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T. Dahou, F. Defoort, B. Khiari, M. Labaki, C. Dupont, et al.. Role of inorganics on the biomass char gasification reactivity: A review involving reaction mechanisms and kinetics models. Renewable and Sustainable Energy Reviews, 2021, 135, pp.110136. 10.1016/j.rser.2020.110136 . hal-03491288

HAL Id: hal-03491288

https://hal.science/hal-03491288v1

Submitted on 22 Aug 2022

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Role of Inorganics on the Biomass Char Gasification Reactivity: A Review Involving Reaction Mechanisms and Kinetics Models

T. Dahou[1,2,3,4], F. Defoort[1], B. Khiari[5], M. Labaki[6], C. Dupont[7], M. Jeguirim[2,3*]

[1] Université Grenoble Alpes, CEA, LITEN, DTBH, 17 avenue des Martyrs, 38054 Grenoble CEDEX 09, France

[2] Université de Haute-alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

[3] Université de Strasbourg, France

[4] Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME), 20 avenue du Grésillé, BP 90406, 49004 Angers CEDEX 01, France

[5] Ecole Nationale d'Ingénieurs de Carthage, 45 rue des entrepreneurs, Tunis, Tunisie

[6] Laboratory of Physical Chemistry of Materials (LCPM)/PR2N, Faculty of Sciences, Lebanese University, Fanar, P.O. Box 90656, Jdeidet El Metn, Lebanon

[7] IHE Delft Institute for Water Education, Westvest 7, 2611 AX Delft, The Netherlands

* Corresponding author details: mejdi.jeguirim@uha.fr ; Tel.: +33-389-336-729

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Abstract

This review article presents the effects of the inorganic elements and compounds on gasification and their mechanisms of action. The influence of inorganics on the gasification reaction have been described in the literature. However, the specific phenomena involved and the mechanisms of action are not stated with consensus. Therefore, the present review gathers the various mechanisms proposed by authors. Some have been demonstrated to be unlikely such as the mechanisms involving intercalation compounds or mechanical actions. In order to give more practical applications of this work, the review also gathers the gasification kinetic models that take these inorganic effects into account.

Highlights

- Char morphology and its inorganic content influence strongly the gasification kinetics
- AAEMs have catalytic effects that enhance the gasification kinetics
- Al, Si and P have an inhibiting effect on the char gasification kinetics
- K and Si are of particular interest in terms of occurrence and activity
- Catalytic mechanisms by intercalation or mechanical actions are not likely to occur

Key words: biomass char; gasification; inorganic elements and compounds; reactivity; catalytic effect; inhibitory effect; kinetics

Word Count:

Declaration of interest: none.

Abbreviations:;;;;;;;;;;;;;;.

AAEMs	Alkali and Alkaline Earth Metals
BET	Brunauer-Emmett-Teller
daf	dry ash free
E_a	activation energy
f (X)	reaction model describing the reaction mechanism
HHV	High Heating Value
k_0	pre-exponential constant
k	rate constant
LHV	Low Heating Value
P_{H2O}	partial pressure of the steam
R	universal gas constant
SSA	Specific Surface Area
T	reaction temperature
X	conversion rate
XRD	X-ray diffraction

1. Introduction

Lignocellulosic biomass is an abundant, clean and carbon-neutral renewable and sustainable source of energy. It constitutes an alternative to fossil fuels, in order to reduce global warming, environmental pollution and the energy crisis. Gasification is one of the most promising thermal processes to convert biomass materials into different types of fuels (syngas, biofuel, etc.),

provided that the overall efficiency is improved, the technology cost reduced and the emissions controlled. Inorganic elements and compounds, which are present in biomass and biomass-derived products, play a major role in directing the char behaviour and toxic emissions. This can be problematic for the gasifier operation if it is not understood and controlled. Besides, char reactivity is an important factor influencing the efficiency of the operation. Accurate models for predicting the behaviour and the effects of inorganics in biomass and biomass chars are essential to overcome some of the challenges facing the widespread use of biomass gasification and to design cost-effective large-scale gasifiers.

However, the mechanisms of action of these inorganic elements and compounds have been studied but there does not seem to be a clear consensus in the literature. Therefore, the present review discusses the various mechanisms proposed by some authors. To provide a better understanding of these mechanisms, the biomass composition and the inorganic elements observed effects are precisely described. Finally, the present article also provides a review of the various models that integrate the effect of the inorganics.

2. Biomass and its composition

2.1. Biomass definition

The European Parliament directive 2009/28/EC of 23 April 2009 on the promotion of the use of energy from renewable sources defines biomass as "the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste" [1]. Therefore, biomass is a feedstock that includes a variety of different resources. Vassilev *et al.* have classified biomass into six groups: wood and woody biomass, herbaceous and agricultural biomass, aquatic biomass, animal and human

biomass wastes, contaminated biomass and industrial biomass wastes (semi-biomass), and biomass mixtures [2]. In this review, as the focus is on the gasification process, only the first two groups —i.e. dry land-based vegetation— are studied. For simplification purpose, these groups are referred to as biomass or lignocellulosic biomass.

2.2. Biomass composition

Biomass composition is complex and involves several hundreds of compounds, divided between organic and inorganic fractions detailed below. However, some compounds do not perfectly fit with these two groups. For example, N- and S-compounds can be in both fractions, while oxalates are considered as organic minerals [3].

2.2.1. Organic fraction

Biomass is typically composed of organic-constituent elements, namely C, O, H, N and S [2]. The proportion of these elements in lignocellulosic biomass, expressed in dry ash-free (daf) basis, is reported in Table 1. The typical content of coal, the main solid fossil fuel, is also presented. Usually, a higher ratio of carbon and sulfur and a lower ratio of oxygen are recorded for coal, compared to lignocellulosic biomass [2].

Table 1. Typical elemental composition in C, O, H, N and S (% daf basis) of biomass and coal (data from [2]).

	Biomass	Coal
C	40 – 60	60 – 90
O	30 – 50	5 – 30
H	3 – 10	4 – 6
N	0.1 – 5	1 – 3
S	0.01 – 1	0.2 – 10

In addition to the composition difference, the biomass energy content is lower than solid fossil fuels. The lower heating value (LHV) of biomass is usually 15 – 20 $MJ.kg^{-1}$, whereas it is 20 – 40 $MJ.kg^{-1}$ for solid fossil fuel. Differences between biomass and solid fossil fuels in terms of composition and LHV can be correlated with H/C and O/C ratios, as shown in the Van Krevelen diagram (Figure 1). Such difference can be explained by the fact that C – H and C – O bonds have low energy contents compared to C – C bonds [4].

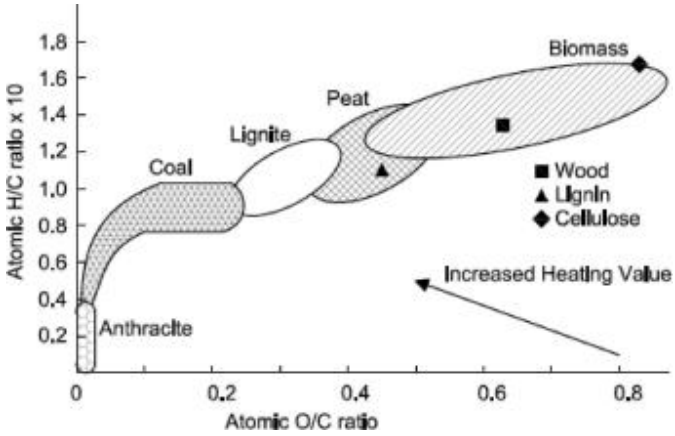

Figure 1. Van Krevelen diagram for various solid fuels (Reproduced with permission from [4]).

The organic fraction of the lignocellulosic biomass is organized in three types of macromolecules: cellulose, hemicellulose and lignin. The lignocellulosic biomass structure is represented in Figure 2.

Cellulose is a linear and partly crystalline glucose polymer with an average polymerization degree around 10 000 for wood [5,6] and an average molecular weight around 100 000 [4]. It constitutes 40 – 50 % of the biomass by weight [4,7].

Hemicelluloses are polysaccharides whose units are glucose, xylose, galactose, arabinose and mannose. It is a branched macromolecule with a random and amorphous structure and with an average molecular weight lower than 30 000. It represents 20 – 40 % of the biomass weight [3,4].

Lignin is a highly branched polyaromatic macromolecule. Its building blocks are made up of a three-carbon chain attached to an aromatic ring of six carbon atoms, with zero to two methoxyl groups. These building blocks (depicted in Figure 2) are linked mainly through ether bonds and arranged irregularly, forming an amorphous three-dimensional structure that varies among biomass species [3,4].

The exact arrangement of these macromolecules is a subject of ongoing research. The biomass structure seems to be formed of cellulose macromolecules linked by hydrogen and Van der Waals bonds in microfibrils, themselves grouped in fibres [5]. This rigid matrix would then be covered by hemicelluloses and lignin macromolecules.

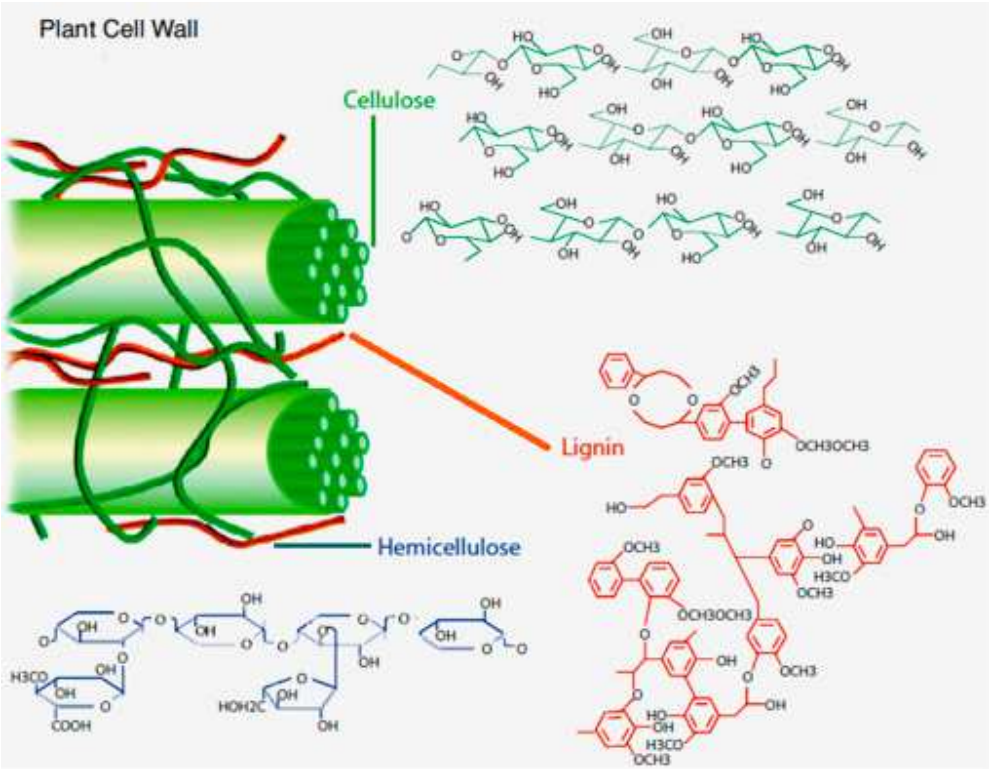

Figure 2. Lignocellulosic biomass structure (Reproduced with permission from [8]).

