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Kinetic modelling of steam gasification of various woody biomass chars: Influence of inorganic elements

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ABSTRACT

A study was performed on the influence of wood variability on char steam gasification kinetics. Isothermal experiments were carried out in a thermobalance in chemical regime on various wood chars produced under the same conditions. The samples exhibited large differences of average reaction rate. These differences were linked neither with the biomass species nor age and may be related to the biomass inorganic elements. A modelling approach was developed to give a quantitative insight to these observations. The grain model was used on one biomass of reference for temperatures between 750 and 900 °C and steam partial pressures between 0 and 0.27 bar. The model was applied to the other samples through the addition of an integral parameter specific to each sample. A satisfactory correlation was found between this parameter and the ratio pota ssium/silicium. This result highlighted the catalytic effect of potassium and inhibitor effect of silicium on the reaction.

1. Introduction

In the present energy context, there is a growing interest worldwide for heat, power and biofuels production from biomass (Sims et al., 2010), notably through gasification (Karmakar and Datta, 2011; Xiao et al., 2011). The knowledge of biomass char steam gasification kinetics is of major importance in the design of advanced gasifiers since this reaction is the limiting phenomenon in the transformation (Dupont et al., 2007) and therefore controls conversion. Due to the limited availability of biomass, gasifiers will have to be supplied with various feedstocks, of different species and coming from different places of growth.

Previous studies have shown that the kinetics of char steam gasification could be very different according to the biomass with a factor of more than twenty for chars prepared in an identical way (Moilanen, 2006; Septien et al., 2009). A simple calculation based on the Arrhenius law shows that even a difference of only a factor of four between two biomasses would imply to change the operating reactor temperature of 100 °C to achieve the same level of conversion. It could therefore strongly impact the process control. It is therefore of great importance to study the intrinsic kinetics of steam gasification of chars from various biomasses.

When series of chars are prepared and gasified under identical conditions, the differences of reactivity may only be attributed to differences of morphological structure and of inorganic elements content.

In her very complete review on lignocellulosic chars gasification rate, Di Blasi reports that surface area, and consequently morphological structure, seems to be less influential on gasification reactivity than content in inorganic elements, and particularly soluble minerals (Di Blasi, 2009). This latter parameter seems therefore to be the most important parameter to consider for understanding the differences of gasification behaviour of chars from different biomasses.

Numerous studies deal with the influence of the content in inorganic elements in the case of gasification of charcoal with steam or CO_2, for instance (Everson et al., 2008; Kajitani et al., 2002; Lee and Kim, 1995; Ochoa et al., 2001; Zhang et al., 2010) or of biomass chars with CO_2, such as (Cetin et al., 2004; Huang et al., 2009; DeGroot and Shafizadeh, 1984; Struis et al., 2002; Seo et al., 2010). There are fewer studies in the case of steam gasification of biomass chars (Kajita et al., 2009; Moilanen, 2006; Yip et al., 2009; Zhang et al., 2008; Zhu et al., 2008). Hence, as underlined by Di Blasi (2009), there is at the moment a significant need to better understand the influence of the inorganic elements content on steam gasification kinetics of biomass chars.

To estimate the influence of inorganic elements on gasification reactivity, most authors use the same biomass and then choose either to impregnate the solid of inorganic elements (Hawley et al., 1983; Huang et al., 2009) or to leach it with aqueous or acid solution (Kajita et al., 2009; Marquez-Montesinos et al., 2002; Yip et al., 2009). Possible differences of morphological structure between the biomass samples are avoided thanks to these methods. However, biomass structure may be modified by these treatments and the location of the impregnated inorganic elements may not be comparable with those of the indigenous ones. Moreover, the

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efficiency of leaching is not total (Etiégni and Campbell, 1991; Marquez-Montesinos et al., 2002; Yip et al., 2009). The other option is to directly compare different biomass feedstocks with different inorganic elements contents (Moilanen, 2006). This may induce some bias due to the differences of morphological structure but has the advantage of considering inorganic elements in their natural form and location inside the solid.

Generally speaking, the alkaline (sodium, potassium) and alkaline earth (calcium, magnesium) metallic (AAEM) species are recognized to increase the reaction rate (Zhang et al., 2008; Zhu et al., 2008), on the contrary to silicium.

