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KINETIC MODELING OF BIOMASS GASIFICATION AND COMBUSTION

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Abstract

This review critically examines char conversion kinetics in oxidizing or reducing atmosphere. In kinetic analysis the devolatilization of biomass and the conversion of char are usually investigated by means of separate experiments, although some kinetic models are also available of biomass combustion. The large majority of the char conversion kinetics consists of a global reaction with activation energies of 196-200kJ/mol (carbon dioxide gasification), 138-271kJ/mol (steam gasification), 75-229kJ/mol (char oxidation) and a power law dependence on the partial pressures of the gasifying agents. The rate expressions usually also incorporate a structural contribution. The wide range of variation of kinetic parameters is due to the different char properties (biomass characteristics and pyrolysis conditions) and mainly to the simplifications introduced in the mathematical treatment of the data.

1. INTRODUCTION

Air gasification of biomass is a process where solid conversion is made to occur in the presence of reduced oxygen, so that temperatures are lower than those encountered in combustion. The limited oxygen supplied is used to burn only a small part of the fuel, either solid or gas, in order to provide the heat needed for char gasification, biomass pyrolysis, drying and, of course, pre-heating. The main product is then a gaseous combustible which can be processed in a second step. In direct (grate-fired) combustion the supply of underfire air, whose role is to gasify the fuel, is coupled with the addition of overfire air to burn the gaseous products. The energy content of the gas produced through gasification depends on numerous factors such as: reactor type, fuel type and form, oxidizing agent, etc. In addition to air, the oxidizing agent can also be oxygen, steam or a mixture of these compounds. When air is used, the gaseous products mainly consist of CO, N₂, H₂, CH₄ and minor quantities of other hydrocarbons. The resulting gas has a low calorific value (3.8-5.6 MJ/m³ against 38 MJ/m³ of natural gas). This can be increased by using oxygen or steam but in the latter case sufficient heat should be provided because steam gasification is an endothermic process. In some cases, steam is added to air to increase the level of H₂ in the produced gas (Bridgwater (1995)). Direct combustion involves the oxidation of biomass with excess air, giving hot flue gases which are used to produce steam in the heat exchange section of of boilers, with steam used to produce electricity (Bain et al. (1998)). Different technologies are applied for gasification or combustion of biomass as discussed in several reviews on this subject (Bridgwater (1995), Beenackers and Maniatis (1996), Maniatis (2001)).

2. CHEMICAL AND PHYSICAL PROCESSES OF BIOMASS GASIFICATION AND COMBUSTION

2.1 Gasification/combustion of biomass particles

Conversion of biomass in combustors and gasifiers results from a strong interaction between chemical and physical processes. In wood combustion and gasification the external gas phase reactions, the surface char reactions and the internal pyrolysis reactions at the surface of the virgin solid are coupled together (Bryden and Ragland (1997)). The coupling degree depends, among the other parameters, by the size of the particle and the conditions of the reaction environment.

Mukunda et al. (1984) investigate the combustion of wood (teak) spheres (10-25mm diameter) in air. After forced ignition, burning takes place. It is observed that the process consists of separate stages. During flaming pyrolysis the sphere diameter and weight are reduced by about 10% and 70-80%, respectively, and the volatile species produced burn in the gas phase with a flame enveloping the sphere. During heterogeneous combustion of char the density decreases by about 10-25%, indicating

the possibility of internal reactions with oxygen diffusing from the outer surface through the porous structure.

Combustion of small-sized (maximum sizes of about 15-20mm) wood particles in fluidized-bed reactors (temperatures) is investigated by de Diego et al. (2002,2003), who also report a two-stage process where devolatilization is followed by combustion. For the small-scale reactor, batch-wise operated, it appears that most of the volatiles generated from the pyrolysis of wood particles burn in the free-board of the reactor and not around the particle. Therefore, the volatile evolution during the first stage is the same using air or nitrogen. A flame around the particle appears only at the conclusion of the devolatilization process, indicating that wood devolatilization and char combustion are sequential processes for the conditions typical of fluidized-bed reactors. These conclusions can also be drawn from the experiments carried out by other researchers (for instance, Winter et al. (1996), Leckner et al. (1999)). The most probable explanation for this behavior is that as long as volatiles are continuously released with sufficiently fast rates, oxygen is prevented from reaching the surface of the fuel particle (De Diego et al. (2003)). Another consideration to be made is that, when the particle size is small, devolatilization is completed before the particle surface attains temperatures high enough for the heterogeneous reactions to become active. Hence homogeneous combustion reactions are favored versus heterogeneous combustion of char.

Mukunda et al. (1984), in their experiments of wood sphere burning, observe that for the largest sizes (diameters of 25mm), some overlap between the wood devolatilization and char combustion takes place. The work presented by Ragland et al. (1988) and Bryden and Ragland (1996, 1997) is focused on the conversion of chunk wood or whole-tree sized fuels for conditions typical of large boilers. In (Ragland et al. (1988)) experiments are carried out with samples of yellow poplar and spruce (15 cm diameter) inserted onto the grate of a spreader stoker boiler with characteristic temperatures above the bed of about 1473K. It is observed that chunk wood burns as a shrinking sphere (rate of about 1.8mm/min) consisting of a relatively thin layer of char (5-15mm) surrounding the core of unburned wood. Successive experiments (Bryden and Ragland (1997)) also carried out with thick wood samples (thickness above 10cm) under condition typical of packed-bed reactors confirm that the processes of drying, pyrolysis and combustion/gasification are highly coupled.