2.2.2. Inorganic fraction

In addition to the organic fraction, biomass contains inorganic elements, namely Cl, Ca, K, Si, Mg, Al, Fe, P and Na. Some other elements can also be found as trace elements (<1 % of the inorganic content), for instance, Mn, Ti, B, Be, Rb, Cr, Ni, Cu, Se and Zn [9].

Inorganic elements are often referred to as the ash content since the inorganics quantification in biomass is usually measured by combustion of the biomass in the air at 550 °C to form ash [10]. The standards for ash yield measurement are slightly different for biomass and solid fossil fuels. Ashes are formed at 815 °C for the latter [11]. In the case of biomass, such a high temperature can volatilize alkali and alkaline earth compounds, in particular KCl, and provokes the release of inorganic carbon as CO_2 from alkali and alkaline earth carbonates, in particular $CaCO_3$ [12,13]. The ash content of wood and woody biomass is typically 0.1 – 8 %. It is typically 0.9 – 20 % for herbaceous and agricultural biomass, with straws presenting the highest ash content, grasses the lowest and other residues, such as husks and shells, presenting average values [2]. In comparison, the ash yield of solid fossil fuels at 815 °C is commonly 4 – 30 %. Solid fossil fuels contain therefore more inorganic elements than wood and woody biomass, but can have the same inorganics content of certain herbaceous and agricultural biomasses.

Few extensive studies are available regarding the inorganic fraction [2,3,9] while more data are available regarding the inorganic composition of biomass ashes, obtained from combustion. This is partly due to the higher concentration of inorganic compounds in ashes, which makes the characterization easier compared to that of raw biomass in which detection issues can occur. However, results given in this section are only about the inorganic fraction of raw biomass and not about ashes.

Biomass composition differs from solid fossil fuels. Inorganic elements in biomass are mainly Si, K and Ca, while those in solid fossil fuels are rather Si, Al, Fe and Ca [2]. More specifically, Vassilev *et al.* [2] identify the main inorganic elements in several biomass subgroups:

- Wood and woody biomass: Ca > Si > K > Mg > Al > P
- Herbaceous and agricultural biomass:
    - Grass: Si > K > Ca > P > Mg > Al
    - Straw: Si > K > Ca > Mg > P > Al
    - Other residues such as shells and husks: K > Si > Ca > P > Mg > Al

These rankings represent the trends obtained from mean values calculated for each subgroup. However, in each subgroup, individual biomass species can have slightly different compositions that modify the order of richness of the main inorganic elements.

The above mentioned inorganic elements are present in the form of various compounds. However, as stated by Vassilev *et al.* [3], "the direct methods for determination of the structural components [of raw biomass] are very rare". Nevertheless, they collected data for 197 samples coming from 25 published research works and from their own results of characterization carried out for 8 biomass samples in order to establish a list of the inorganic compounds present in the biomass. The identified inorganic compounds are:

- Silicates such as SiO_2, Ca-silicates or aluminosilicates;
- Oxides and hydroxides such as $Mg(OH)_2$, $Ca(OH)_2$ or Fe_2O_3;
- Sulphates, sulphites and sulphides (not typical in lignocellulosic biomass) such as $CaSO_4$ or K_2SO_4;
- Phosphates such as Ca-phosphates, Ca-Mg-phosphates or K-phosphates;
- Carbonates such as $CaCO_3$ or $CaMg(CO_3)_2$;

- Chlorides such as KCl or K-Ca-chloride;
- Nitrates such as KNO_3 or Ca-nitrates;
- Other inorganic matter such as metals or glass (not typical in clean lignocellulosic biomass).

The available data do not allow linking the organic elements to a specific biomass subgroup. Moreover, there is a high variability due to the inorganic content dependence on several factors such as biomass genetics, its environment or the fraction of biomass considered [3].

For example, silicates and in particular silica are typically found in soil. The presence of these compounds in biomass can be either due to their formation in the biomass (authigenic fraction) or to the formation outside of the plant and the consequent accumulation in the biomass (detrital fraction). The detrital fraction of silicates can be issued from the fixation of fine particles, displaced from the soil by the water or the wind to the plant surface. These fine particles can also be introduced into the plant by water suspensions. In the particular case of silica, the authigenic fraction is formed by silicic acid absorption from the soil solutions that precipitates in the biomass structure. When present, silica gives rigidness to the plant tissues as in the case of husk, straw, bark and other supportive tissues. Other compounds can also have disparate origins. Other examples of authigenic compounds (i.e. formed in the biomass) are sulphates, nitrates and chlorides that come from the evaporation and the precipitation of water in the biomass [3].

3. The pyrogasification of biomass

Though it is not widely used in the literature, the term of pyrogasification could rather be used to refer to the gasification process. Indeed, it is usually decomposed in three main steps: biomass drying, biomass pyrolysis and residual char gasification [7,14–16]. These steps are overlapping

and are themselves groups of various reactions. Figure 3 shows a more detailed scheme of the pyrogasification steps with the intermediary and final products.

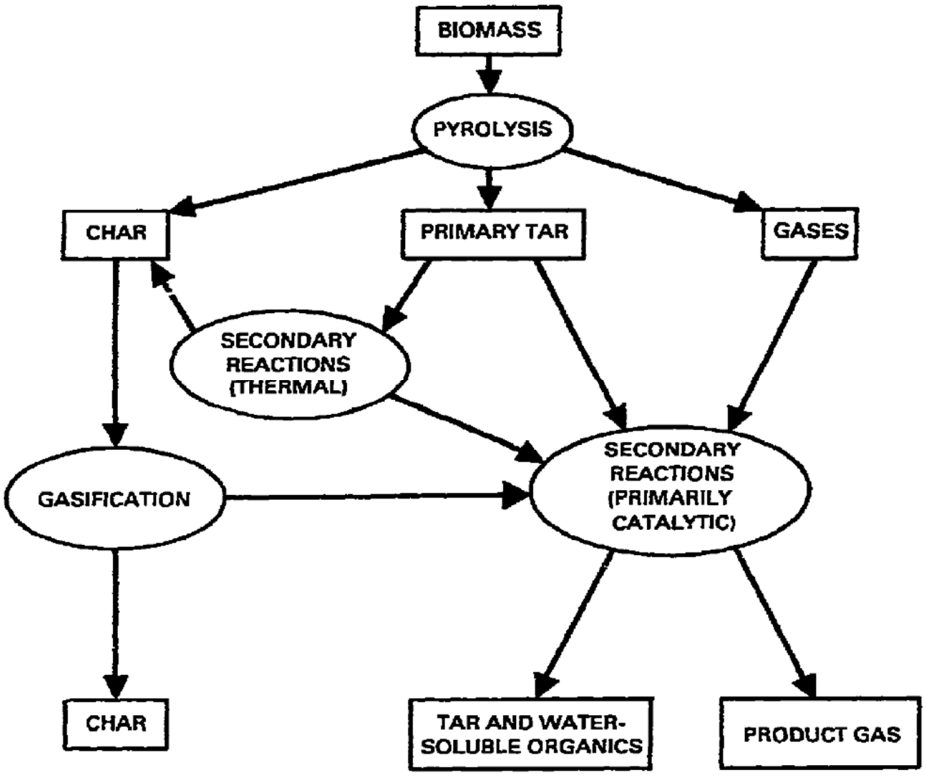

Figure 3. Biomass pyrogasification steps (Reproduced with permission from [17]).

Dupont *et al.* [18] show that in typical fluidized bed conditions, i.e. 800 – 1000 °C at atmospheric pressures, and in the case of small particles, i.e. 0.5 mm, the pyrolysis and the steam gasification steps can be considered as successive ones. The steam gasification is slower than the pyrolysis step and is therefore the limiting step in the pyrogasification process. The pyrolysis is controlled by both the chemical reaction and the heat transfer while the steam gasification is only controlled by the chemical reactions and is independent of the mass and heat transfers.

Therefore, the knowledge of the gasification reaction kinetics is essential to the design of the reactors presented above. This applies to any reactor and can be easily understood in the case of the dual fluidized bed reactor. The gasification kinetics need to be controlled so that enough char goes to the combustion side to produce the heat necessary to the process.

Therefore, in this investigation, the focus is made on the limiting phenomenon: the gasification reaction kinetics.

3.1.Pyrolysis reactions

Pyrolysis is a thermal decomposition in the absence of oxygen. Three fractions are formed: gas, liquid and solid. The liquid is constituted of two phases: organic, i.e. tars, and aqueous. The solid fraction is called the char. Depending on the heating rate and the final temperature, these fractions are formed in various proportions [19]. Figure 4 shows typical product distribution for fast, intermediate and slow pyrolysis at around 500 °C.

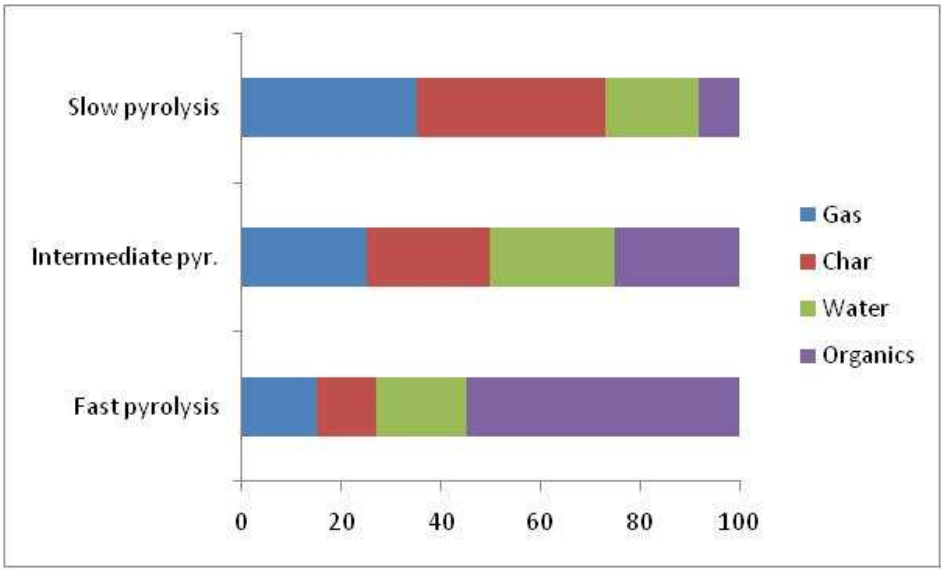

Figure 4. Typical product distribution for the fast, intermediate and slow pyrolysis at ~500 °C.

Fast pyrolysis —or high heating rate pyrolysis— corresponds to residence times inferior to 2 seconds or heat flux superior to 10^5 W.m^{-2} [6,20]. It produces mainly liquid that is called bio-oil. Intermediate pyrolysis corresponds to residence times of around 5 to 30 seconds or heat flux around 10^4 W.m^{-2} [6,20]. Half of its products are liquid while the other half are divided between gas and char [21]. Slow pyrolysis — or low heating rate pyrolysis, or carbonization — corresponds to residence times of several hours or heat flux inferior to 10^3 W.m^{-2} [6,20]. It produces char, liquid and gas in approximately the same proportions, with the liquid being in a slightly lower quantity. The liquid obtained from slow pyrolysis is constituted of approximately one third (~10 % of the total products) of organic fraction and two-thirds of the aqueous fraction (~20 % of the total products).

