{k_{5f}}{k_{5b}} p_{H2}{}^{0.5} \quad \text{, hydrogen inhibition model (second version)} \tag{6.3.}$$

According to Hüttinger and Merdes[26], it is not possible to determine which is the dominating hydrogen inhibiting mechanism by looking at the reaction rate because the equations are identical, with exception of the second version of the hydrogen inhibition model.

It is quite common to reduce equation 6 to the following expression[20,24]:

$$r = \frac{K_1 p_{H2O}}{1 + K_2 p_{H2O} + K_3 p_{H2}} \tag{7}$$

where K_2 and K_3 represent a ratio between rate constants but are not rate constants themselves.

Other authors[19,29] rather use empirical equations to model the chemical kinetics. In this work, the kinetic parameters have been obtained according to the oxygen exchange model, equations 2 and 3, and also according to n[th] order kinetics.

INFLUENCE OF FUEL TYPE

Several studies have focused on the influence of wood type on CO_2 gasification[30,31,32] and steam gasification[2,14,17,20,33,34,35]. A general conclusion is that the ash content, composition and its catalytic properties explain the differences among the fuels. In particular, Hansen et al.[20] refer to the potassium content of the ashes as being especially relevant.

Moilanen et al.[14] present their results from steam atmospheric gasification of chars from different origins: wood, black liquor, cellulose fibres, peat and coal. All chars, apart from peat, present an increasing reaction rate with conversion, especially wood.

Stoltze et al.[17] find that the gasification of hardwood is 2-3 times slower than straw, probably due to the different char structure and composition. However, since the density of the hardwood char is 5 times higher than the one of straw, in a volume basis the reactivity of wood char is double than of straw. The direct consequence of this fact is that the gasifiers for wood char only require half the volume of a straw gasifier.

Finally, it is important to mention that the pyrolysis conditions also have influence on the char reactivity, as several investigations have proved.

TREATMENT OF THE EXPERIMENTAL RESULTS

There are two definitions of the reactivity commonly used:

$$r = -\frac{1}{(m(t)-m_f)} * \frac{d(m(t)-m_f)}{dt} \qquad (8)$$

$$r_w = -\frac{1}{(m_0-m_f)} * \frac{d(m(t)-m_f)}{dt} \qquad (9)$$

where m_o is the char mass at the beginning of the gasification and m_f is either negligible, or represents the mass of ash, or – as in this work- the residual mass after gasification. The degree of conversion is obtained as:

$$X(t) = 1 - \frac{m(t)-m_f}{m_0-m_f} \qquad (10)$$

Therefore, the relation between the two definitions of reactivity presented above is:

$$r_w = r * (1-X) \qquad (11)$$

It is widely accepted that the reactivity depends on the degree of conversion but there is no agreement about how to define one representative value of reactivity for each experiment.

The representative value of reactivity from an experiment is most frequently obtained as the average reactivity between two degrees of conversion: 0-50%[36], 0-70%[16], 0-75%[10], 40-60%[20], 10-50%[37], 60-80%[30].

Bandyopadhyay et al.[38] selects the representative value of reactivity as the reactivity at 5% conversion. Using an earlier value might introduce error because of the gas changing, but a later value would not correspond to a known condition of the sample inside the sample cup holder (depth, mainly).

Stoltze et al.[16] propose a mass-weighed mean reactivity in order to give less importance to the latest stages of conversion.

Finally, other researchers consider the reactivity as a function of the chemical reactivity, dependent of temperature and reactants partial pressure but independent of conversion, and of a structural factor, solely dependent on the degree of conversion[13,39].

Still, it is possible to find other methods to obtain reactivity[11,19].

EXPERIMENTAL SECTION

Kinetics for a Norwegian birch and a Danish beech have been determined. Apart from their origin there are also other differences between the woods. The beech sample is first received as wood chips whose surface has been exposed to the ambient and that partially contains bark. The birch sample comes from a wood log that has been cut into small cubes of 1x1x1cm, removing the bark. The proximate and ultimate analysis is shown in Table 1 and the ash analysis in Table 2.

Table 1 Proximate and ultimate analysis of birch and beech wood.

Proximate analysis	Moisture	Volatile matter[*]	Fixed carbon	Ash
Birch wood	11.13%	78.7%, mf	20.9%, mf	0.37%, mf
Beech wood	14.16%	75.2%, mf	24.2%, mf	0.56%, mf
Ultimate analysis	C	H	N	O (by diff.)
Birch wood (wt%, mf)	48.7	6.4	0.078	44.45
Beech wood (wt%,mf)	48.1	6.4	0.081	44.82

* Pyrolysis conditions: Heating at 24 °C/min until 600 °C, held for 30 min, natural cooling.

Table 2 Ash analysis of birch and beech wood (%).