Although qualitative evidence has largely been given on the major importance of the inorganic elements content on char gasification rate, none of the existing kinetic models is able to take this parameter into account. Hence, all these models are only related to one biomass. Only Zhang et al. (2008) have recently made an interesting attempt to develop a quantitative approach of the influence of the inorganic elements in the description of steam gasification of biomass chars. Two parameters, called c and p, were added in the random-pore model (Bhatia and Perlmutter, 1980), as previously made by Struis on coal chars (Struis et al., 2002). The originality lies in the correlation of these parameters with the potassium content of the twelve biomasses used for the development of the model. However, the correlation was not explicitly given and it is therefore difficult to test the model performance and its physical meaning.

Based on this background, the present study aims at better understanding steam gasification kinetics of biomass chars and developing a kinetic model valid for various biomass chars, by considering in a quantitative way the influence of the inorganic elements contained in the biomass chars. To achieve this goal, gasification experiments were performed in thermobalance on chars from 21 different biomass samples under different operating conditions of temperature and steam partial pressure.

2. Methods

2.1. Biomass samples

The biomass used in this study consisted in 21 samples of wood chips, from common species of woods, coming from various places in France and of different ages, including Short Rotation Forestry and Short Rotation Coppice.

The samples properties were measured following the European standards on biofuels. In particular, ash content was measured at 550 °C and ash composition was measured for the following elements (SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, K_2O, Na_2O). The main results are given in Table 1. These properties were presented and discussed in detail elsewhere (Dupont et al., 2010).

It has to be kept in mind that these values should be taken with caution due to the hardly-avoidable uncertainty of properties measurement of heterogeneous solid.

For all samples, ash was mainly composed of calcium. Potassium and silicium were the other two important components, followed by magnesium. The ash content as well as the relative amounts of elements were quite different among the samples.

No correlation could be found between properties and species. The older the tree, the lower the ash content. This seems logical since the proportion of bark, which contains the highest amount of ash in wood, is higher in young wood.

2.2. Experimental procedure

2.2.1. General description

To ensure good representativeness, 30 g of each sample of wood chips was sampled following the standard XP CENT/TS 14780.

The sample was pyrolysed under N_2 atmosphere in a low heating rate furnace (a few °C min^{-1}). It was kept at the final temperature of 450 °C during 4 h. Then the produced char, which counted for about 25%w of the initial biomass, was ground with a mortar and sieved below 50 μm. Char was assumed to be ground homogeneously enough to prevent any segregation when sieving. Char gasification with steam took place in a Thermo Gravimetric Analysis (TGA) device operating at atmospheric pressure (SETARAM Setsys coupled with steam generator Wetsys). The device is depicted in Fig. 1. Five milligrams of the sample was placed in the crucible of the thermobalance. This crucible was a cylinder of 2.5 mm height and 8 mm diameter. The sample was heated at a rate of 24 °C min^{-1} to the gasification temperature under a N_2 gas flow of 0.05 L min^{-1} to end pyrolysis. After the gasification temperature was reached and no mass loss was observed, the gas was switched to a mixture of H_2O/N_2 (0–27 vol%, with an uncertainty below 4%)

Table 1
List of samples and of their composition in major inorganic elements.

Sample name	Species	Si	Na	K	Ca	Mg	Al	Ash
		mg/kg dry biomass						wmf%
1	Spruce	661	33	236	1003	151	95	0.6
2	Beech, hornbeam, oak	370	8	653	2665	358	26	1.1
3	Beech, oak	651	12	561	858	207	57	0.8
4	Pine	291	11	112	2177	263	57	0.6
5	Beech	584	13	403	3349	427	43	0.9
6	Softwoods	3619	86	1520	6576	733	507	3.3
7	Hornbeam	224	4	523	2451	126	25	0.6
8	SRF[a] poplar	498	30	1175	12,248	692	98	4.1
9	Birch	85	10	328	1746	249	17	0.7
10	Beech	757	27	1442	3795	532	24	1.8
11	Oak	119	11	561	4545	262	16	1.5
12	SRC[b] willow	841	14	654	2926	273	79	1.5
13	SRC poplar	642	19	1784	7661	675	86	2.5
14	Poplar	763	48	1855	15,879	1600	102	4.3
15	Reference sample (beech)	260	18	403	1196	313	38	0.6
16	Oak	112	6	531	4894	386	21	1.6
17	Pine, spruce	375	12	1250	1909	198	64	1.1
18	Pine	252	19	164	1157	297	58	0.5
19	SRF poplar	366	20	1222	10,034	778	86	2.7
20	SRC poplar	632	48	2019	6987	753	158	2.6
21	Hornbeam, oak	108	8	549	6679	253	11	2.1

[a] SRF: Short Rotation Forestry.
[b] SRC: Short Rotation Coppice.