Moreover, increasing the temperature of the pyrolysis promotes the tar decomposition into gases [20]. Therefore, in the pyrogasification conditions, the tars represent less than 10 % of the products.

As a first assessment, the kinetics of the pyrolysis of a given biomass can be considered as the sum of the kinetics of the pyrolysis of its macromolecular constituents, i.e. cellulose, hemicellulose and lignin [22]. Research on the pyrolysis kinetics and the constituent degradation is still ongoing. However, it seems that each constituent degrades over a different temperature range, as represented in Figure 5. Hemicellulose seems to be the least stable and degrades between 200 and below 300 °C. Then cellulose seems to decompose between 250 and 350 °C. Finally, lignin is more likely to break down over the widest range, from 200 to above 500 °C [23].

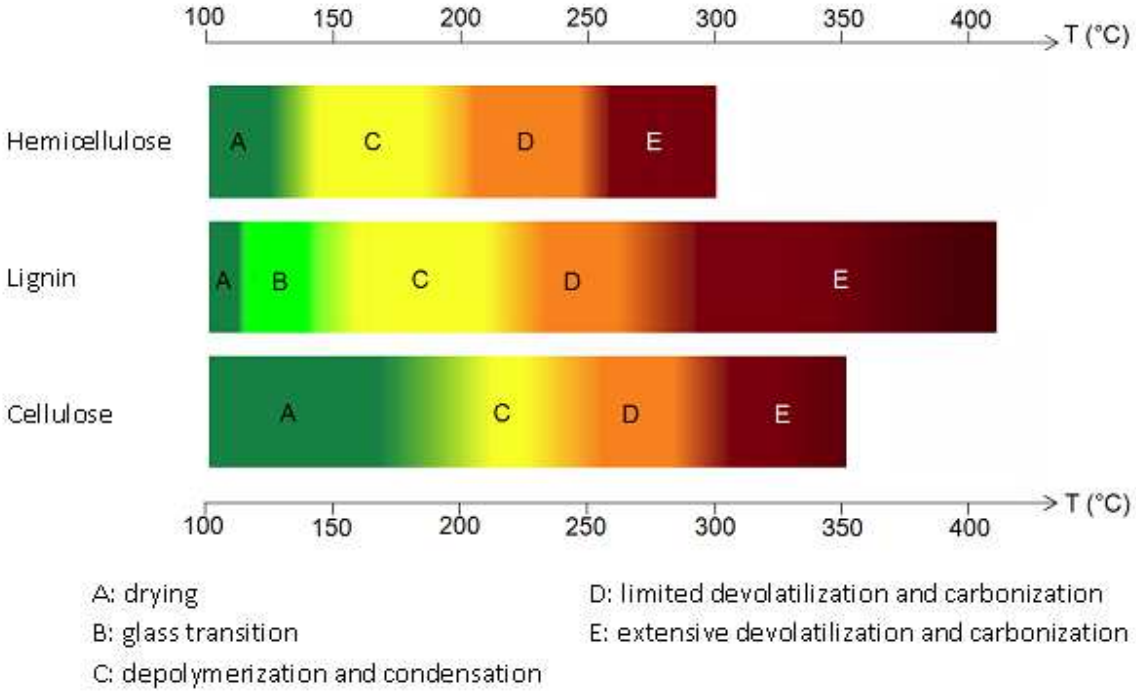

Figure 5. Thermal stability of hemicellulose, lignin and cellulose (Adapted from [23]).

These literature observations show that most of the biomass constituents are degraded below 450 °C, which means when most of the pyrolysis process is completed.

3.2.Gasification reactions

Gasification is the partial oxidation of the carbonaceous part of biomass that produces syngas, or synthesis gas, which is mainly a mixture of CO and H_2.

3.2.1. Reaction equations

The main known reactions, as well as their associated enthalpy at 25 °C, are presented in Table 2. It includes reactions with carbon, oxidation reactions, water-gas shift reaction, methanation reactions and steam-reforming reactions [14].

Table 2. Typical gasification reactions and their associated enthalpy at 25 °C [14].

Carbon reactions	
$C + CO_2 \leftrightarrow 2\ CO$ (Boudouard)	+ 172 kJ.mol^{-1}
$C + H_2O \leftrightarrow CO + H_2$ (Water gas or steam)	+ 131 kJ.mol^{-1}
$C + 2\ H_2 \leftrightarrow CH_4$ (Hydrogasification)	- 74.8 kJ.mol^{-1}
$C + 0.5\ O_2 \rightarrow CO$	- 111 kJ.mol^{-1}
Oxidation reactions	
$C + O_2 \rightarrow CO_2$	- 394 kJ.mol^{-1}
$CO + 0.5\ O_2 \rightarrow CO_2$	- 284 kJ.mol^{-1}
$CH_4 + 2\ O_2 \leftrightarrow CO_2 + 2\ H_2O$	- 803 kJ.mol^{-1}
$H_2 + 0.5\ O_2 \rightarrow H_2O$	- 242 kJ.mol^{-1}
Shift reaction	
$CO + H_2O \leftrightarrow CO_2 + H_2$	- 41.2 kJ.mol^{-1}
Methanation reactions	
$2\ CO + 2\ H_2 \rightarrow CH_4 + CO_2$	- 247 kJ.mol^{-1}
$CO + 3\ H_2 \leftrightarrow CH_4 + H_2O$	- 206 kJ.mol^{-1}
$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$	- 165 kJ.mol^{-1}
Steam-methane reforming reactions	
$CH_4 + H_2O \leftrightarrow CO + 3\ H_2$	+ 206 kJ.mol^{-1}
$CH_4 + 0.5\ O_2 \rightarrow CO + 2\ H_2$	- 36 kJ.mol^{-1}

There are heterogeneous reactions between the carbon from the biomass and the gas atmosphere as well as homogeneous reactions between the gases. These homogeneous reactions can occur between the reactive gases and the produced gases, or between several produced gases.

It can be noted that the reaction between carbon and the gasifying agent, i.e. CO_2 or H_2O, is endothermic. This explains the energy required for the gasification process described in the section presenting the gasifier technologies.

3.2.2. Factors influencing the gasification

Biomass gasification can be carried out using different gasifying environments. Table 3 lists possible gasifying agents (air, oxygen, steam and carbon dioxide) and the characteristics of each one. Combinations of several gasifying agents can also be used. The gaseous environment during gasification influences the gasification process, in particular, the repartition of the products and the energy content of the resulting gas [15].

Table 3. Characteristics of gasifying agents [24].

Gasifying agent	Characteristic
Air	- Partial combustion for heat supply of gasification - Moderate char and tar content
Oxygen	- Enhanced carbon conversion characteristics - Enriched H_2, CO and CH_4 in producer gas and reduced tar levels
Steam	- Improved heating value of producer gas (10-15 $MJ.Nm^{-3}$) - Enriched H_2 in producer gas
Carbon dioxide	- High heating value of producer gas - High concentration of H_2 and CO in the producer gas and reduced CO_2

In terms of kinetics, at equal oxygen content in the gas flow, steam gasification is faster than CO_2 gasification [25]. For example, in their study on woodchip char at 900 °C, Ahmed *et al.* [26] observed that the use of steam instead of CO_2 divides the gasification time by almost three and increases the gasification rate by a factor of almost two.

For both gasifying agents, the reaction rate increases with the steam or CO_2 partial pressure increase. An example from Marquez-Montesinos *et al.* is shown in Figure 6 for the gasification of grapefruit skin char at different steam partial pressures.

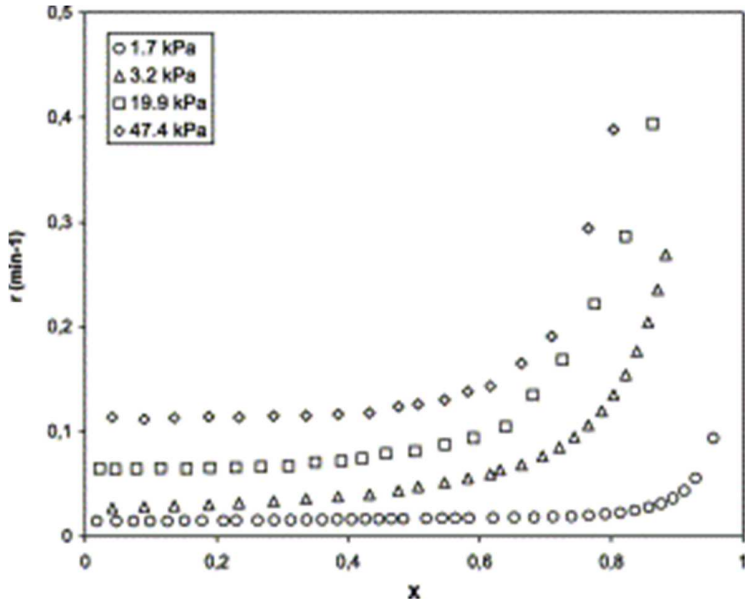

Figure 6. Reactivity versus conversion curves for steam gasification of grapefruit skin char at different partial pressures of steam (Reproduced with permission from [27]).

In the same way, the reaction rate increases when the gasification temperature increases. An example is given in Figure 7 from the same study from Marquez-Montesinos *et al.* under a CO_2 atmosphere.

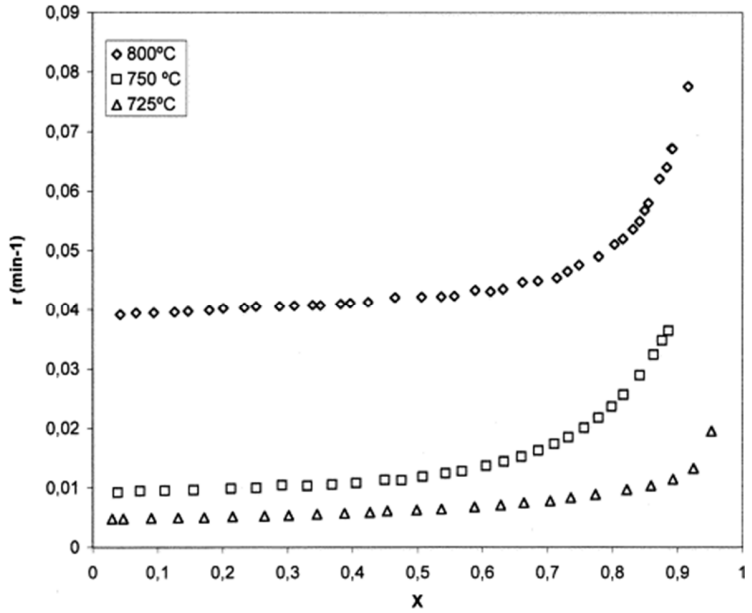

Figure 7. Reactivity versus conversion curves for CO_2 gasification of grapefruit skin char at different temperatures (Reproduced with permission from [27]).

In identical operating conditions, biomass samples can have different kinetic behaviours. For example, Dupont *et al.* [28] measured the reactivity of 20 biomass species of various types — wood, short rotation coppice and forestry, agricultural residue and microalgae— in steam gasification experiments performed in a thermogravimetric analyzer at 800 °C. They found a factor of more than 30 between the reactivities of the fastest and the slowest biomass samples, with gasification times ranging from a few minutes to several hours. The reactivity values are presented in Figure 8.a.