Species	Si	Al	Fe	Ca	Mg	K	Na	Ti	S
Beech	1.2	0.14	1.8	25	7.1	28	2	0.029	0.75
Birch	0.03	0.01	0.17	30	4.8	28	0.08	0.007	0.64
Species	P	Cl	Cu	Zn	Ni	Pb	Cd	Hg	
Beech	2	0.29	0.03	0.2	0.02	0.01	<0.001	<0.001	
Birch	3.4	0.03	0.06	0.06	0.01	0.02	<0.001	<0.001	

Both woods have been pyrolysed at the Technical University of Denmark, Department of Energy Engineering (DTU, ET), in a macro-TGA, heated at 24 °C/min to 600 °C, held at that temperature for 30 min and then cooled down to room temperature naturally. Both chars were thereafter crushed and sieved to 45-63 μm.

The instrument used for the reactivity study is a Pressurised Thermogravimetric Analyser (PTGA) at ReaTech, a modified Du Pont Thermogravimetric Analyser. The sample (~5 mg) is placed on a small platinum tray, hanging on a horizontal balance arm. The sample temperature is measured with the help of two thermocouples, near to, but not in contact, with the sample. This investigation is limited to atmospheric pressure although the instrument is prepared for high pressure operation. Rathmann et al.[40] and Sørensen[35] give a detailed description of the PTGA and Hansen et al.[20] describe the modifications required for the instrument to tolerate steam.

Once the char sample is introduced into the PTGA, it is first dried in N_2 during 10 min at 200 °C, then is heated at 24 °C/min to 1000 °C and held at this temperature for 30 min. After this the sample is cooled to the gasification temperature and when conditions are stable, the steam is allowed into the reaction chamber. The sample is hold isothermal until the gasification reaction is complete and then the temperature is raised to 1000 °C to complete the reaction. The sample size is ca. 10 mg and the gas flow 1000 ml/min.

The objective of increasing the temperature up to 1000 °C previous to gasification is to simulate the history of the particle in the two-stage gasifier at DTU, ET. This is also the reason for the heating rate of 24 °C/min. During the 30 min. period at 1000 °C

in the nitrogen atmosphere some fraction of the catalytic species K and Na devolatilise and are carried away from the sample and therefore the char could be less reactive.

The experimental matrix for this investigation is shown in Table 3.

Table 3 Experimental matrix for H_2O gasification experiments

P_{H2O} (bar)	T(°C)							
	750	800	With H₂	850	with H₂	900	with H₂	950 with H₂
0.1	○●	○●●	①	○○●	①❶❸	○●	①❶❸	③❸
0.3	○○●●	○●	❷❷❸	○●	❸	●	②❸	
0.5	○●	○○●	①❶	○●	①❶		③	③

(○,①,②,③) Birch char; (●,❶,❷,❸) Beech char. The numbered symbols indicate the partial pressure of hydrogen (x10 bar).

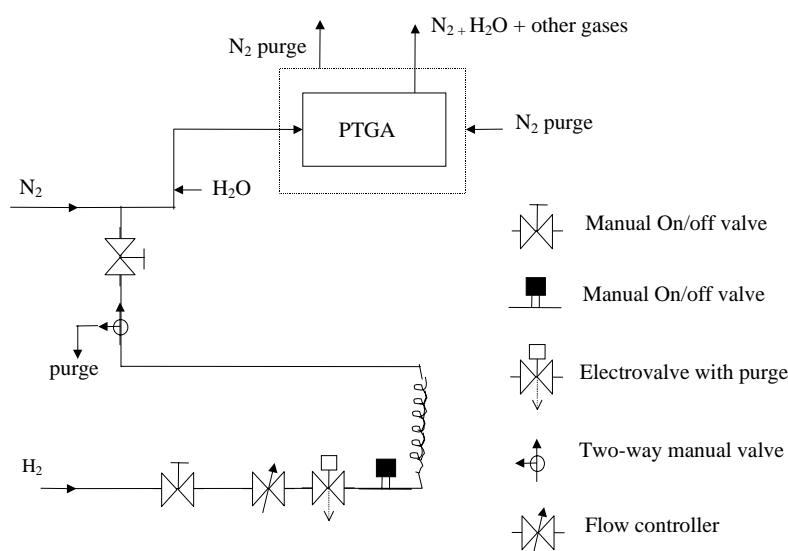The design of the installation is described in Fig. 1.

Fig. 1 Schematic drawing of the installation set-up.

RESULTS AND DISCUSSION

GASIFICATION RATE

Fig. 2 shows the mass loss curve for one of the experiments. The initial and final weights for the gasification reaction are also indicated. Fig. 3 shows the reactivity as a function of the degree of conversion, i.e. the reactivity profile, for the same experiment according to equations 8 and 9. In addition, the figure shows the average reactivity (from eq. 8) between 20 and 80% conversion.