The coupling between the processes of wood/biomass devolatilization and char conversion is dependent on both sample properties (size, initial moisture content, etc.) and external conditions. When combustion of char is a process independent of the devolatilization stage, three main regimes are introduced (Basu and Fraser (1991), Winter et al. (1996)). In the regime III, char combustion is controlled by bulk diffusion. The reaction occurs at the exterior surface of the particle. Once the particle size is reduced, it is likely that the rate of oxygen diffusion in the pores becomes comparable to the reaction rate. This leads to limited penetration of oxygen into the char. The conversion regime II lasts until the char particle becomes so small that the diffusion rate is much faster than the chemical reaction rate. In this way, the oxygen completely penetrated the porous particle and the conversion regime I is established.

2.2 Char reactivity

A huge amount of literature has been produced on the reactivity and the heterogeneous kinetics of coal and coal char gasification and combustion (Laurendeau (1978), Smith (1982), Bews et al. (2001), Hurt and Calo (2001)). In contrast, only a relatively small number of studies is available on wood/biomass char. Two main differences are encountered in comparison with coal chars: the ash content is very low and the pore structure is highly directional, typical of that of wood and its intrafibrillar cavities (Standish and Tanjung (1988)). The nature of the carbonaceous material includes both the state of the

carbon itself (i.e. amorphous or crystalline) and the internal structure of the particle (e.g. porous or dense) (Standish and Tanjung (1988)).

The char reactivity is usually defined in terms of the conversion rate per remaining mass (Risnes et al. (2001)):

$$R = -\frac{1}{M} \frac{\partial M}{\partial t} = \frac{1}{1-X} \frac{\partial X}{\partial t} \quad (1)$$

where M is the mass of the organic portion of the sample, dM/dt is the conversion rate and X is the degree of conversion

$$X = \frac{M - M_0}{M_0 - M_\infty} \quad (2)$$

(M₀ and M_∞ are the initial and final values of the sample mass).

The reactivity is measured versus conversion and, to obtain chemical kinetics, it may be splitted into a chemical kinetic term, r_c and a structural term, r_s, which should take into account the effects of available internal surface, available active/reactive sites and pore evolution: R=r_cx r_s.

Usually, the structural contribution is expressed in terms of S(X)/S₀, that is, the relative change in available surface area during reaction (Janse et al. (1999)), Di Blasi et al. (1999)), or c_f, that is, the number of active carbon sites (Barrio and Hustad (2001), Barrio et al. (2001), Ollero et al. (2003)). Although a large part of the experimental work on wood/biomass gasification is focused on the application of fixed- or fluidized-bed reactors for determining the gas composition on dependence of the fuel properties and operating conditions, some effort has also been devoted to determine the effects of different parameters (pyrolysis conditions, wood/biomass variety, pretreatments, gasification conditions) on the char reactivity and to formulate models for the kinetic and structural terms.

2.3 Influences of the pyrolysis conditions

The reactivity of coal char in oxidizing environments is known to be affected by the heating rate and final temperature during pyrolysis (and related residence times). Pyrolysis conditions also affect the properties and reactivity of biomass chars. Janse et al. (1998) examine chars produced from pine wood by means of a screen heater and a packed-bed reactor. Heating rate during pyrolysis is varied between 1 and 300K/s for a final temperature of 600C. It is observed that fast heating leads to a more reactive char, with the time needed for complete conversion decreased by about one order of magnitude for the range of heating rates given above. On the other hand, variations in the final temperature between 500-600C (values of interest in fast pyrolysis) or the retention time (20-100s) do not appear to play an important role. The negligible role played by this range of final temperature is also confirmed by Branca and Di Blasi (2003), who consider chars produced from thick particles of different wood species. Also, the heating rate during pyrolysis is observed to affect the shape of the rate curve during thermogravimetric measurements of char combustion. Differential curves, instead of integral data used in the majority of previous literature (Janse et al. (1998)), allow the existence to be shown of a low-temperature shoulder and a high-temperature peak in the rate of weight loss (Branca and Di Blasi (2003)). The first is attributed to char devolatilization and the latter to combustion. Fast heating rates during pyrolysis highly reduce the importance of the first reaction zone and, as shown in the following, alter the values of the kinetic constants. The presence of two reaction zones in the rate of weight loss during char combustion is also reported by Shafizadeh and Sekiguchi (1984), Marcilla et al. (2000), and Varhegyi et al. (2001, 2002).

Indeed, weight loss starts at relatively low temperature and occurs at a certain extent also in inert environment. This process is indicated as char devolatilization. More specifically, low-temperature

cellulosic chars (Shafizadeh and Sekiguchi (1984)) undergo devolatilization according to three sequential stages, corresponding to the pyrolysis of partially decomposed and intact glycosyl units and decomposition of paraffinic and carbonyl groups. Chars obtained at temperatures above 673K only show the last stage. As expected, the amount of solid left at the conclusion of the devolatilization process (and burned in the presence of oxygen) becomes successively higher with the formation temperature.