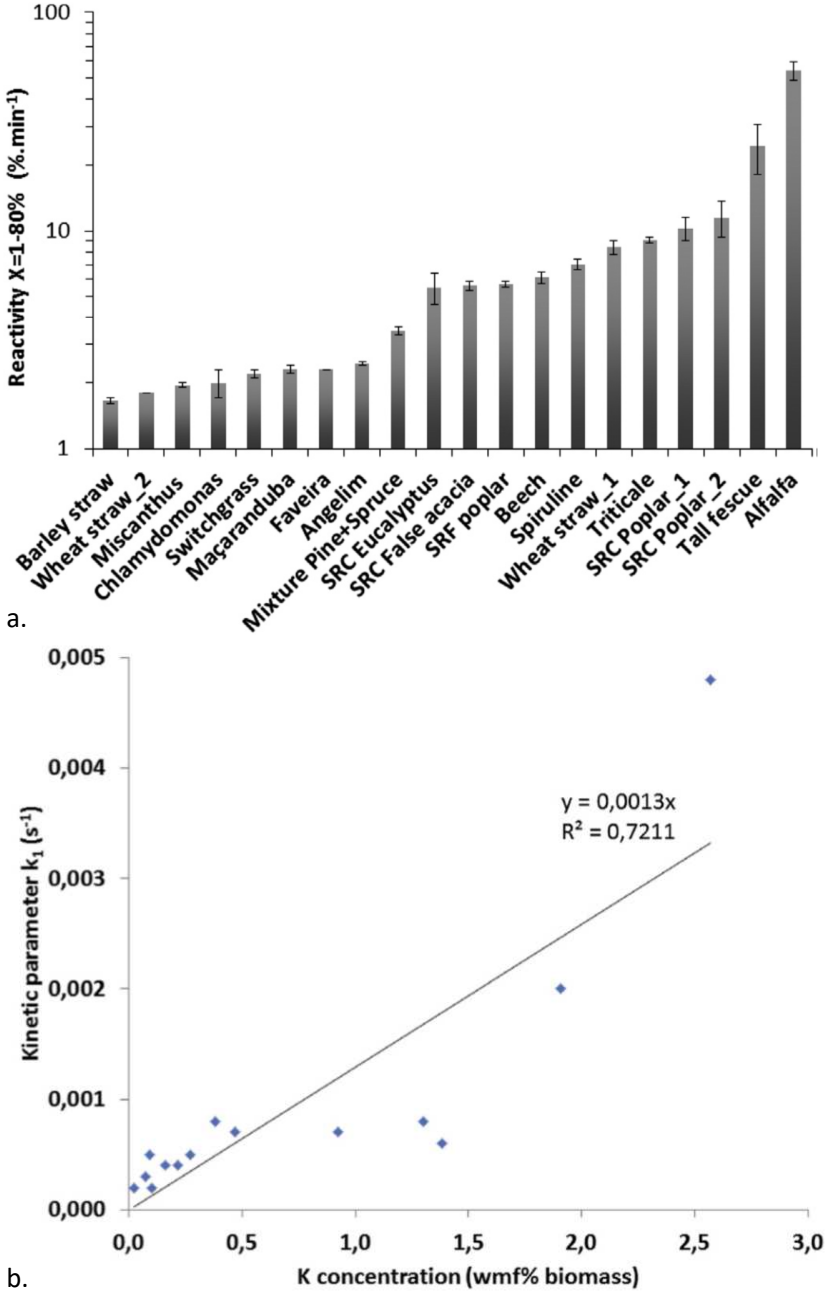

Figure 8. a. Reactivity between 1 and 80% of conversion of several biomass samples; b. Correlation between their kinetic parameter k_1 (where the conversion is $X(t)=k_1t$) and potassium concentration (Reproduced with permission from [28]).

Other parameters than CO_2 or H_2O partial pressure and temperature can affect the reactivity of the chars. This can occur including in conditions where only the chemical reaction is limiting, i.e. where heat and mass transfer do not play a role. The two main parameters mentioned in the literature are the morphological structure of the char and its inorganic material composition [25]. As synthesized in Di Blasi's review [25], the morphological structure is particularly influenced by the release of the volatile species during the pyrolysis which is controlled by the operating conditions of this step. It is shown that high heating rate pyrolysis produces a char that is more reactive in gasification than low heating rate pyrolysis. Chars from low heating rate pyrolysis keep their natural porosity while chars from high heating rate pyrolysis form larger cavities (Figure 9) [25,29]. This larger surface area in the case of high heating rate pyrolysis along with the higher content in oxygen and hydrogen results in more available active sites [30].

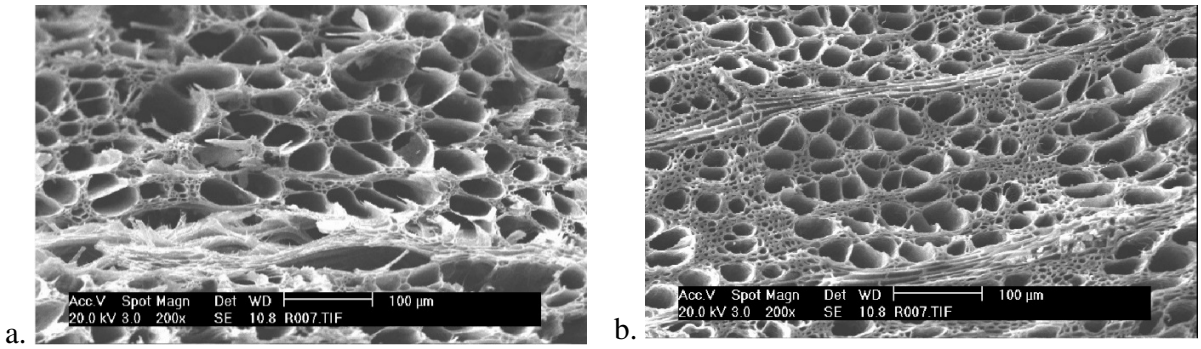

Figure 9. SEM observations of beech chars produced from: a. high heating rate pyrolysis (100 °C.s^{-1}), b. low heating rate pyrolysis (0.05 °C.s^{-1}) (Reproduced with permission from [29]).

It seems that, for similar conditions for the production of the char, the influence of the morphological structure is weaker than the influence of the inorganic composition, though no clear conclusion is given in the literature [32,33]. The differences in terms of gasification

reactivity of the biomass samples, illustrated above in Figure 8 [28], are attributed to the differences in their inorganic composition. In particular, in that study Dupont *et al.* observed that biomass species that gasify fast are rich in potassium (**Figure 8**.a) whereas those that gasify slowly are rich in silicon or phosphorus.

The present work focuses on the effect of the inorganic elements on char gasification. These effects are discussed in detail in the following section.

4. The effects of inorganic elements on the gasification process

This section reviews the literature on the effects of inorganic compounds on gasification. It is designed to be as extensive as possible regarding biomass. It also includes references on other feedstocks such as graphite or coal. Indeed, several studies are conducted on these solid fossil fuels and can be relevant in the study of biomass. They are reported here mostly in the form of reviews and, more occasionally research articles of particular interest are cited.

The articles cited are reported in Table 4. They are organized by:

- gasifying agent: H_2O and CO_2;
- type of feedstock: biomass and graphite and/or coal;
- mode of preparation of the feedstock to highlight the effects of the inorganic compounds: raw biomass or char (i.e. inherent inorganic compounds), washed biomass or char (i.e. with removal of the inherent inorganic compounds), sample mixed with an inorganic compound in its solid form and sample impregnated with a solution of the inorganic compound.

Table 4. References on the effects of inorganic elements, organized by gasifying agent, type of feedstock and mode of addition of the inorganic compounds if necessary.

		H_2O		CO_2	
		Biomass	Graphite and/or coal	Biomass	Graphite and/or coal
Experimental works	Raw biomass or char	• Dupont, 2011 [34] • Dupont, 2016 [28] • González-Vázquez, 2018 [35] • Hognon, 2014 [36] • López-González, 2014 [37] • Romero Millán, 2019 [38]	—	• DeGroot, 1990 [39] • Kannan, 1990 [40] • Link, 2010 [41] • Strandberg, 2017 [42] • Umeki, 2012 [43]	—
	Washed biomass or char	—	—	• Jiang, 2017 [44] • Kannan, 1990 [40] • Kramb, 2017 [45] • Zahara, 2018 [46]	—
	Mixed with solid inorganic compound	—	• Hüttinger, 1986a [47] • Hüttinger, 1986b [48] • Wen, 1980 [49]	• Arnold, 2017 [50] • Bach-Oller, 2019 [51] • Jiang, 2017 [44]	• Wen, 1980 [49]
	Impregnated with inorganic solution	• Feng, 2018a [52] • Lv, 2016 [53] • Yip, 2009 [54] • Zhang, 2008 [55]	• Delannay, 1984 [56] • Meijer, 1994 [57]	• Bach-Oller, 2019 [51] • Bennici, 2019 [58] • Bouraoui, 2016 [59] • DeGroot, 1984 [60] • Feng, 2018b [61] • Huang, 2009 [62] • Kirtania, 2017 [63] • Kramb, 2016	• Struis, 2002 [67] • Ding, 2017 [68]

		[64] • Kramb, 2017 [45] • Lahijani, 2013 [65] • Perander, 2015 [66]
Reviews	• Baker, 1984 [17] • Arnold, 2019 [70] • McKee, 1983 [71] • Nzihou, 2013 [72]	• Moulijn, 1984 [69]

Concerning experimental works on biomass, it can be noted that more studies have been published on CO_2 gasification than on steam gasification. In particular, studies under a CO_2 atmosphere cover a wider range of contact modes between the biomass and the inorganic compounds. This can be explained by the fact that producing a steam atmosphere is more challenging experimentally than working with a CO_2 bottle.

4.1. Assessment of the inorganic effects on char gasification

4.1.1. Effects of all inorganic compounds

4.1.1.1. Methodologies used in literature

It is shown that, unlike pyrolysis kinetics, gasification kinetics cannot be explained by the macromolecular composition of the biomass [37,38]. On the contrary, some inherent inorganic elements are known to have a significant influence on char gasification kinetics. To highlight the catalytic and inhibitory effects of inorganic elements, several methods are applied in the literature. Studies use raw biomass or biomass char [28,34–42], biomass or char washed with deionized water and/or with acid to remove the inherent inorganic matter [40,44–46,52–54], or biomass or char with added inorganic compounds [40,44,45,50,51,53,55,57,59–61,63–66,73]. The latter can be prepared through solid mixing [44,50,51,73] or through impregnation with a

solution containing the inorganic compound [45,51,53,55,57,59–61,63–66,73]. In the case of washed samples and impregnated samples a particular attention should be given. In particular, the char physical properties should not be affected to not distort the conclusions on inorganic effects. Moreover, inorganic compounds used for impregnation can change form when they crystallize. For example, a K_2CO_3 solution could induce the presence of K bonded to the biomass through ion exchange and $KHCO_3$ crystals as well as K_2CO_3 crystals in the dried sample [51,64]. However, impregnation is the major addition method used in literature since it is simple to carry out and allows a close contact between the inorganics and the biomass.

Few authors compared the effects of various addition methods. Elliott *et al.* [74] and Bach-Oller *et al.* [51] observed a slightly stronger catalytic effect of K_2CO_3 in the case of impregnation compared to dry mixing. However, Elliott *et al.* did not observe this difference in the case of Na_2CO_3. The curves for both inorganic compounds from Elliott *et al.* are shown in Figure 10. These results suggested an activity through the gas phase. The slight decrease in activity with dry mixing could be explained by a lower volatilization of the inorganic compound in this case due to mass transfer limitations.