It is important to notice that the shape of the reactivity profile is very dependent on the reactivity definition. For the following discussion, the reactivity has been obtained according to equation 8.
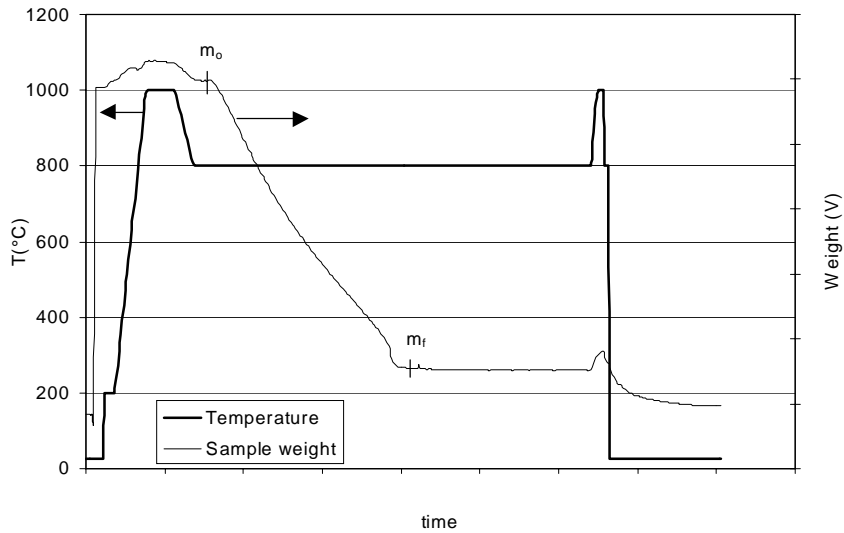

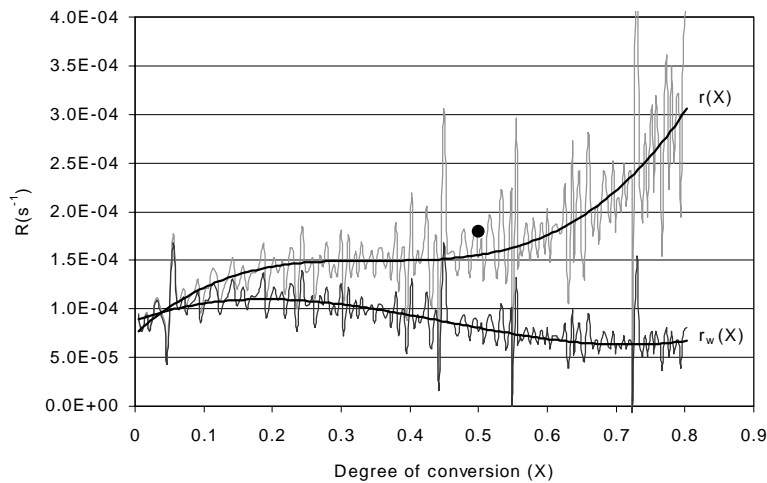Fig. 2 Temperature and weight signal as a function of time. Experimental data.

Fig. 3 Reactivity as a function of conversion.
(●: Average reactivity between 20 and 80% conversion).

PURE STEAM EXPERIMENTS

Fig. 4 shows the reactivity of the pure steam experiments as a function of temperature and steam partial pressure. The representative reactivity value has been obtained as the reactivity at 50% conversion. The continuous line shows the nth order reaction model for the birch experiments. The figure shows that beech is more reactive than birch at

low temperatures (750-800 °C). The kinetic parameters obtained according to n^{th} order kinetics are shown in Table 4 together with results from other references.
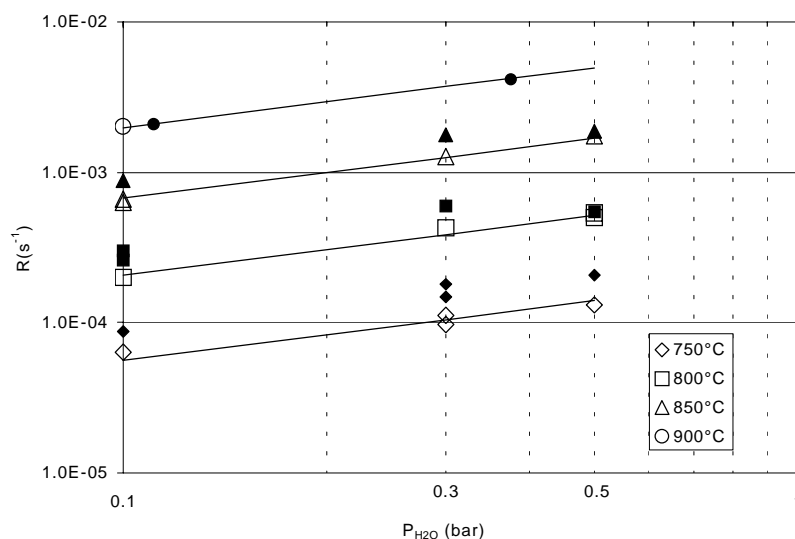

Fig. 4 Reactivity as a function of steam partial pressure and temperature.
(Filled symbols: beech, hollow symbols: birch).

Table 4 Kinetic parameters comparison for steam gasification experiments.