The influences of the pyrolysis conditions (temperature, heating rate and residence time) on CO₂ gasification of acacia and eucalyptus char are investigated by Kumar and Gupta (1994). Slow carbonization (4K/min) is made for temperatures of 800-1200C and residence times of 1-3h. Rapid carbonization is achieved with a heating rate of 30K/min at temperatures of 800C and 1h residence time. For all the conversion temperatures it is observed that the reactivity of chars is significantly reduced as the pyrolysis temperature is increased. The authors attribute this result to an increased structural ordering of the carbon matrix, lowering the concentration of reaction sites. Similar to the results obtained for char combustion, higher heating rates during pyrolysis are seen to cause higher reactivity of char in CO₂ atmospheres. This result is attributed to the reduced amount of deposited pyrolytic carbon in rapidly carbonized wood (this provides lesser active reaction site concentration than char formed from primary reactions of wood decomposition). Moreover, fast decomposition is suggested to produce defective carbon microcrystallites having a higher concentration of active reaction sites. Increasing the residence time provokes effects similar to temperature, again improving structural ordering in the resulting char.

The influence of pressure during pyrolysis on the reactivity of the resulting chars is investigated by Plante et al. (1988), by considering conventional pyrolysis char (from poplar) generated under vacuum and atmospheric pressure. The vacuum pyrolysis char is found to be more reactive than that generated under atmospheric conditions. The higher content of oxygen observed in the former case (15 against 10%) is indicated as responsible for this behavior (reactivity about 20% higher). It should be noted that this result is consistent with the lower reactivity of char generated by secondary reactions (whose amount is highly reduced for pyrolysis under vacuum) reported by Kumar and Gupta (1994).

The influences of the thermal conditions during char formation are also reported by Whitty et al. (1998) for black liquor char. It is observed that prolonged exposure to high temperatures decreases the reactivity because of thermal annealing and, in the presence of CO, deposition of solid carbon as a consequence of the reaction $2CO \rightarrow C + CO_2$. The carbon deposit causes a decrease in the initial rate of gasification. High pressure during pyrolysis gives rise to a more compact char with a lower internal surface area.

The effects of the pyrolysis conditions on the reactivity of RDF char (pyrolysis in a fixed-bed reactor with heating rates of 0.5-1.5K/s and final temperatures in the range 500-800C) in combustion and CO₂ gasification are investigated by Cozzani (2000). A clear trend of the CO₂ reactivity with the pyrolysis temperature is not found. On the contrary, for combustion, the reactivity is observed to decrease by a factor of about 5 for the range of pyrolysis temperatures given above. This result is again explained by a reduction in the active surface area to the total surface area (this slightly increases with the pyrolysis temperature). On the other hand, the higher temperatures needed for the CO₂ gasification are considered to be the cause for the reduced influence of the active surface area on the char reactivity.

Given the small sample quantity used in thermogravimetry, the stages of devolatilization and char gasification are sequential. Therefore, char reactivity studies are usually carried out with samples obtained from previous (separate) pyrolysis experiments. An exception is the study carried out by Fushimi et al. (2003) for treatment with steam of cellulose, lignin and bagasse samples in a thermogravimetric system (heating rates between 5 and 100K/min for temperatures of 673-1073K). Rapid heating is observed to increase the reactivity of lignin char owing to macropores resulting from

the rapid release of volatiles. It also prevents char agglomeration and condensation of fragments on the char surface.

More recently, further data have been made available (Cetin et al. (2004, 2005)) on the influences of the pyrolysis conditions (heating rate, temperature and pressure) on the properties and reactivity of biomass (pine, eucalyptus and bagasse) char in CO₂ atmosphere (pressures between 1-20bar). Again, reactivities are observed to increase by increasing the heating rate (higher surface area) and by decreasing the pressure during pyrolysis. For very high heating rates the char particles are observed to undergo a molten phase with consequent creation of smoother surfaces and spherical cavities. The formation of macropores associated with the high heating rates, causing an increase in the surface area, enhances the char reactivity (the micropore network is reduced in consequence of the melting). Increasing the pressure leads to the formation of larger char particles, owing to swelling and formation of particle clusters following melting and fusion. Although pyrolysis pressure effects on reactivity are smaller than those of melting observed at high heating rates, the decrease in the reactivity with pressure increase is higher than expected by the measured decrease in the surface area. Therefore, it is concluded that pyrolysis pressure impacts directly on the reactivity of char due to graphitisation in the structure at high pressures.

2.4 Influences of the gasification/combustion conditions

Standish and Tanjung (1988) present experiments on char particles (Indonesian rubber tree) made with a tube furnace. Pre-heating to the desired temperature is achieved in nitrogen with a retention time of about 10min. The temperature is varied in the range 900-1100C in CO₂ atmospheres. The usual Arrhenius dependence on temperature is found with an activation energy of about 210kJ/mol. The effects of CO₂ concentration are summarized by a reaction order of 0.71 in this variable (concentrations between 20-100%) and are higher at low concentrations, possibly owing to CO inhibition. However, while complete conversion of char is observed at high CO₂ concentrations, at low values it is not achieved even for very long retention times. The authors attribute this result to a possible reduction in the active sites by nitrogen absorption. The time for complete conversion presents a nearly linear dependence ($n=1.05$) on the initial particle radius R_0 (values between 4.5-20mm). The change in the particle size, during conversion, can be approximated by $R=R_0(1-X)^{1/3}$. Furthermore, the particle density remains constant up to conversions of 75%. These results indicate that gasification takes place along a thin zone at the particle surface "while the interior pore structure remained essentially intact and indistinguishable from the structure of the unconverted particle". Hence gasification can be described in accordance with the shrinking core model.