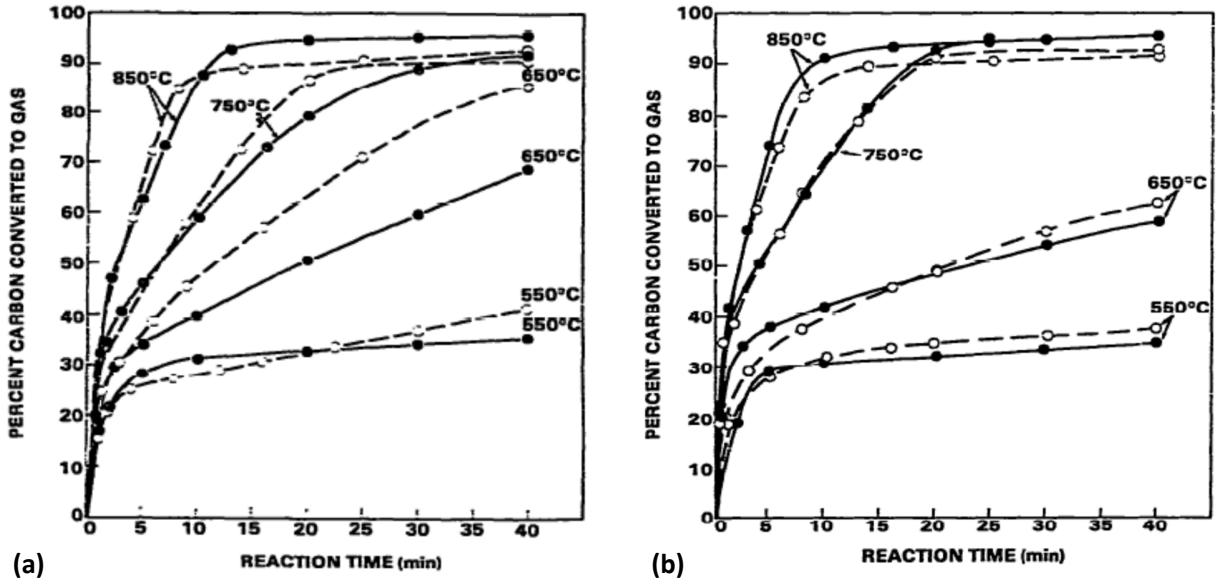

Figure 10. Carbon conversion to gas for the catalyzed steam gasification of Douglas fir with dry-mixed (solid line) and solution impregnated (dotted line) (a) potassium carbonate and (b) sodium carbonate (Reproduced with permission from [74]).

4.1.1.2. Catalytic effects

From these studies, it appears that alkali and alkaline earth metals (AAEMs) tend to have a catalytic effect that enhances biomass gasification kinetics. More specifically, alkali metals, and in particular K which is more present in biomass than Na, are reported to be more active than alkaline earth metals. No significant effect is observed for Mg in the literature [46,55]. The catalytic activity of AAEMs are reported to be, in decreasing order, K, Na, Ca and Mg [54,55,62]. An example of the obtained curves of carbon conversion as a function of temperature for several catalysts is given in Figure 11 [62] during the CO_2 gasification of Chinese Guangzhou fir. It can be noted that González-Vázquez *et al.* [35], as well as Bennici *et al.* [58], did not observe a catalytic effect of Ca but a rather negative effect on gasification kinetics under steam

and CO_2 atmospheres respectively. However, the conclusion of González-Vázquez *et al.* comes from a correlation analysis on several pure biomasses and not from a phenomenological analysis. Observations from Bennici *et al.* come from experiments on impregnated washed biomass but no further explanations are given in the results.

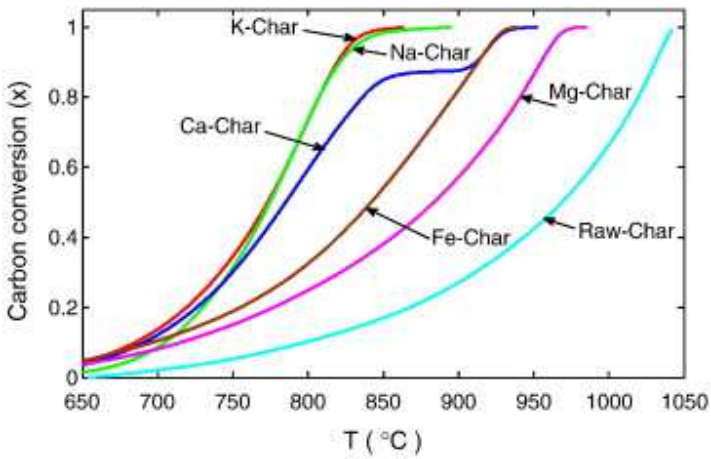

Figure 11. Carbon conversion during the CO_2 gasification of chars from Chinese Guangzhou fir catalyzed with different inorganic elements (Reproduced with permission from [62]).

Catalytic gasification uses this effect to improve the gasification process. Catalysts usually studied are compounds of AAEMs as well as some heavy metal compounds such as Fe-compounds and Ni-compounds [70]. Among these elements, those inherent to the biomass are mainly K, Ca and Mg, the others are usually found in low amounts in the biomass. Therefore, biomass species naturally rich in these elements —especially K which has the highest catalytic activity— tend to have the highest gasification reactivity.

4.1.1.3. Inhibitory effects

However, other elements present in the biomass can have the opposite effect and slow the gasification down. In particular, Al, Si and P are reported to inhibit the gasification [28,41,55,59,70]. In the case of lignocellulosic biomass, Al and P are usually found in low amounts whereas Si can reach high concentrations.

From these general observations of the effects of the inorganic elements on gasification, as well as from the knowledge of the typical inorganic composition of lignocellulosic biomass, the importance of K and Si can be highlighted. Understanding the influence of compounds of these two elements is of particular interest. Therefore it is the focus of the following sections.

4.1.2. The specific effects of K and Si

Catalysts containing K used in gasification are mostly K_2CO_3 and KOH which are compounds naturally found in biomass [70]. KNO_3 or KCl are also studied [45,59,65]. Kramb *et al.* [64] observed the same effect on CO_2 gasification kinetics with the addition of K by KNO_3 as with the addition of K_2CO_3. The result for K-compounds is in accordance with the observations of Hüttinger *et al.* [47,48] who found the following relative activity : KOH ~ K_2CO_3 ~ KNO_3 > K_2SO_4 > KCl. They also demonstrated that the intermediate species KOH was formed from all salts.

It is important to note that the K catalytic effect can be influenced by the presence of Ca. Indeed, apparent promoting effects can be obtained when combining K and Ca catalysts [70,72]. This promoting effect occurs until an optimal concentration of $CaCO_3$ added with K_2CO_3 to the biomass. After this optimum is reached, further addition of $CaCO_3$ can be detrimental [70].

The inhibiting effect of Si is observed with inherent Si from the biomass [28,41,51,55,70] and with Si from the bed material or added for investigation purpose [40,50,59].

4.2. Proposed mechanisms for the K-catalysis

The catalytic effects of AAEMs, in particular K, and the inhibiting effect of elements such as Si are well described in the literature. However, authors propose hypotheses but the mechanisms of such effects remain poorly known. This section presents first the inorganic compounds behaviour during the char formation through pyrolysis and then the proposed mechanisms of action of these inorganics during gasification.

Several mechanisms are proposed in the literature to explain the catalysis of gasification by K-compounds. Authors agree on the fact that the alkali compounds added as catalysts or inherent to the biomass are not the active compounds. However, there is no consensus concerning the active intermediate. The active species mentioned in literature reviews [70,72] are K_xO_y (non-stoichiometric), K_2O, K-O-C, K-C and C_nK.

4.2.1. Mechanism with intercalation compounds

One of the mechanisms suggested in the literature is a mechanism involving intercalation compounds C_nK. Intercalation compounds C_nK are compounds where potassium is inserted between two graphitic layers. Biomass chars are disorganized carbon structure but contain a fraction of graphitic structures. McKee [71] mentions the catalytic cycle involving an intercalation compound C_nK, possibly $C_{48}K$ or $C_{60}K$, suggested by Wen [49]. A mechanism is described for CO_2 as a gasifying agent as well as for steam. In both cases, there four steps that are not elementary reactions. First, there is a carbothermic reduction of the carbonate to obtain metallic potassium and carbon monoxide (Eq. 1.). Then, metallic potassium reacts with the carbon to form the intercalation compound C_nK (Eq. 2.). In the case of steam gasification, steam reacts with the intercalation compound C_nK which form nC, KOH and H_2 (Eq. 3.). Then, the formed potassium hydroxide reacts with carbon monoxide to regenerate the carbonate and

produce dihydrogen (Eq. 4.). In the case of CO_2 gasification, the compound $(2C_nK).OCO$ is formed and transforms into CO and $(2nC).K_2O$ (Eq. 5.). The latter reacts with an additional CO_2 molecule to form $(2nC).K_2CO_3$ and to finally regenerate K_2CO_3 (Eq. 6.).

$$K_2CO_{3(c)} + 2\ C_{(c)} = 2\ K_{(g)} + 3\ CO_{(g)} \quad \text{(Eq. 1)}$$

$$2\ K_{(g)} + 2\ nC_{(c)} = 2\ C_nK_{(c)} \quad \text{(Eq. 2)}$$

$$2\ C_nK_{(c)} + 2\ H_2O_{(g)} = 2\ nC_{(c)} + 2\ KOH_{(g)} + H_{2(g)} \quad \text{(Eq. 3)}$$

$$2\ KOH_{(g)} + CO_{(g)} = K_2CO_{3(c)} + H_{2(g)} \quad \text{(Eq. 4)}$$

$$2\ C_nK_{(c)} + CO_{2(g)} = (2C_nK).OCO_{(c)} = (2nC).K_2O_{(c)} + CO_{(g)} \quad \text{(Eq. 5)}$$

$$(2nC).K_2O_{(c)} + CO_{2(g)} = (2nC).K_2CO_{3(c)} = 2\ nC_{(c)} + K_2CO_{3(c)} \quad \text{(Eq. 6)}$$

However, there is no direct evidence of the formation of C_nK during gasification to our knowledge. It is shown that these compounds can be formed at moderate temperature, i.e. around 250 °C, and can be detected through X-ray diffraction (XRD). However, these compounds are not stable at gasification temperatures, i.e. above 700 °C, and they are hydrolyzed by steam at ambient temperature [71,75]. Therefore, such a mechanism is not likely in the gasification conditions of the present case.

4.2.2. Mechanisms with a mechanical action

Physical effects of the alkali compounds are also discussed in the literature. Alternatively to the chemical action of intercalation compounds, they could also have a mechanical action. It is known that the intercalation of K increases the distance between graphitic planes [76], as illustrated in Figure 12. Therefore, it is suggested that intercalation of AAEMs in the graphitic layers could open up the structure and make it more easily available for the reaction [71].

However, as discussed previously, the formation of such compounds in gasification conditions is unlikely.