Reference	Char origin	N^{th} order kinetics		
		E(kJ/mol)	k_o	n
This work[*]	Birch	237 ± 0.4	$2.62 \cdot 10^8 \pm 5 \cdot 10^6 s^{-1} bar^{-n}$	0.57 ± 0.03
This work[+]	Beech	211 ± 6.1	$1.71 \cdot 10^7 \pm 1 \cdot 10^7 s^{-1} bar^{-n}$	0.51 ± 0.05
Capart et al.[12]	Woodchar	138	$1.79 \cdot 10^3 \ s^{-1} atm^{-n}$	1.00
Hemati et al.[13]	Woodchar	198	$1.23 \cdot 10^7 \ s^{-1} atm^{-n}$	0.75
Richard et al.[8]	Fir wood	104.5 ± 8		
Li et al.[9]	Black liquor	210 ± 10		
Whitty[19]	Black liquor	230		0.56
Timpe et al.[10]	Poplar	271		
	Cattails	262		
Moilanen et al.[14,15]	Wood	196, 217		
	Black liquor	226		
Stoltze et al.[16,17]	Straw	151	$4.77 \cdot 10^7$ %/min	~0.5
(Large TGA)	Wood chips	119	$1.76 \cdot 10^6$ %/min	~0.5
Rensfelt et al.[2]	Poplar wood	182	$1.2 \cdot 10^8 \ min^{-1}$	
	Straw	182	$5.9 \cdot 10^7 \ min^{-1}$	
Groeneveld [18]	Wood char	217	$10^6 – 10^7 s^{-1} m^{2.1} mol^{-0.7}$	0.7

[*] $R_{sqr} = 0.9919$, [+] $R_{sqr} = 0.9784$

From the above comparison one can see that the activation energy varies between 105 and 270 kJ/mol. Most values for E lie between 180 and 270 kJ/mol and the parameters obtained in this investigation are well within this range. The reaction order obtained is

also similar to the values found in literature, eventually among the lower values. These data will be further discussed in Fig. 7.

H_2 INHIBITION EFFECT

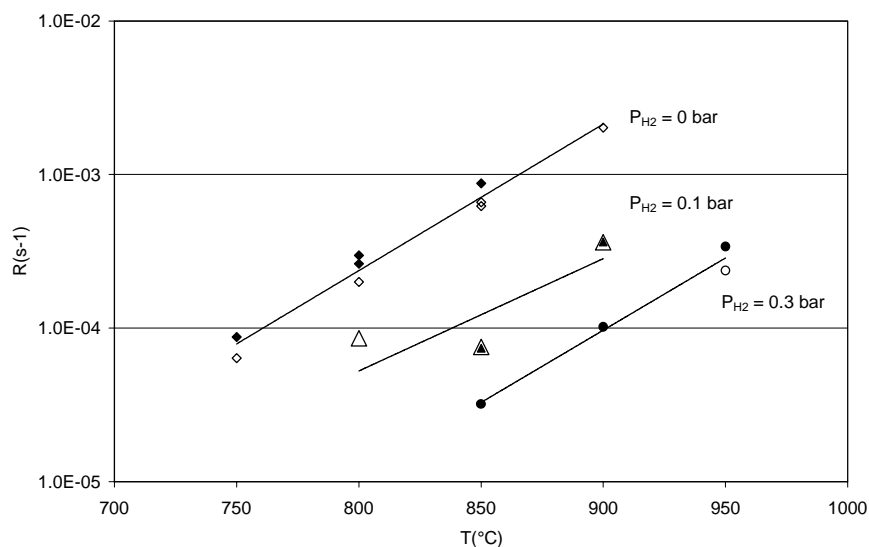The experiments show that the presence of hydrogen inhibits the steam gasification reaction, as presented in Fig. 5.

Fig. 5 Inhibition effect of H_2 as a function of temperature and H_2 partial pressure.
(P_{H2O}= 0.1 bar, filled symbols: beech, hollow symbols: birch)

The equations 6 and 6.1 have been used to model the reaction. Table 5 shows the kinetic parameters obtained in this investigation. In spite of the high uncertainty of the model parameter calculation, the model fits well the experimental results (See Fig. 6).

Table 5 Kinetic constants for H_2O/H_2 gasification of birch and beech char.

Wood species	E_{1f} (kJ/mol)	k_{o1f} ($s^{-1}bar^{-1}$)	E_{1b} (kJ/mol)	k_{o1b} ($s^{-1}bar^{-1}$)	E_3 (kJ/mol)	k_{o3} (s^{-1})
Beech	199	$2.0 \cdot 10^7$	146	$1.8 \cdot 10^6$	225	$8.4 \cdot 10^7$
Birch	214	$7.6 \cdot 10^7$	284	$2.1 \cdot 10^{12}$	273	$1.6 \cdot 10^{10}$