Moilanen and Muhlen (1996) observe that steam gasification of peat char presents a rate slightly faster than that observed in CO₂ environment. The gasification rates decrease by increasing the pressure (up to 1.5MPa and temperatures between 1023 and 1223K). Moreover, H₂ and CO inhibit the gasification process.

The reactivity of char in CO₂ atmospheres increases with conversion, at low and intermediate levels, as a consequence of the increase of the surface area during the course of gasification (Tancredi et al. (1996)). At high conversion levels (beyond 70%) a very steep rise is observed, which cannot be plausibly explained by the development of the surface area. According to Tancredi et al. (1996), this behavior may be caused by an increased catalytic effect of the metallic constituents (especially Na and K) of ash, following the increase of their concentration during char conversion.

The important role played by inorganic material on peat char is also evidenced by Moilanen and Muhlen (1996). It is observed that the gasification rate slightly increases with conversion for CO₂ atmospheres, whereas the steam gasification rate increases to a maximum before decreasing as

conversion progresses. Chars obtained from demineralized peat present considerably lower reactivity and, in the presence of steam, the negative burn-off behavior disappears. The observed behavior in steam gasification implies that active substances contained in the char are deactivated as conversion increases (for instance calcium). Deactivation can result from sintering and agglomeration, the formation of new mineral compounds or the occurrence of reactions between the mineral compounds and the gasifying agents.

The gasification (CO₂, H₂O) reactivity of grapefruit peels, carbonized at 700C for 2h (particles 1-1.6mm thick), is observed (Marquez-Montesinos et al. (2002)) to increase with conversion (especially for H₂O atmosphere) more than expected from the increase in the surface area. This is again attributed to the enhanced catalytic effects exerted by some ash compounds (mainly potassium and lower amounts of sodium), that is, to the increase in the ratio between carbon and the catalytically active substances. The reduction in the ash content of the char, by means of acid washing, or the pressure causes a decrease in the reactivity.

A high heating rate during char pre-heating (before attaining the gasification temperature) also increases the reactivity (Plante et al. (1988)). As for the gasification conditions, the rate of char conversion increases with pressure especially for high temperatures. The effects of pressure are more important for the less reactive char produced at atmospheric conditions (versus vacuum pyrolysis) (Plante et al. (1988)). Prolonged exposure of char to high temperature reduces the reactivity by thermal annealing (Whitty et al. (1998), black liquor char). These effects appear as a reduction in the porosity (and surface area) and a rearrangement of the char structure at a molecular level.

Barrio and Hustad (2001) and Barrio et al. (2001) report that the presence of CO and H₂ inhibits char gasification in atmospheres bearing CO₂ (birch char) and H₂O (birch and spruce char), respectively. The same conclusions are also reported in relation to CO during CO₂ gasification of wheat straw and spruce (Risnes et al. (2001)) and olive stone (Ollero et al. (2003)) chars. No significant difference is seen between birch and spruce char gasified with steam are observed. The differences between chars, obtained from different wood species, are also small in combustion (Branca and Di Blasi (2003)). In relation to this problem De Groot and Shafizadeh (1984) write that "the distinction between hardwoods and softwoods is apparently insignificant, apart from the catalytic effects of the ash content". Probably this issue is also the main factor for the large differences exhibited by biomass (agricultural residues) char with respect to wood both in combustion (Di Blasi et al. (1999)) and gasification (Risnes et al. (2001), Ollero et al. (2003)).

An enhancement of the reactivity in steam of chars generated from alkali salt impregnated wood is reported by Hawley et al. (1983). The effects of pre-pyrolysis addition of catalysts to wood on the reactivity in CO₂ of the resulting char is also the subject of the study by De Groot and Shafizadeh (1984)). The carbonates of sodium and potassium are found to be equally effective as gasification catalysts. The transition metal salts are the most effective catalysts initially but their activity is highly reduced well before the gasification is complete.

3.KINETICS OF BIOMASS/CHAR COMBUSTION AND GASIFICATION

Analysis of biomass decomposition in oxidative/reducing environments is a problem of interest for the design and development of combustion and gasification systems. Indeed, adequate kinetic mechanisms should be coupled with the description of transport phenomena (heat, mass and momentum transfer) in order to provide detailed process simulation. Kinetic models for the heterogeneous reactions of char combustion and gasification are also of great practical importance. For instance, in steam and carbon dioxide atmospheres, the required residence time for char gasification may be 10-100 times greater than for pyrolysis of thick particles at temperatures between 800 and 100C (Edrich et al. (1985)), so that the related kinetics play a key role for reactor sizing.

3.1 Kinetics of wood/biomass devolatilization in oxidizing atmosphere

Compared with inert atmospheres, a relatively few investigations (Vovelle et al. (1982), Aho and Houtari (1985), Cordero et al. (1991), Ghaly and Ergudenler (1994), Momoh et al. (1996), Ghetti et al. (1996), Mansaray and Ghaly (1996), Bilbao et al. (1997), Di Blasi and Branca (1999), Liu et al. (1999), Branca and Di Blasi (2004), Calvo et al. (2004), Jauhiainen et al. (2004)) have been carried out of wood/biomass degradation in air or in the presence of oxygen. In all cases, as consequence of the small sample mass and the mild thermal conditions applied to reduce the effects of heat and mass transfer intrusions and to control the reaction exothermicity, the thermogravimetric curves show two main reaction zones. The first zone corresponds to solid devolatilization and the second to char combustion.

