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How inorganic elements of biomass influence char steam gasification kinetics

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ABSTRACT

A study was performed to elucidate the influence of biomass type on char steam gasification kinetics. Isothermal experiments were carried out in a thermobalance in chemical regime on nineteen biomass chars produced under the same conditions. The reactivity obtained varied of a factor of more than thirty. This large difference appeared to be correlated with the biomass inorganic elements. In particular, the catalytic effect of potassium (K) as well as the inhibiting effect of silicon (Si) and phosphorus (P) were highlighted. Three different types of rate evolution versus conversion could be observed depending on the ratio K/(Si + P) and were correlated with the ash surface composition after gasification. Conversion could be satisfactorily predicted versus time through simple models taking into account the influence of inorganic elements and thus further useable in simulation of industrial gasifiers fed by various biomass types.

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1. Introduction

Due to the energy context, there has been for several years an increasing interest worldwide for heat, power and biofuels production from unused biomass through the advanced process of gasification [7]. Since the reaction of char steam gasification is the limiting phenomenon under typical gasification conditions, it controls conversion and the knowledge of its kinetics is therefore crucial to design and control gasifiers, in particular fixed beds, and thus to succeed in process industrial implementation. Due to the limited availability of biomass, gasifiers will have to cope with various feedstocks, of different species, coming from different places and hence of variable nature.

Literature studies have shown that the kinetics of char steam gasification could be very different according to biomass, with a factor of more than twenty for chars prepared in an identical way [11]. As stated in a previous paper [4], a simple calculation based on the Arrhenius law shows that even a difference of only a factor of four between two biomasses implies to change the operating reactor temperature of 100 °C to achieve the same level of conversion. This significant impact on process control highlights the importance of studying 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. As highlighted in Di Blasi's review [3], surface area, and consequently morphological structure, seems to be less influential on steam gasification reactivity than content in inorganic elements, and particularly soluble minerals. This latter parameter seems therefore to be the most important parameter to consider for understanding the differences of steam gasification behaviour of chars from different biomasses.

In recent years there have been several studies dealing with the influence of biomass inorganic elements on char steam gasification. The majority of these studies was focused on woody biomass, even if some tests were carried out on agricultural biomass by Zhang et al. [17] or on microalgae by Hognon et al. [6]. These studies emphasized the catalytic effect of alkaline (sodium Na, potassium K) and alkaline earth metallic (calcium Ca, magnesium Mg) species [9,10,17,18], on the contrary to silicon Si [4,14,15] and phosphorus P [6]. However, the effect of inorganic elements was mostly addressed in a qualitative way. Indeed, studies were generally

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Nomenclature

k	Intrinsic kinetic parameter s^{-1}
k_i	Kinetic constant s^{-1}
m_i	Char mass before gasification kg
m_f	Char mass after gasification kg
P_{H_2O}	Steam partial pressure Pa
r	Gasification rate $\%.min^{-1}$ or $\%.s^{-1}$
r_{integ}	Average reactivity $\%.min^{-1}$
SEM-EDX	Scanning Electron Microscopy coupled with Electronic Dispersive X-ray
SRF/SRC	Short Rotation Forestry/Coppice
t	Time s
T	Temperature K
TGA	Thermo Gravimetric Analysis
wmf%	Moisture-free mass percent
X	conversion

based on the comparison of a few different biomass samples, which prevents to draw significant correlations from results.

Few attempts of quantitative empirical approaches have been made up to now on the influence of inorganic elements on biomass steam gasification. Zhang et al. [17] added two parameters in the random-pore model [1], as previously made by Struis et al. (2002). The originality lay in the correlation of these parameters with the content in K of the twelve biomasses used for the development of the model. However, the correlation was not explicitly given and the model performance as well as its physical meaning are therefore difficult to assess. In a previous work from our team [4], a model was developed on twenty-one woody biomasses by adding a linear function of ratio K/Si in the shrinking-core model. The model obtained gave correct estimation of the average conversion rate under the conditions explored and showed the catalytic effect of K and inhibiting effect of Si, but this approach did not describe possible differences of conversion profiles versus time and the associated phenomena. More recently, it has been proposed in a study on five lignocellulosic and algae feedstock [6] that conversion profile would be correlated with ratio K/(Si + P). Simple zeroth order and first order kinetic models were proposed to fit the two behaviours observed, but the associated parameters could not be linked with inorganic elements due to the limited samples number. These different conversion profiles led authors to consider that gasification occurs through parallel reactions. This principle was applied to two biomass feedstock – acid-washed or not – by Kajita et al. [9]. One reaction was said to be non catalytic – following first-order kinetic law – and one to be catalytic – following zeroth order kinetic law – with K as the main catalytic species. However, no correlation was proposed to describe this catalytic influence of K. Moreover, Si was not measured, which prevented to evaluate the impact of this element. Similarly, Umeki et al. performed experiments on nine biomasses and made an attempt to model the evolution of catalytic effect of inorganic elements versus conversion during gasification under various conditions through parallel reactions [15]. As in Refs. [6], the influence of Si on conversion profile was highlighted. Nevertheless, according to the authors, model results are promising when CO_2 is the gasifying agent but more work is required to catch the trends associated to steam gasification.

Based on this background, the present work aimed at:

- characterizing in thermobalance the kinetic behaviour of a large set of biomass types during char steam gasification
- then using the results to elucidate the role of biomass type on steam gasification kinetics and more specifically correlating the conversion profile observed with inorganic elements contained in biomass
- finally deriving models i) able to predict conversion versus time from inorganic elements composition and ii) simple enough to be useable in process applications.

2. Materials and methods

2.1. Biomass samples

Biomass samples were selected among species potentially useable as feedstock in gasification processes [5]. They were classified as follows:

- Wood: beech, angelim, faveira, maçaranduba, mixture Scot pine + spruce
- SRF/SRC (Short Rotation Forestry/Coppice): SRF of poplar and eucalyptus, SRC of poplar (numbered 1 and 2)
- Agricultural biomasses: alfalfa, barley straw, miscanthus, switchgrass, tall fescue, triticale, two wheat straws (numbered 1 and 2).

Two samples of microalgae tested in Ref. [6] were also used, as potential feedstock for gasification in third generation biorefinery: *Chlamydomonas reinhardtii* and *Arthrospira platensis* (*Spirulina platensis*).

Sampling was carried out following standard CENT/TS 14780. The samples properties were measured following the standards on solid biofuels. The main results are given in Table 1. 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 biomass resources [8].

In agreement with previous studies on biomass characterization [2,5,16], ash amount was found to increase from wood samples, with values between 0.4 and 1.9 wmf%, then to SRF/SRC and perennial crops (miscanthus, switchgrass) samples, with values between 1.1 and 4.6 wmf%, and finally to the other agricultural biomasses samples, with values between 6.8 and 14.7 wmf%. Ash content from microalgae was found to be similar to this last family. As expected, the dominating inorganic elements were observed to be different among biomasses:

- Most woody biomasses, including SRC/SRF, as well as alfalfa, mainly contain Ca and K and small amounts of Si;
- Perennial crops, straws and the woody biomass faveira contain large/very large amounts of Si, then significant amounts of K and Ca;
- Fescue mainly contains K, and also significant amounts of Si.
- The two microalgae tested are rich in K and Ca while poor in Si like most woody biomasses, but also contain large amounts of Na, Mg and P.

2.2. Experimental procedure

Most samples were received in the form of millimetre-particles. To ensure good representativeness, 30 g of each of these samples was sampled following the standard CENT/TS 14780 and then 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

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