Table 6 compares these results with the few kinetic parameters found in the literature. Although there is a certain agreement in the value of E_3, the other values are somewhat different. This could be explained by the high uncertainty of the calculation, as also mentioned by Hansen et al.[20] or by the differences in char origin.
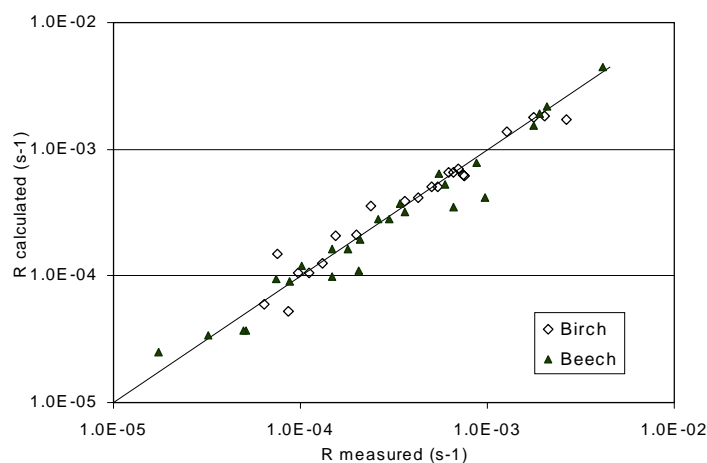
Fig. 6 Calculated reactivity values versus experimental values.

Table 6 Comparison of kinetic parameters for H_2O/H_2 gasification.

Reference	Char origin	Langmuir-Hinshelwood kinetics				
		E_{1f} (kJ/mol)	E_{1b} (kJ/mol)	E_3 (kJ/mol)	E_{1f}-E_3 (kJ/mol)	E_{1b}-E_3 (kJ/mol)
This work	Birch	214	284	273	-59	11
This work	Beech	199	146	225	-26	-79
Hansen et al. [20]	Wheat straw	149	140*	257*	-108	-117
Sørensen et al. [41+]	Wheat straw	158	126	269	-111	-143

* Calculated values, implied in the kinetic model.
+ Recalculation from Hansen et al.[20] experiments.

Fig. 7 compares all the kinetic parameters obtained with those found in literature, with and without hydrogen inhibition, by means of a kinetic compensation diagram. A solid line has been drawn for each of the Langmuir-Hinshelwood constant. Most of the values lie within the same line what might be a sign of consistency in spite of the disparity in activation energies. The kinetic parameters according to n[th] order kinetics are somewhat more scattered although still aligned. The differences between kinetic parameters can be also due to parameters not studied in this investigation like the number of active sites or the effect of temperature on the active sites behaviour. The three sets of kinetic parameters for birch (Langmuir-Hinshelwood kinetics) represent three valid numerical solutions in the model fitting.
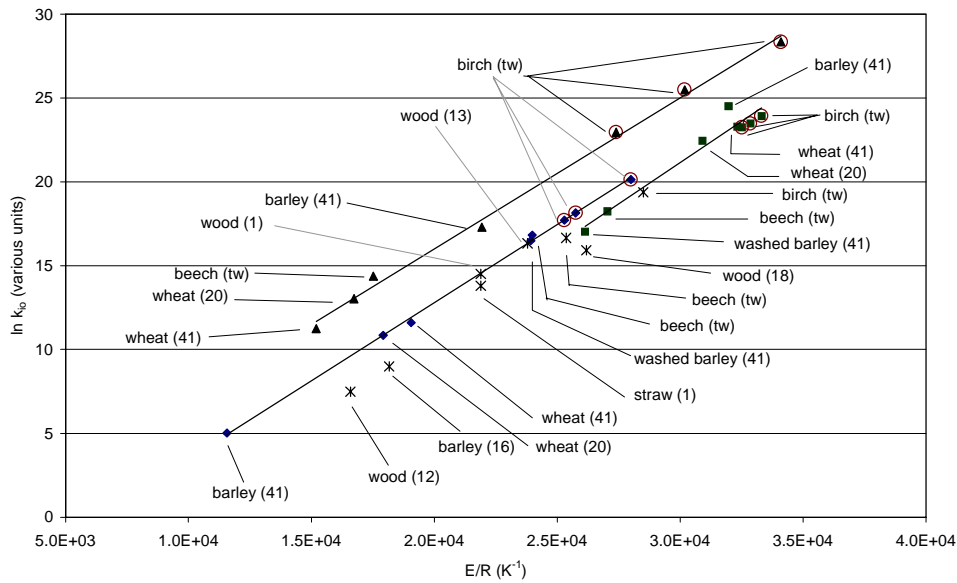
Fig. 7 Kinetic compensation diagram for H_2O and H_2O/H_2 gasification.
($*$: n^{th} order, $\blacklozenge$: k_{1f}, $\blacktriangle$: k_{1b}, $\blacksquare$: k_3, tw: this work)

EFFECT OF FUEL TYPE

With respect to reactivity, the results have shown no large differences between birch and beech. There are however certain differences regarding the effect of temperature on the reactivity profile, and the shape of the profile itself. Fig. 8 shows several reactivity profiles, normalised with respect to their reactivity at 20% conversion to allow comparison. The final increase in gasification rate is more drastic for beech than for birch, especially noticeable for beech at lower temperatures.