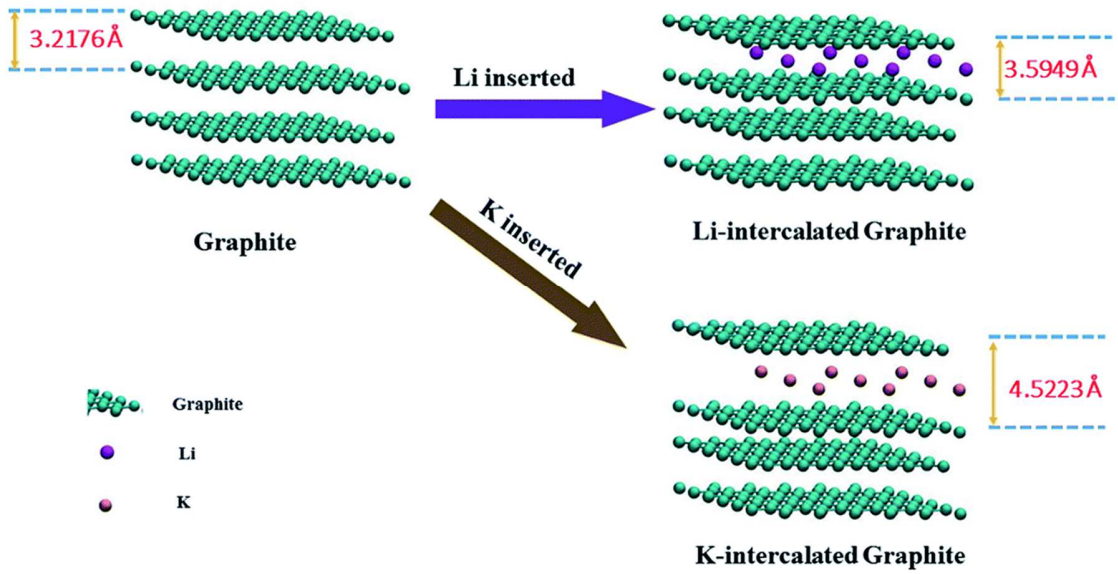

Figure 12. Li and K intercalation in graphite with the resulting interlayer spacing (Reproduced with permission from [76]).

Another mechanical action could be through swelling. Elliott *et al.* [74] observed that AAEMs can induce swelling during the pyrolysis which could increase the number of active carbon sites available for the gasification reaction. However, gasification of Douglas fir with Na_2CO_3 at two concentrations, 1.5×10^{-3} and 3.0×10^{-3} mole Na per g sample, showed similar improved rates while only the higher Na_2CO_3 concentration induced swelling of cellulose samples. Similarly, Na_2CO_3 added to Douglas fir through dry-mixing has a catalytic effect while it does not induce swelling. Therefore, they demonstrate that the swelling phenomenon is not involved in the catalysis of gasification by AAEMs.

4.2.3. Mechanisms for a carbon atom

McKee [71] proposes a mechanism in three steps from potassium carbonate. As in the intercalation mechanism, the cycle starts with the carbothermic reduction of the carbonate to obtain metallic potassium and carbon monoxide (Eq. 1.). McKee suggests that it is the limiting step. Then, metallic potassium reacts with steam which forms potassium hydroxide and dihydrogen (Eq. 7.). Finally, the formed potassium hydroxide reacts with carbon monoxide to regenerate the carbonate and produce dihydrogen, similarly to the intercalation mechanism (Eq. 4.). A similar reaction pathway is proposed for CO_2 as a gasifying agent (Eq. 8. and 9.) and both can also be applied to sodium carbonate.

$$K_2CO_{3(c)} + 2\ C_{(c)} = 2\ K_{(g)} + 3\ CO_{(g)} \qquad \text{(Eq. 1)}$$

$$2\ K_{(g)} + 2\ H_2O_{(g)} = 2\ KOH_{(g)} + H_{2(g)} \qquad \text{(Eq. 7)}$$

$$2\ KOH_{(g)} + CO_{(g)} = K_2CO_{3(c)} + H_{2(g)} \qquad \text{(Eq. 4)}$$

$$2\ K_{(g)} + CO_{2(g)} = K_2O_{(c)} + CO_{(g)} \qquad \text{(Eq. 8)}$$

$$K_2O_{(c)} + CO_{2(g)} = K_2CO_{3(c)} \qquad \text{(Eq. 9)}$$

Equations (Eq. 1) and (Eq. 7) are demonstrated through detection of a larger amount of $K_{(g)}$ that would be expected from dissociation of K_2CO_3 alone, and by the decrease of $K_{(g)}$ and formation KOH after steam injection. Little information is available on the kinetics of Equations (Eq. 7) and (Eq. 4) but they have strongly negative free energies at gasification temperatures indicating that they are thermodynamically feasible.

Moulijn *et al.* [69] propose a mechanism from the literature review for the case of CO_2 gasification, which could also be applied to gasification in H_2O or O_2. This mechanism starts with the carbothermic reduction of K_2CO_3 that forms metallic K (Equation (Eq. 1)). The gasification agent then transfers oxygen to K to form K_xO_y. This compound reacts with an additional O that

will afterward reacts with solid C to form CO as presented in Equations (Eq. 10) and (Eq. 11). However, Moulijn *et al.* state that "the detailed structure of K_xO_y, and K_xO_{y+1} is not clear".

$$K_xO_y + CO_{2(g)} = CO_{(g)} + K_xO_{y+1} \quad \text{(Eq. 10)}$$

$$K_xO_{y+1} + C_{(c)} = K_xO_y + CO_{(g)} \quad \text{(Eq. 11)}$$

In conclusion, these mechanisms are a first approach to understand the behaviour of alkali carbonates in the catalysis of steam gasification. It highlights that the general role of potassium is to bring the gasifying agent into contact with the carbon. However, char is not constituted of single carbon atoms. Carbon atoms are linked to each other in structures with various levels of organization, and to other atoms, mainly hydrogen and oxygen, especially on char surface. Therefore, some authors propose more detailed mechanisms mentioning the active sites on char surface, i.e. the functional groups or particular carbon atoms of the structure that are available for reaction.

4.2.4. Mechanisms for carbon structures

The work of Delannay *et al.* [56] on graphite suggests a mechanism following four steps illustrated in Figure 13. First, water reacts with one carbon from the graphitic layer to form a phenol group. This phenol group then reacts with KOH to form a K-O-C phenolate group. With heat, the latter decomposes to either metallic K and CO or to K_2O, CO and C. Finally, KOH is regenerated from the reaction of K_2O with H_2O. The observation of the produced gases supports this mechanism. Two stages can be identified: the production of hydrogen and hydrocarbons at high rate corresponding to step 1 and then the production of CO and H_2 at a slower rate corresponding to steps 2 to 4 with step 3 being limiting.

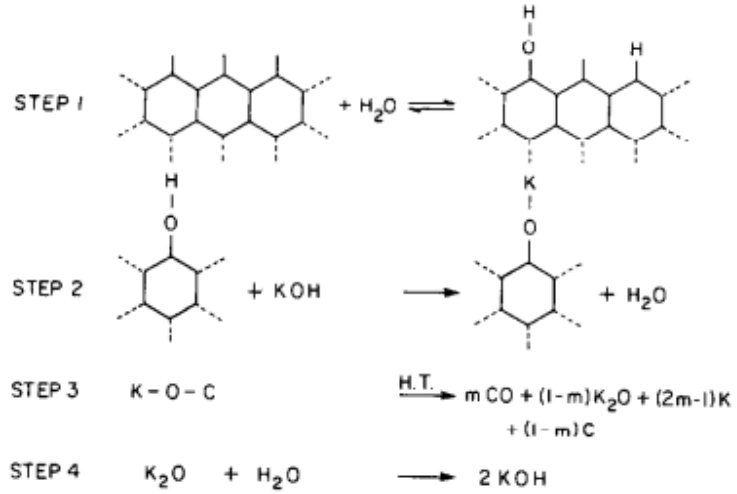

Figure 13. Mechanistic model for the reaction of water with graphite in the presence of KOH (Reproduced with permission from [56]).

Feng *et al.* [61] support also the idea of the K-O-C group formation as an active site. They worked with biomass chars impregnated with AAEMs before or after the pyrolysis, i.e. "AAEM pre-loaded biochar" or "AAEM post-loaded biochar" respectively. They proposed mechanisms for each case as illustrated in Figure 14.

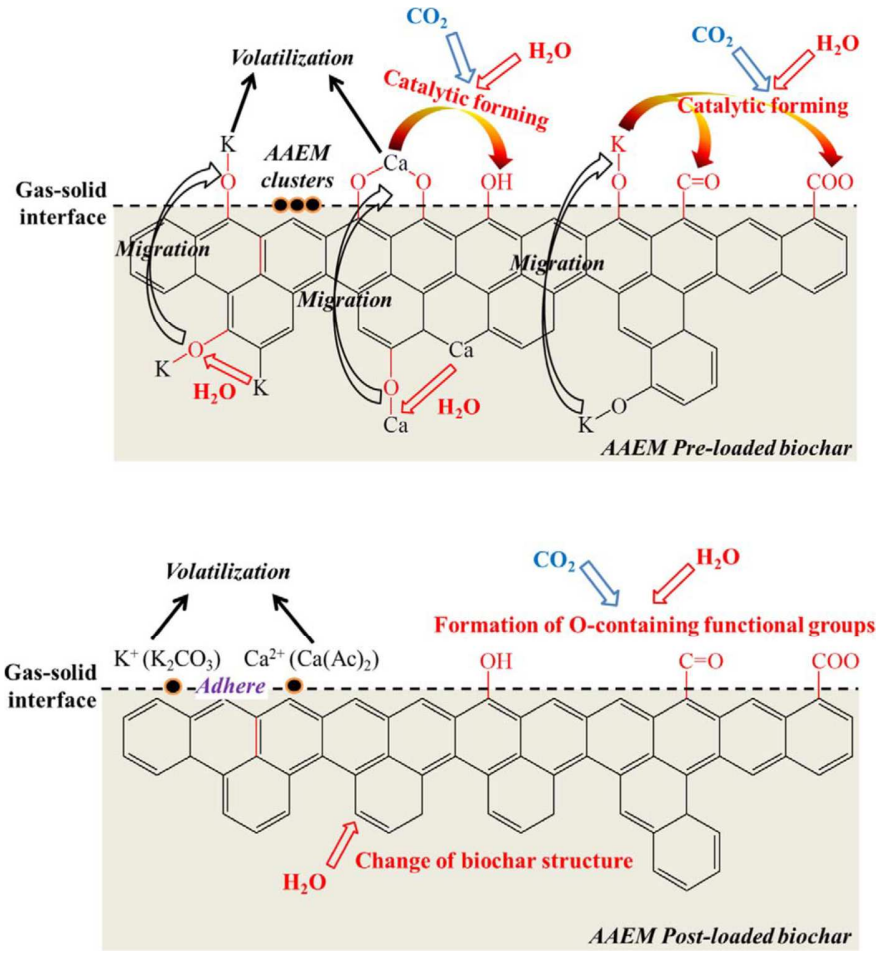

Figure 14. Mechanisms of pre-loaded AAEMs and post-loaded AAEMs on biochar (Reproduced with permission from [60]).