The large majority of the studies simply proposes two global reactions with nth-order rates in the mass fraction. For the devolatilization step, the activation energies are roughly comprised between 94-63kJ/mol (Aho and Houtari (1985)), 83-93kJ/mol (Cordero et al. (1991), 94-89kJ/mol (Ghaly and Ergudenler (1991), 101-136kJ/mol (Momoh et al. (1996)), 79kJ/mol (Ghetti et al. (1996)), 143-188 (Mansaray and Ghaly (1999)), 63-99 kJ/mol (Liu et al. (2002), and 90-131 kJ/mol (Calvo et al. (2004)). For the combustion step, the activation energies include 320-170kJ/mol (Aho and Houtari (1985)), 65-83kJ/mol Cordero et al. (1991), 38-39kJ/mol (Ghaly and Ergudenler (1991), 35-65kJ/mol (Ghetti et al. (1996)), 11-17kJ/mol (Mansaray and Ghaly (1999)), 87-124kJ/mol (Liu et al. (2002), and 34-148kJ/mol (Calvo et al. (2004). It can be observed that for the devolatilization step, with the exception of (Mansaray and Ghaly (1999)), low activation energies are reported by all the authors. This result stems primarily from the high simplification introduced by the one-step reaction model to describe a process which is complicated by the composite nature of the biomass fuels and by the contribution of the main constituents in the thermogravimetric curves, as extensively discussed for decomposition in inert atmospheres. Variations between the kinetics for the combustion steps are much wider, probably because of the stronger role played by the nature of the samples especially by the content and composition of ashes which act as catalysts for the combustion process. It should also be noted that, in all cases, the measurements and the related kinetic evaluations are limited to one heating rate only, so that compensation effects are not avoided.

Improvements are represented by models where the devolatilization step is described by two reactions (Bilbao et al. (1997), Di Blasi and Branca (1999), Jauhiainen et al. (2004)) combined with a one-step reaction for the combustion stage. Bilbao et al. (1997) assume that the devolatilization rates of pine wood sawdust are linear in the mass fraction and correspond mainly to hemicellulose and cellulose decomposition with the activation energies of 78 and 193kJ/mol, respectively. Power law dependences on the mass fractions are used by Di Blasi and Branca (1999) and Jauhiainen et al. (2004). In the former case, wood and several agricultural residues examined for a heating rate of 20K/min produce ranges of activation energies for the two reactions of 90-73kJ/mol and 92-83kJ/mol. Jauhiainen et al. (2004), in the analysis of thermogravimetric measurements of olive solid waste for heating rates between 5-20K/min, attribute the two devolatilization steps to holocellulose (activation energy of 151kJ/mol) and lignin (activation energy of 66kJ/mol), respectively. Apart from material and experimental conditions, the differences in the kinetic parameters estimated by these authors can be attributed mainly to the use of integral (Di Blasi and Branca (1999)) or differential (Bilbao et al. (1997), Jauhiainen et al. (2004)) data. Differences are also observed for the combustion step with activation energies of 148kJ/mol (Bilbao et al. (1997)), 71-90kJ/mol (Di Blasi and Branca (1999)) and 133 kJ/mol (Jauhiainen et al. (2004)).

Only in one case (Branca and Di Blasi (2004), three reactions are used for the devolatilization stage, as usually done for pyrolysis models, combined with a further reaction for char combustion. Weight loss

curves of two wood species (beech and Douglas fir) measured in air for four heating rates between 5-40K/min and a final temperature of 873K are examined. The rates of the first three reactions are linear in the solid mass fraction and the activation energies are 106, 226 and 114kJ/mol, respectively. The fourth step presents a power-law dependence ($n=1.54$) on the solid mass fraction and an activation energy of 183kJ/mol.

As already observed, apart from sample characteristics which consider both biomass and wood species, differences consist in the use for the kinetic analysis of one or several heating rates, integral or differential data and linear or power law dependences of the reaction rate on the solid mass fraction. Apart from these considerations, there are also other reasons which motivate the need for further investigation on this topic. Apart from the kinetics for wood by Branca and Di Blasi (2004), and olive waste by Jauhiainen et al. (2004), kinetic constants have been estimated by means of only one experiment, so that compensation effects are not avoided. Furthermore, integral (TG) data have been generally used. These, contrary to differential (DTG) data, do not allow a distinction to be made between well-fitting and poorly fitting models and do not show whether the model is able to describe the multiple peaks and other fine details of the experiments.

3.3 Structural models for char conversion

Despite the great effort made by different researchers to correlate the kinetic rates of carbon gasification to the physical and chemical properties of the material and the reaction conditions, a generalized unified law does not exist. In general the char reactivity depends on conversion, temperature and concentration of reactants (Ollero et al. (2003)). For lignocellulosic chars it increases with conversion and, as already discussed, it can also exhibit a maximum or a minimum. It can be understood that there are essentially two contributions to be taken into account, that is, the intrinsic kinetic law, which essentially describes the dependence on temperature and concentrations of reactants, and structural variations during conversion. As pointed out by Dutta and Wen(1977) in relation to coal chars "the variety of rate-conversion curves is due to the fact that different coal/char samples vary greatly from one another with respect to their pore structures and the change of such pore structures with conversion and temperatures". A group of studies examines the first issue assuming structural models already available in the literature. The most popular structural models have been summarized by Janse et al. (1998) and include the power-law (grain) model (Kristiansen (1995)), the pore-tree model (Simmons and Finson (1979)), the random pore model (Bathia and Perlmutter (1980)), the random capillary model (Gavalas (1980)), and the bifurcated pore model (Tseng and Edgar (1989)).