Moilanen and his co-workers[14,21] also obtain increasing reactivity profiles with conversion, except for peat. They expect such increasing reactivity because of pore development structure, enhanced by the catalytic effect of the ash, since the ratio catalyst/carbon increases with char conversion. Stoltze et al.[16] obtain similar profiles with barley straw. Rensfelt et al.[2] find as well increasing reactivity with conversion, and a characteristic shape of the reactivity profile for each fuel, having each fuel the same curve independent of temperature. However, for washed barley chars, Sørensen et al.[41] find a decreasing reactivity as a function of conversion.

The ash analysis presented in Table 2 shows very similar values for the potassium content of both woods, but there is some variation regarding other ash components. It cannot be known from the experiments whether the differences in the reactivity profiles are due to these other ash components or to a different porosity evolution as the conversion proceeds.
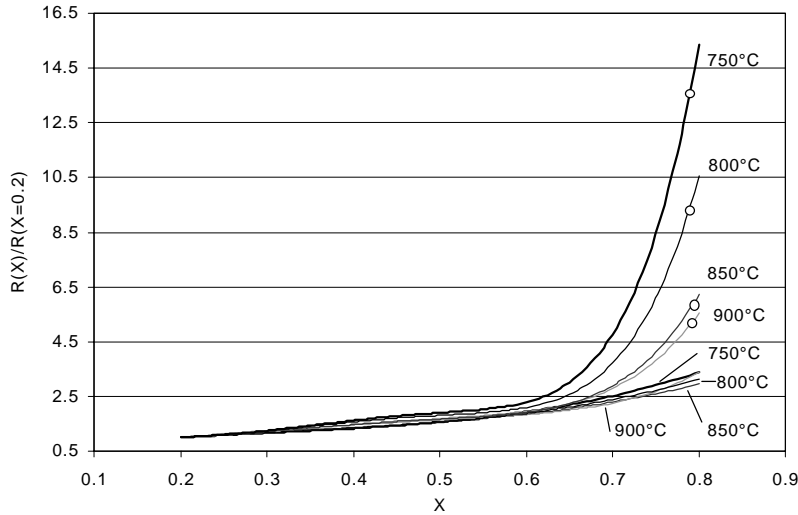
Fig. 8 Reactivity profiles for H_2O experiments. (O: beech experiments).

INFLUENCE OF REACTIVITY DEFINITION

In this section, six different procedures are used to select a representative reactivity value (r_c) from the same experiments, using the reactivity definition (eqn. 8). All the definitions are explained in Table 7.

Table 7 Representative reactivity definitions compared in this section.

	Description	X	Definition of r_c
1	Reactivity at 20% conversion	0.2	$r_c = r$ (X=0.2)
2	Reactivity at 50% conv.	0.5	$r_c = r$ (X=0.5)
3	Reactivity at 80% conv.	0.8	$r_c = r$ (X=0.8)
4	Average reactivity (20-80% conv.)	0.2-0.8	r_c= average r between X=0.2 and 0.8
5	Structural profile f(X) assumed [35,39,42]	0.2-0.8	$r=r_c(T, P_{H2O})*f(X)$
6	Time for 80% conversion	0-0.8	$r_c=1/t$(X=0.8)

The kinetic parameters for the nth order kinetic model have been obtained using these definitions of reactivity for the pure steam gasification experiments of birch. All the activation energies lie between 228-238 kJ/mol and the reaction orders between 0.54 and 0.58, apart from definition 3. The frequency factors are somewhat more scattered, lying between $5 \cdot 10^7$ and $3 \cdot 10^8$. Regarding the uncertainty of the calculation, definitions 2, 5 and 4 seem to give more precise results and it is interesting to notice that the error of the reaction order calculation does not depend on how a representative reactivity value is defined.

It is very important to analyse the influence of the reactivity definition (eqn. 8 and 9) on the kinetic parameters. Since all representative reactivity definitions are related to a fixed degree of conversion (or a fixed interval), the difference between r and r_w will be a multiplying factor, independent of temperature and pressure, and therefore absorbed in the frequency factor. This means that whether equation 8 or 9 is used, the activation energy and the reaction order calculation will give the same result.

CONCLUSIONS

(1) The kinetic parameters according to the nth order reaction model for steam gasification of wood char are E= 237 kJ/mol, k_0= $2.62 \cdot 10^8$ and n= 0.57 for birch, E= 211 kJ/mol, k_0= $1.71 \cdot 10^7$ and n= 0.51 for beech char.

(2) Hydrogen inhibits the steam gasification reaction. The char gasification reaction with steam and hydrogen can be modelled based on Langmuir-Hinshelwood kinetics. The model fits well the results.

(3) The type of wood affects very little the kinetic parameters but shows some influence on the reactivity profile.

(4) The definition of the reactivity will not affect the activation energy or the reaction order calculation.