In the case of pre-loaded biochar, i.e. char from the pyrolysis of an impregnated biomass, AAEM are linked to the carbon matrix. Unlike in the mechanism of Delannay *et al.*, where the gasifying agent reacts on a carbon, here the reaction occurs on K-matrix sites to form the K-O-C groups inside the carbon matrix. The AAEMs migrate to the gas-solid interface which implies that these groups break and form again, contributing to the condensation of aromatic rings, i.e. the formation of larger rings from small ones. Moreover, due to their valence state, K is bonded to

only one carbon site while Ca is bonded to two. Therefore, K is less strongly bonded to the carbon matrix so the bond can easily break to provide active sites for the aromatic condensation which explains the stronger effect of K compared to Ca.

In the case of post-loaded biochar, AAEMs are present only on the surface and are not incorporated into the carbon matrix. The fact that bonds are weaker facilitates the volatilization of the AAEMs and explains the lower reactivity of these chars.

4.2.5. Explanation of the reactivity changes at high conversion

For some biomass species, an acceleration of the gasification is observed at high conversion [28,34,55,59]. For example, results at 800 °C from Bouraoui *et al.* presented in Figure 15 show that, for samples of impregnated beech wood, a high K/Si ratio leads to an increase in reactivity with conversion.

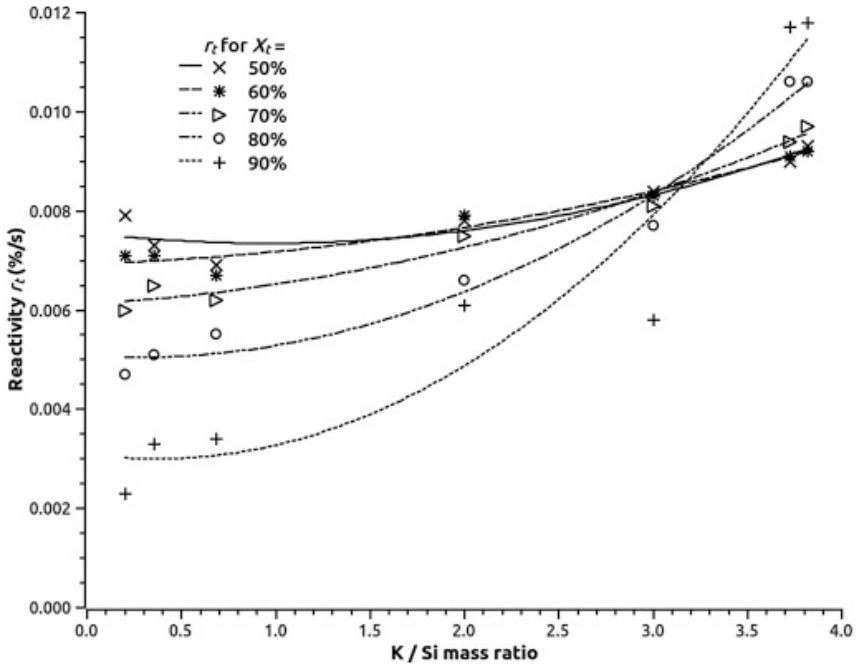

Figure 15. Reactivity at 800 °C at several conversion values as a function of the K/Si ratio of samples of impregnated beech wood (Reproduced with permission from [59]).

This gasification acceleration seems to be linked to significant alkali content and could be explained by several factors. At the end of the gasification, the alkali compounds are more concentrated which could enhance the catalytic effect [34,55]. It could also be due to the sudden disintegration of the porous structure of the char, leading to a higher active surface area available to react. Lastly, it could be related to the release of alkali metals previously inactive, such as intercalated alkali [55].

On the opposite, for other biomass species with high alkali content — in particular K — the gasification rate strongly decreases at very high conversion values. This behaviour can be observed in the case of K catalysis and can be attributed to the collapse of the numerous pores and channels formed which induces a decrease of the surface available for the reaction [70]. It

could also be explained by interactions between AAEMs and silica to form silicates either making the AAEM compounds not available for catalysis or forming liquid phases that encapsulate the remaining char [41,42].

4.3. Proposed mechanisms for the inhibiting effect of Si

In literature there seems to be an agreement about the fact that the inhibiting effect of Si on gasification is rather due to an inhibition of the catalysis from other elements. It is shown that Al, Si and P compounds can react with the catalytic AAEM compounds [28,46,55,70]. They form aluminates, silicates and phosphates with the AAEMs which are stable and non-catalytic compounds. Subsequently, the AAEMs are not available anymore to catalyze the gasification.

Some studies also report that melted phases containing Si can encapsulate the remaining char. For example, as discussed in the previous section, Strandberg *et al.* [42] explained the low reactivity at high conversion of a Si- and K-rich wheat straw by the melted ashes that induced a physical inhibition (Figure 16).

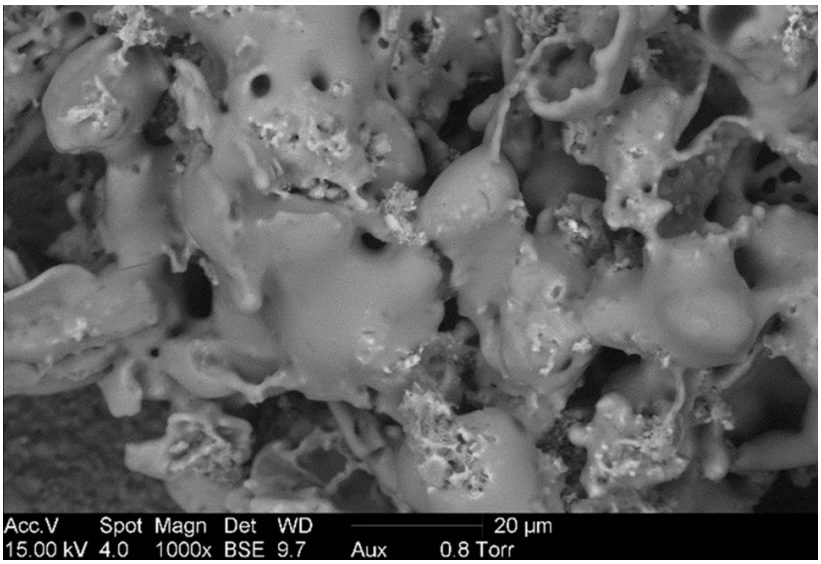

Figure 16. SEM observation of a wheat straw char at 90% gasification conversion, with melted ashes (Reproduced with permission from [42]).

However, few studies are conducted to directly investigate the mechanism of action of Si on the gasification kinetics. Published works focused either on the gasification kinetics or on the agglomeration issues related to this element. Therefore, the previous conclusions came from studies highlighting the effects of Si and looking at literature results from agglomeration publication. To our knowledge, there is no direct study investigating both the gasification kinetics and the residue characterization with Si.

Finally, the apparent promoting effect of Ca on K-catalysis is attributed to the preferential reaction of this element with silica to form silicates [50]. K then avoids deactivation and can keep its catalytic activity.

4.4. Proposed models

To describe the gasification of biomass, a first approach can be to simulate the system at its thermodynamic equilibrium. However, this method is reported to give good results in the case of high temperature entrained flow gasifiers but not in the case of fluidized bed reactors [15]. In this last case, which is the case related to the present review, the system does not reach its thermodynamic equilibrium. Therefore, kinetic models have to be designed.

Various kinetic models are used in the literature to describe the steam gasification of biomass. Generally, such kinetic models are of the form of Equation (Eq. 1212).

$$r = k(T) \times g(P_{H_2O}) \times f(X) \quad \text{(Eq. 1212)}$$

Where k(T) describes the dependence on the reaction temperature T, f(X) is a function of the conversion X that takes into account the change in the char structure during the reaction, and $g(P_{H2O})$ describes the dependence on the partial pressure of the steam which is the gasifying agent.

The temperature dependent factor k(T) follows an Arrhenius law (Eq. 13.).

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad \text{(Eq. 13)}$$

With k_0 a pre-exponential constant and E_a the activation energy.

The steam partial pressure dependent factor $g(P_{H2O})$ follows a power law (Eq. 14.).

$$g(P_{H_2O}) = {P_{H_2O}}^n \quad \text{(Eq. 14)}$$

For the function f(X), there is no consensus in literature about its form. Different models can be used which depend on the conditions. Models commonly used for f(X) are listed in Table 5 which is adapted from Romero Millán *et al.* [38].

Table 5. Common models for the surface function f(X) (Adapted from [38]).

Model	f(X)
0th order	1
1st order – Volumetric model	$1 - X$
2nd order	$(1 - X)^2$
3rd order	$(1 - X)^3$
n^{th} order	$(1 - X)^n$
One dimensional	$\frac{1}{2X}$
Two dimensional	$\frac{1}{-\ln(1 - X)}$
Three dimensional	$\frac{3}{2} \times \frac{(1 - X)^{\frac{2}{3}}}{1 - (1 - X)^{\frac{1}{3}}}$
Contracting area	$2 \times (1 - X)^{\frac{1}{2}}$
Contracting volume – Shrinking core model – Grain model	$3 \times (1 - X)^{\frac{2}{3}}$
Random pore model	$(1 - X) \times \sqrt{1 - \psi \times \ln(1 - X)}$

Volumetric model, grain model and random pore model, sometimes including modifications, are the most used models for steam gasification [34–38,55,77].

However, these models do not achieve a good description of the experimental data for biomass samples showing catalytic effects.

To take these effects into account, authors have proposed modifications to the models presented above. Table 6 summarizes the available kinetic models taking into account the effects of inorganic elements on gasification [34,36–38,43,50,55,64,67,68].

Table 6. Gasification kinetic models taking into account the effects of inorganic elements.

Model	Gasification agent – Feedstock	Reference
Grain model with additional factor $a_i = 0.1812\frac{m_K}{m_{Si}} + 0.5877$	Steam – Biomass	Dupont, 2011 [34]
If $\frac{K}{Si+P} > 1$, 0th-order model If $\frac{K}{Si+P} < 1$, 1st-order/volumetric model	Steam – Biomass	Hognon, 2014 [36]
If $\frac{K}{Si+P} > 1$, 0th-order model $f(X) = 0.15 \times \frac{K}{Si+P} + 0.7$ If $\frac{K}{Si+P} < 1$, 1st-order/volumetric model $f(X) = (1 - X)^{-1.62\times\frac{K}{Si+P}+1.64}$	Steam – Biomass	Romero Millán, 2019 [38]
Grain model with additional term $k_a \times X^{n_a}$ with $n_a = 0.254[Ca] + 3.4 \times 10^{-2}$	Steam – Biomass	López-González, 2014 [37]
Sum of rates of three regimes: Catalytic with deactivation of catalyst, $f(X) = \exp(-\xi X^2)$ Non-catalytic, 1st-order/volumetric model Catalytic with no deactivation of catalyst, 0th-order model	CO_2 – Biomass	Umeki, 2012 [43]
Random pore model with additional factor $1 + (cX)^p$ where c and p are correlated to K	Steam – Biomass	Zhang, 2008 [55]
Random pore model with additional factor $1 + c \times (1 - X)^p$	CO_2 – Coal	Arnold, 2017 [50]
Random pore model with additional factor $1 + (g + 1) \times (bt)^g$	CO_2 – Coal	Struis, 2002 [67]
Sum of rates correlated to [Ca] and to [K], with for each: Random pore model with additional factor $1 + (g + 1) \times (bt)^g$ where ψ, b and g are correlated to the metal concentration	CO_2 – Biomass	Kramb, 2016 [64]
Random pore model where $\psi = f \times \exp(-\phi \times \tau)$, ϕ is a coefficient and τ is a dimensionless time	CO_2 – Coal	Ding, 2017 [68]

These modified models describe well gasification kinetics with catalytic effects due to inorganic elements. However, they are semi-empirical models with no true physical meaning. Therefore, a better understanding of the phenomena involved in catalysis and catalyst inhibition should allow the design of a unified phenomenological model. Besides, some models are developed for CO_2 as a gasifying agent but are not validated to describe steam gasification as the phenomena occurring seem to differ according to the gasifying agent. It is for example the case of the three regime model designed by Umeki *et al.* [43].