Attempts are also made to modify the most popular structural models proposed for the heterogeneous reactions of coal to take into account the peculiarities of biomass/wood chars. These models, such those by Struis et al (2002) for the CO₂ gasification of fir char, do not include any kinetic law but are somewhat empirical in that they use adjustable parameters to take into account the variations in the char reactivity with temperature and/or catalysts. In this case isothermal thermogravimetric data are used to modify the Bathia and Perlmutter model, which takes into account the changes in the char reactivity exclusively in terms of structural changes. Modification are introduced to take into account the higher reactivity (than predicted by random pore models) at high conversion (beyond 70%). The parameters of the empirical model vary with the reaction temperature and the pre-treatments of the sample.

In some cases (Risnes et al. (2001), Barrio et al. (2001a,b), Ollero et al. (2003)) the structural contribution is approximated by $F(X)$ (a 5-6th order polynomial in the conversion X), which is assumed to be invariant over the temperature and pressure ranges examined. As pointed out by Risnes et al. (2001), such an invariance should be properly checked. Then a representative reactivity is introduced.

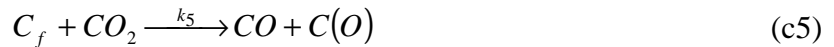
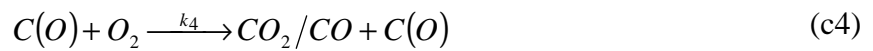
3.4 Kinetic models of char gasification

In the majority of kinetic analyses, the model consists of a global reaction rate expressed as:

$$r = k_0 \exp(-E_i/RT) P_i^n \{S(X)\} S_0, \quad i = O_2, CO_2, H_2O$$

for the combustion reaction $C + O_2 \rightarrow CO/CO_2$, the CO_2 gasification reaction $C + CO_2 \rightarrow 2CO$ and the H_2O gasification reaction $C + H_2O \rightarrow CO + H_2$.

In reality, the heterogeneous conversion of char occurs through several steps, which include the inhibiting effects of some compounds, as discussed above. Semi-global mechanisms of char combustion are summarized by Hurt and Calo (2001). The simplest of the Langmuir-Hinshelwood kinetic form is:



where k_1 - k_5 are Arrhenius rate constants. The reaction c1 represents the chemisorption of oxygen on active sites and the reactions c2 the formation of CO through desorption (similar to the gasification mechanisms, C_f is the number of active or available sites and $C(O)$ a carbon-oxygen complex which occupies the site). Formation of CO_2 by surface reaction is also observed (reaction c3) or by interaction of the gas phase oxygen with surface complexes (reaction c4) which may or may not involve the generation of a new complex $C(O)$ on the product side. The reaction rate of CO_2 and carbon (reaction c5) is much slower than that of O_2 and carbon. Therefore, reaction c5 is usually excluded as a significant step, when considering the carbon-oxygen reaction. Semi-global mechanisms have been modeled in terms of kinetic laws of the Langmuir-Hinshelwood form. The simplest of these, taking into account reactions c1-c2, is:

$$r_c = \frac{k_1 k_2 P_{O_2}}{k_1 P_{O_2} + k_2} \quad (14)$$

whose parameters, however, have not yet been evaluated for the chars of interest in this review.

The carbon dioxide gasification of char has been extensively studied and the following oxygen exchange mechanism is postulated (Laurendau (1978)):



where k_1 , k_2 and k_3 are the usual Arrhenius rate constants, C_f represents an active carbon site and $C(O)$ a carbon-oxygen complex. The presence of CO produces an inhibiting effect by lowering the steady-state concentration of $C(O)$ by the reaction a2. The gasification rate, in accordance with reactions a1-a3 and applying the steady-state assumption for the $C(O)$ complex, can be expressed as:

$$r_c = \frac{k_1 P_{CO_2}}{1 + (k_2/k_3)P_{CO} + (k_1/k_3)P_{CO_2}} \quad (\text{a5})$$

where P_{CO_2} and P_{CO} are the partial pressure of CO_2 and CO . When the CO concentrations are small and/or the inhibiting effect exerted by this species is not taken into account, a simple global model can be applied.

The steam gasification of char also takes place according to several steps as reported by Barrio et al. (2001). They also point out that, compared with CO_2 , H_2O gasification is more complicated because, in addition to the main gasifying agent, the effects of H_2 , CO_2 and CO should also be taken into account, owing to the equilibrium of the water gas shift reaction. Barrio et al. (2001) report different mechanisms indicated as "oxygen exchange" and "hydrogen inhibition":

The steps to be considered are:



(k_1 - k_7 are Arrhenius rate constants). The oxygen exchange mechanism consists of steps b1-b3. The hydrogen inhibition mechanism may consist either of steps b1, b3 and b4-b5 or steps b1, b3 and b6-b7. For the oxygen exchange mechanism, hydrogen inhibition is due to the equilibrium of the dissociation reactions b1-b2. For the first hydrogen inhibition mechanism, the formation of the $C(H)_2$ complex is the reason of the inhibition. In the other case, a dissociative chemisorption of H_2 on the active sites occurs and in this way the active sites become not accessible for the oxygen transfer with steam. In all cases, the surface rate equation is formally identical:

$$r_w = \frac{k_1 P_{H_2O}}{1 + (k_1/k_3)P_{H_2O} + f(p_{H_2})} \quad (7)$$

where P_{H_2O} and P_{H_2} are the partial pressures of H_2O and H_2 , respectively, and $f(p_{H_2})$ depends on the selected mechanism. The following expressions are obtained for the oxygen exchange

$$f(p_{H_2}) = \frac{k_2}{k_3} P_{H_2} \quad (8)$$

the hydrogen inhibition by formation of the $C(H)_2$ complex

$$f(p_{H_2}) = \frac{k_4}{k_5} P_{H_2} \quad (9)$$

and the hydrogen inhibition by formation of $C(H)$ complex

$$f(p_{H_2}) = \frac{k_6}{k_7} P_{H_2}^{0.5} \quad (10)$$

The problems encountered for the determination of the intrinsic kinetics of biomass pyrolysis are extensively discussed in previous literature. The important role played by the presence of oxygen and the onset of the exothermic combustion reactions whose rate, at high temperatures, may become much faster than the typical response time of measuring devices and feedback control systems are also pointed out (Di Blasi et al. (1999)). High external heating rates, which are encountered in combustion, make worse the situation and the attempts made to reproduce them at a laboratory scale, as observed by Janse et al. (1998), "would result in mass/heat transfer controlled conditions for the laboratory equipment of the kinetic measurements, and the results would reflect the hydrodynamics of that specific piece of equipment instead of the true combustion rate". Hence the kinetic expression obtained under moderate thermal conditions are extrapolated to those more severe of the practical combustors. The role of diffusional effects in TGA gasification tests (CO₂) is investigated by Ollero et al. (2002, 2005). These are particularly important as the gasification process requires the transport of reactant and heat from the external bulk gas phase to the internal particle surface, where the chemical reactions take place. Diffusional effects can be important also for thermogravimetric conditions and consequently the experiments should be accurately carried out and proper consideration should be given to the interpretation of the data. A two-dimensional model developed for a better understanding of these problems (Gomez-Barea et al. (2005)) shows that temperature and partial pressures of carbon dioxide are the key parameters and that the role of diffusion is a function of the conversion degree. Therefore, the assessment of diffusional effects should be made for the entire range of conversions and operating conditions.

Experiments carried out to determine the gasification rates usually foresee a pre-heating period (in N₂) up to high temperatures (1000C) and a retention period (10 min) (Ollero et al. (2002)). Then the sample is cooled down (25K/min) to the desired temperature again in an inert environment. Finally the gasification tests are carried out under isothermal conditions at selected temperatures. Isothermal data are thus used to evaluate the reaction kinetics.

The kinetics of biomass/char gasification are described by a one-step global reaction by several authors for CO₂ (Groeneveld and Van Swaaij (1980), De Groot and Shafizadeh (1984), Plante et al. (1988), Bandyopadhyay et al. (1991), Tancredi et al. (1996), Henrich et al. (1999), Risnes et al. (2001), Barrio and Hustad (2001), Ollero et al. (2003)) or steam (Rensfelt et al. (1978), Groeneveld and Van Swaaij (1980), Richard et al. (1982), Hemati et al. (1988), Li et al. (1991), Molainen et al. (1994), Moilanen and Saviharju (1997), Barrio et al. (1991)) atmospheres. There is quite good agreement in relation to the activation energy of the global reaction, especially for CO₂ gasification. For wood gasification in CO₂, the value is around 200kJ/mol (values between 196-200kJ/mol with the corresponding ln of the pre-exponential factors of 20 and 21) with the exponent n (for CO₂ partial pressure) roughly between 0.4 and 0.6. The kinetics of wheat straw char are roughly the same as wood (Risnes et al. (2001)) but those of chars from olive residues present much lower values (133kJ/mol, Ollero et al. (2003)), presumably owing to the high potassium content of the ashes. The differences between the activation energies estimated for the steam gasification of wood char are higher than in the case of CO₂ with values comprised between 138 and 271 kJ/mol, though the majority of the evaluations are around intermediate values of 180-210 kJ/mol. The exponent n for the steam partial pressure varies between 0.5-1.

The more complicated Langmuir-Hinshelwood kinetics are considered only in a few cases (Hawley et al. (1983), Barrio and Hustad (2001), Barrio et al. (2001), Ollero et al. (2003), Klose and Wolki (2005)), often with the sole evaluation of the rate constants.

3.5 Kinetic models of char combustion

The majority of the kinetic models of wood char combustion, using integral thermogravimetric (TG) dynamic data for parameter estimation, is based on a one-step global reaction with a power-law dependence on the oxygen partial pressure and the solid mass fraction (this accounting for structural effects). Significant variation is shown by kinetic parameters, with activation energies of 160kJ/mol for cellulosic chars (Kashiwagi and Nambu (1992))) and 75-140kJ/mol for other feedstocks (Adanez et al. (1991), Magnaterra et al. (1994), Janse et al. (1998), Di Blasi et al. (1999)).