(5) The method to select a representative reactivity value from one experiment has more influence on the frequency factor than on the activation energy and reaction order. The accuracy of the calculation might also be affected.

ACKNOWLEDGMENTS

REFERENCES

1. Gil, J., Aznar, M.P., Caballero, M.A., Francés, E. & Corella, J. (1997). Biomass gasification in fluidized bed at pilot scale with steam-oxygen mixtures. Product distribution for very different operating conditions, Energy and Fuels, Vol. 11, pp. 1109-1118.

2. Rensfelt, E., Blomkuist, G., Ekstrom, S., Espenäs, B.G. & Liinanki, L. (1978). Basic gasification studies for development of biomass medium-btu gasification processes, Energy from Biomass and Wastes, IGT, 14-18 August 1978. Paper No. 27, pp. 466-494.

3. Bilbao, R., García, L., Salvador, M.L. & Arauzo, J. (1998).Steam gasification of biomass in a fluidized bed, effect of a Ni-Al catalyst, Biomass for Energy and Industry. 10th European Conference and Technology Exhibition, 8-11 June 1998, Würzburg, Germany, pp. 1708-1711.

4. Rapagnà, S., Jand, N. & Foscolo, P.U. (1998). Utilisation of suitable catalysts for the gasification of biomasses, Biomass for Energy and Industry. 10th European Conference and Technology Exhibition, 8-11 June 1998, Würzburg, Germany, pp. 1720-1723.

5. Evans, R., Knight, R. A., Onischak, M. & Babu, S.P. (1987). Process performance and environmental assessment of the Renugas process, Energy from Biomass and Wastes X, IGT, pp. 677-696.

6. Paisley, M.A. et al. (1999).Commercial demonstration of the Battelle/FERCO biomass gasification process: Startup and initial operating experience,Proceedings of the 4th Biomass Conference of the Americas, Oakland, CA,USA, pp.1061-1066.

7. Zschetzsche, A., Hofbauer, H. & Schmidt, A. (1998). Biomass gasification in an internal circulating fluidized bed, Proceedings of the 8th EC on Biomass for Agriculture and Industry, Vol. 3, pp. 1771-1777.

8. Richard, J.R., Cathonnet, M. & Rouan, J.P. (1982). Gasification of charcoal: Influence of water vapor, Fundamentals of Thermochemical Biomass Conversion, pp. 589-599. Elsevier Applied Science Publishers.
9. Li, J. & van Heiningen, A.R.P. (1991). Kinetics of gasification of black liquor char by steam, Industrial & Engineering Chemistry Research, Vol. 30, No, 7, pp. 1594-1601.
10. Timpe, R.C. & Hauserman, W.B. (1993). The catalytic gasification of hybrid poplar and common cattail plant chars, Energy from Biomass and Wastes XVI, Institute of Gas Technology, March 2-6, 1992, pp. 903-919.
11. Kojima, T., Assavadakorn, P. & Furusawa, T. (1993). Measurement and evaluation of gasification kinetics of sawdust char with steam in an experimental fluidized bed, Fuel Processing Technology, Vol. 36, pp. 201-207.
12. Capart, R. & Gélus, M. (1988). A volumetric mathematical model for steam gasification of wood char at atmospheric pressure, Energy from Biomass 4. Proceedings of the 3rd contractors'meeting, Paestum, 25-27 May, pp. 580-583.
13. Hemati, M. & Laguerie, C. (1988). Determination of the kinetics of the wood sawdust Steam-gasification of charcoal in a thermobalance, Entropie, No. 142, pp. 29-40.
14. Moilanen, A., Saviharju, K. & Harju, T. (1993). Steam gasification reactivities of various fuel chars, Advances in Thermochemical Biomass Conversion, Blackie Academic & Professional, 1993, pp. 131-141.
15. Moilanen, A. & Saviharju, K. (1997). Gasification reactivities of biomass fuels in pressurised conditions and product gas mixtures, Developments in Thermochemical Biomass Conversion, Blackie Academic & Professional, 1997, pp 828-837.
16. Stoltze, S., Henriksen, U., Lyngbech, T. & Christensen, O. (1993). Gasification of straw in a large-sample TGA, Nordic Seminar on Solid Fuel Reactivity, Chalmers University of Technology, Gothenburg, Sweden, 24 November 1993.
17. Stoltze, S., Henriksen, U., Lyngbech, T. & Christensen, O. (1994). Gasification of straw in a large-sample TGA, Part II Nordic Seminar on Biomass Gasification and Combustion, NTH, Trondheim, 21 June 1994.
18. Groeneveld, M.J. (1980). The co-current moving bed gasifier, Ph.D.thesis, Twente University of Technology, Enschede, Netherlands.
19. Whitty, K.J. (1997). Pyrolysis and gasification behaviour of black liquor under pressurized conditions, Academic Dissertation, Report 97-3, Åbo Akademi, Department of Chemical Engineering.
20. Hansen, L.K., Rathmann, O., Olsen, A. & Poulsen, K.(1997). Steam gasification of wheat straw, barley straw, willow and giganteus, Risø National Laboratory, Optics and Fluid Dynamics Department, Project No. ENS-1323/95-0010
21. Moilanen, A. & Mühlen, H.J. (1996). Characterization of gasification reactivity of peat char in pressurized conditions. Effect of product gas inhibition and inorganic material, Fuel, Vol. 75, No. 11, pp. 1279-1285.
22. Whitty, K.J. (1993). Gasification of black liquor char with H2O under pressurized conditions, Report 93-4, Department of Chemical Engineering, Combustion Chemistry Research Group.
23. Barrio, M.& Hustad, J.E. CO2 gasification of birch char and the effect of CO inhibition on the calculation of chemical kinetics, *This conference*.
24. Mühlen, H-J., van Heek, K.H. & Jüntgen, H. (1985). Kinetic studies of steam gasification of char in the presence of H2, CO2 and CO, Fuel, Vol.64, July, pp. 944-949.