Despite the widely used one-step reaction, as discussed above, differential thermogravimetric (DTG) data show that combustion of lignocellulosic chars is a multi-step process. The most recent kinetic analysis (Branca and Di Blasi (2003)) takes into account both stages and uses differential data. Thermogravimetric curves in air of wood chars, obtained from different species and conventional or fast pyrolysis, show a low-temperature shoulder (devolatilization) followed by a high-temperature peak (combustion). A n-order global reaction provides a very poor description of the differential curves and, in agreement with previous literature, requires relatively low activation energies (114.5 and 167kJ/mol for conventional and fast pyrolysis chars, respectively). The combination with an additional first-order reaction for the devolatilization stage produces accurate predictions of both integral and differential curves. It also gives rise to much higher activation energies of the combustion reaction (183 or 229kJ/mol, depending on the severity of the pyrolysis conditions). The kinetic parameters for the combustion stage are independent of the detail degree in the description of the devolatilization stage. It is worth noting that, for the case of conventional pyrolysis (wood) char, the activation energy (182.6kJ/mol) is significantly higher than that obtained by means of one-step global models and roughly the same as reported for the low-temperature zone of coal char or graphite combustion (the rate of the combustion reaction is nearly linear). The activation energy of the devolatilization reaction also increases with the severity of the pyrolysis conditions (from 114.5 to 218.5kJ/mol), whereas the differences in the char reactivity deriving from the wood species can be taken into account by pre-exponential factors and order of the combustion reaction. The use of two first-order reactions for the devolatilization stage does not improve significantly the accuracy of the predictions. The exponent for the dependence on the partial pressure of oxygen has been reported to vary roughly between 0.5 and 1.

4. CONCLUSIONS

As temperature, retention time and /or pressure established during biomass pyrolysis are increased, the reactivity of the resulting char decreases for both reducing and oxidizing environments. Indeed, the first two parameters cause an increase in the structural ordering of the carbon matrix, in this way lowering the concentration of the active sites (thermal annealing). Apart from reducing the surface area, the pyrolysis pressure is reported to impact directly on the reactivity of char due to an increase of the graphitisation level in its structure. Fast heating rates during pyrolysis are suggested to produce defective carbon microcrystallites having a higher concentration of active reaction sites. Furthermore, it has been recently observed that char particles undergo a molten phase with the consequent creation of smoother surfaces and spherical cavities. The micro-pore network is reduced owing to melting, but the formation of macro-pores is associated with an increase in the surface area. Operating conditions during conversion, and in particular the concentrations of carbon monoxide or hydrogen, also influence the char reactivity, which is a function of conversion and the related changes in the surface area. At high conversions it is also highly affected by the increase in the ratio between carbon and the catalytically active substances present in the ashes. Hence, pre-pyrolysis addition of catalysts to wood is another means to modify reaction characteristics.

Several kinetic models are available of the combustion kinetics for wood and biomass, based on thermogravimetric measurements. Following the small sample mass and the mild thermal conditions

usually employed, the weight loss characteristics show two zones corresponding to the devolatilization and the combustion reactions, respectively. The large part of the kinetic models is highly simplified and consists of two global reactions with n th-order rates in the mass fraction. These are empirical models as the kinetic constants are estimated only for single experiments by means of integral data. In a few cases, more accurate treatments are developed comprising two or three steps for the devolatilization stage coupled with an additional reaction for char combustion. The use of differential data produces higher values for the activation energy of the last step, which are roughly in the range 140-180kJ/mol.

In the mathematical description of char combustion there are essentially two contributions to be taken into account, that is, the intrinsic kinetic law, which mainly describes the dependence on temperature and concentrations of reactants, and structural variations during conversion. Structural models applied for biomass chars are the same as for coals, though modifications are proposed to take into account the peculiarities of the former.

Significant effort has been devoted to determine the parameters for a global reaction of char gasification in carbon dioxide or steam bearing atmospheres, using thermogravimetric isothermal data. There is quite good agreement in relation to the activation energy, especially for carbon dioxide gasification. For wood gasification, the value is around 200kJ/mol (values between 196-200kJ/mol with the corresponding \ln of the pre-exponential factors of 20 and 21) with the exponent n (for carbon dioxide partial pressure) roughly between 0.4 and 0.6. Differences are seen for biomass chars, presumably owing to different contents and compositions of the ashes. A wider range of variation is observed for the steam gasification of wood char with activation energies comprised between 138 and 271 kJ/mol, though the majority of the evaluations are around intermediate values of 180-210 kJ/mol. The exponent for the steam partial pressure varies between 0.5-1. The more complicated Langmuir-Hinshelwood kinetics are considered only in a few cases, often with the sole evaluation of the rate constants.

The majority of the kinetic models of wood char combustion, using integral thermogravimetric dynamic data for parameter estimation, is based on a one-step global reaction with a power-law dependence on the oxygen partial pressure and the solid mass fraction (this accounting for structural effects). Significant variation is shown by kinetic parameters, with activation mainly in the range 75-140kJ/mol. However, differential thermogravimetric data show that combustion of lignocellulosic chars is a multi-step process. A recent model shows that a n -order global reaction provides a very poor description of the differential curves and, in agreement with previous literature, requires relatively low activation energies (115 and 167kJ/mol for conventional and fast pyrolysis chars, respectively). The combination with an additional first-order reaction for the devolatilization stage produces accurate predictions and gives rise to much higher activation energies of the combustion reaction (183 or 229kJ/mol, depending on the severity of the pyrolysis conditions).

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