25. Meijer, R., Kapteijn, F. & Moulijn, J.A.(1994).Kinetics of the alkali-carbonate catalysed gasification of carbon: H_2O gasification, Fuel,Vol.73,No.5, pp.723-730.
26. Hüttinger, K.J. & Merdes, W.F. (1992). The carbon-steam reaction at elevated pressure: formations of product gases and hydrogen inhibitions, Carbon, Vol. 30, No. 6, pp. 883-894.
27. Weeda, M., Abcouwer, H.H., Kapteijn, F. & Moulijn, J.A. (1993).Steam gasification kinetics and burn-off behaviour for a bituminous coal derived char in the presence of H_2, Fuel Processing Technology, Vol. 36, pp. 235-242.
28. Linares-Solano, A., Mahajan, O.P. & Walker, P.L. (1979). Reactivity of heat-treated coals in steam, Fuel, Vol. 58, May, pp. 327-332.
29. Liliedahl, T. & Sjöström, K. (1997). Modelling of char-gas reaction kinetics, Fuel, Vol. 76, No. 1, pp. 29-37.
30. DeGroot, W.F. & Shafizadeh, F.(1984). Kinetics of gasification of Douglas Fir and cottonweed chars by carbon dioxide, Fuel, Vol. 63, February, pp. 210-216.
31. Kannan, M.P. & Richards, G.N.(1990). Gasification of biomass chars in carbon dioxide: dependence of gasification rate on the indigenous metal content. Fuel, Vol. 69, June, pp. 747-753.
32. Illerup, J.B.& Rathmann, O.(1995).CO2 gasification of Wheat straw, barley straw, willow and giganteous, Department of Combustion Research, RISØ National Laboratory, 12th December.
33. Espenäs, B.G. (1993). Reactivity of biomass and peat chars formed and gasified at different conditions, Advances in Thermochemical Biomass Conversion, Blackie Academic & Professional, 1993, pp. 142-159.
34. Moilanen, A. & Kurkela, E. (1995). Gasification reactivities of solid biomass fuels, Preprints of papers, American Chemical Society, Division of Fuel Chemistry, Vol. 40(3), pp. 688-693.
35. Sørensen, L.H.(1994). Fuel reactivity as a function of temperature, pressure and conversion, Ph.D. thesis, Risø National Laboratory, Denmark.
36. Chen, G., Yu, Q. & Sjöström, K.(1997). Reactivity of char from pyrolysis of birch wood, Journal of Analytical and Applied Pyrolysis, Vol. 40-41, pp. 491-499.
37. Zanzi, R., Sjöström, K. & Björnbom, E. (1995). Rapid pyrolysis of agricultural residues at high temperature, Proceedings of the 2nd Biomass Conference of he Americas: Energy, Environment, Agriculture, pp. 630-636.
38. Bandyopadhyay, D., Chakraborti, N. & Ghosh, A.(1991). Heat and mass transfer limitations in gasification of carbon by carbon dioxide, Steel Research, Vol. 62, No. 4, pp. 143-151.
39. Sørensen, L.H., Gjernes, E., Jessen, T. & Fjellerup, J. (1996). Determination of reactivity parameters of model carbons, cokes and flame-chars, Fuel, Vol. 75, No. 1, pp. 31-38.
40. Rathmann, O., Stoholm, P. & Kirkegaard, M. (1995). The pressurized thermogravimetric analyzer at the Department of Combustion Research,, Risø: Technical description of the instrument, Roskilde: Risø National Laboratory, Risø-R-823(EN), Denmark.
41. Sørensen, L.H. et al. (1997). Straw - H2O gasification kinetics. Determination and discussion, Nordic Seminar on Thermochemical Conversion of Solid Fuels, 3rd December, 1997, Chalmers University of Technology, Sweden.
42. Risnes, H., Sørensen, L.H. & Hustad, J.E. CO_2 reactivity of char from Danish wheat, Norwegian spruce and Longyear coke. *This conference*.