5. Trends and Perspectives

In the context of the pyrogasification of biomass, the inorganic content seems to be the most influential parameter on the gasification process but no clear conclusion is available in the literature. For instance, alkali and alkaline earth metals (AAEMs) have a catalytic effect on the gasification reaction, with varying degrees, while Al, Si and P have an inhibiting effect. By crossing this information with the typical inorganic composition of biomass species, it appears that the case of K and Si are of particular interest. However, even though the effects are long known, the mechanisms behind them are still little known.

In the case of the K-catalysis, several mechanisms are proposed with various degrees of detail but none of them makes consensus. Several experimental works and proposed mechanisms reviewed suggest that the catalytic activity is due to the formation of gaseous intermediates. However, the gas phase is usually not directly analyzed probably due to the difficulty of such analysis. It would be interesting to confirm the formation of gaseous intermediates, for example with an online mass spectrometer placed after the gasification system.

In the case of the inhibition of the gasification by Si, authors tend to agree on the fact that it is rather an inhibition of the AAEM-catalysis. The mechanisms of action of these two elements on gasification are therefore linked.

This low level of knowledge on the mechanisms involving the inorganic compounds during the gasification of biomass has impacts at the process design level. It leads to working with kinetic models that can fail to describe the reaction of biomasses when their inorganic content is non-negligible. A long term major perspective is to design a gasification kinetic model that takes into account the inorganic elements influence and that is based on phenomenological parameters. Several models attempting to take this influence into account are available in literature. However, these models are semi-empirical, coming from correlations between the gasification rate or reactivity and the inorganic elements concentrations. The kinetic parameters have no physical meaning or they are not unified, i.e. there are several parameters depending on the conditions and not one equation for all biomass species. The perspective would be to have one single model for all biomass species with unified parameters correlated with physical values.

Even though K and Si were specifically considered in this review due to their high occurrence in biomass species and to their strong activity on gasification kinetics, the influence of other elements must be considered to achieve a proper description of the mechanisms involved. In particular, it has been demonstrated in literature that Ca, which is a main inorganic element in biomass, also interacts with SiO_2. It reacts preferentially with SiO_2 compared to K. The latter then remains available to catalyze the gasification. Moreover, Al and P can form stable compounds with K or Ca in the same way as Si. They are not often the major inorganic elements in biomass but they can reach significant concentrations in some species. These Ca, Al and P influences therefore seem to all be related to the capacity of K to be released and stay into the gas

phase around the carbon matrix. It would then be this capacity that would determine its catalytic effect. As a result, the physical value suggested to be introduced in a future kinetic model is the quantity of volatilized K.

This quantity of volatilized K could be obtained from calculations at thermodynamic equilibrium from the initial biomass composition. With an accurate database, these calculations would take into account the aforementioned reactions. However, the database still is poorly known in some crucial parts of the considered system, for example K-Ca equilibria.

To reach this long term perspective, shorter term perspectives can be suggested:

- The effect on biomass gasification kinetics of the addition of Ca-, P- and Al-species may be investigated.

- The reaction of K and Si inherent to the biomass species could be studied in more details to determine the composition of the resulting K-silicates and K-Si-containing liquids. In particular, quantification of the crystalline phases as well as of the composition of the amorphous phases could be conducted. Such study would help to determine the fraction of volatilized K, i.e. the remaining fraction of K after its reaction with SiO_2.

At a process level, the understanding of the K-catalysis mechanisms, will allow to control the phenomena in order to optimize the gasification process. Since SiO_2 strongly inhibits the K-catalysis, removing the SiO_2 fraction of the biomass would increase its gasification rate. Therefore, Si-rich species may be studied in order to identify if SiO_2 is located in a specific part of the plant that could be put aside. It could also be investigated if SiO_2 has a specific behavior during grinding that would allow removing it through sieving.

6. Conclusions

A promising non-traditional thermoconversion process for bioenergy production is gasification. However, and as far as agricultural residues are concerned, this process may be problematic since such biomasses can have high inorganic contents compared to traditionally used woods. Indeed, such elements can be detrimental to the gasification process by inducing slag formation and/or agglomeration of the gasifier bed. Besides, reactional mechanisms in the gasifiers as well as the corresponding kinetics are still not well elucidated. Empirically, this diversity of reactivity has been correlated to their char morphology but also and mainly to their inorganic content.

This review attempts to contribute to the understanding of the inorganic elements role during biomass steam gasification. In particular, the phenomena involving K and Si during the biomass gasification, evoked in literature, were synthesized, analyzed and compared, especially through the gas phase, and with particular focus on their influence on the reaction kinetics.

Funding

This research was funded by the Agence de l'Environnement et de la Maîtrise de l'Energie.

References

[1] European Parliament. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. 2009.

[2] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass. Fuel 2010;89:913–33. https://doi.org/10.1016/j.fuel.2009.10.022.

[3] Vassilev SV, Baxter D, Andersen LK, Vassileva CG, Morgan TJ. An overview of the organic and inorganic phase composition of biomass. Fuel 2012;94:1–33. https://doi.org/10.1016/j.fuel.2011.09.030.

[4] McKendry P. Energy production from biomass (part 1): overview of biomass. Bioresour Technol 2002;83:37–46. https://doi.org/10.1016/S0960-8524(01)00118-3.

[5] Bajpai P. Structure of Lignocellulosic Biomass. Pretreat. Lignocellul. Biomass Biofuel Prod., Springer, Singapore; 2016, p. 7–12. https://doi.org/10.1007/978-981-10-0687-6_2.

[6] Deglise X, Donnot A. Bois énergie - Propriétés et voies de valorisation. Tech Ing Énerg Renouvelables 2017.

[7] de Lasa H, Salaices E, Mazumder J, Lucky R. Catalytic Steam Gasification of Biomass: Catalysts, Thermodynamics and Kinetics. Chem Rev 2011;111:5404–33. https://doi.org/10.1021/cr200024w.

[8] Bamdad H, Hawboldt K, MacQuarrie S. A review on common adsorbents for acid gases removal: Focus on biochar. Renew Sustain Energy Rev 2018;81:1705–20. https://doi.org/10.1016/j.rser.2017.05.261.

[9] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification. Fuel 2013;105:40–76. https://doi.org/10.1016/j.fuel.2012.09.041.

[10] European Standards. Solid biofuels - Determination of ash content (EN 14775). 2009.

[11] International Organization for Standardization. Solid mineral fuels - Determination of ash (ISO 1171:2010). 2010.

[12] Arvelakis S, Jensen PA, Dam-Johansen K. Simultaneous Thermal Analysis (STA) on Ash from High-Alkali Biomass. Energy Fuels 2004;18:1066–76. https://doi.org/10.1021/ef034065+.

[13] Xiao R, Chen X, Wang F, Yu G. The physicochemical properties of different biomass ashes at different ashing temperature. Renew Energy 2011;36:244–9. https://doi.org/10.1016/j.renene.2010.06.027.

[14] Basu P. Chapter 5 - Gasification Theory and Modeling of Gasifiers. Biomass Gasif. Pyrolysis, Boston: Academic Press; 2010, p. 117–65. https://doi.org/10.1016/B978-0-12-374988-8.00005-2.

[15] Sikarwar VS, Zhao M, Fennell PS, Shah N, Anthony EJ. Progress in biofuel production from gasification. Prog Energy Combust Sci 2017;61:189–248. https://doi.org/10.1016/j.pecs.2017.04.001.

[16] Van Swaaij WPM. Gasification — the process and the technology. Resour Conserv 1981;7:337–49. https://doi.org/10.1016/0166-3097(81)90042-0.

[17] Baker EG, Mudge LK. Mechanisms of catalytic biomass gasification. J Anal Appl Pyrolysis 1984;6:285–97. https://doi.org/10.1016/0165-2370(84)80023-6.

[18] Dupont C, Boissonnet G, Seiler J-M, Gauthier P, Schweich D. Study about the kinetic processes of biomass steam gasification. Fuel 2007;86:32–40. https://doi.org/10.1016/j.fuel.2006.06.011.

[19] Khiari B, Jeguirim M. Pyrolysis of grape marc from Tunisian wine industry: Feedstock characterization, thermal degradation and kinetic analysis. Energies 2018;11:730–44. https://doi.org/10.3390/en11040730.
[20] Bridgwater AV. Pyrolysis of Biomass. In: Van Swaaij WPM, Kersten SRA, Palz W, editors. Biomass Power World Transform. Eff. Use, Singapore: Pan Stanford Publishing; 2015, p. 473–513.
[21] Kordoghli S, Paraschiv M, Tazerout M, Khiari B, Zagrouba F. Novel Catalytic Systems for Waste Tires Pyrolysis: Optimization of Gas Fraction. J Energy Resour Technol Trans ASME 2017;139. https://doi.org/10.1115/1.4034979.
[22] Di Blasi C. Modeling chemical and physical processes of wood and biomass pyrolysis. Prog Energy Combust Sci 2008;34:47–90. https://doi.org/10.1016/j.pecs.2006.12.001.
[23] de Wild P. Biomass pyrolysis for chemicals. University of Groningen, 2011.
[24] Sansaniwal SK, Rosen MA, Tyagi SK. Global challenges in the sustainable development of biomass gasification: An overview. Renew Sustain Energy Rev 2017;80:23–43. https://doi.org/10.1016/j.rser.2017.05.215.
[25] Di Blasi C. Combustion and gasification rates of lignocellulosic chars. Prog Energy Combust Sci 2009;35:121–40. https://doi.org/10.1016/j.pecs.2008.08.001.
[26] Ahmed II, Gupta AK. Kinetics of woodchips char gasification with steam and carbon dioxide. Appl Energy 2011;88:1613–9. https://doi.org/10.1016/j.apenergy.2010.11.007.
[27] Marquez-Montesinos F, Cordero T, Rodríguez-Mirasol J, Rodríguez JJ. CO2 and steam gasification of a grapefruit skin char. Fuel 2002;81:423–9. https://doi.org/10.1016/S0016-2361(01)00174-0.
[28] Dupont C, Jacob S, Marrakchy KO, Hognon C, Grateau M, Labalette F, et al. How inorganic elements of biomass influence char steam gasification kinetics. Energy 2016;109:430–5. https://doi.org/10.1016/j.energy.2016.04.094.
[29] Septien S, Escudero Sanz FJ, Salvador S, Valin S. The effect of pyrolysis heating rate on the steam gasification reactivity of char from woodchips. Energy 2018;142:68–78. https://doi.org/10.1016/j.energy.2017.09.114.
[30] Guerrero M, Ruiz MP, Millera Á, Alzueta MU, Bilbao R. Oxidation Kinetics of Eucalyptus Chars Produced at Low and High Heating Rates. Energy Fuels 2008;22:2084–90. https://doi.org/10.1021/ef700643p.
[31] Di Blasi C. Combustion and gasification rates of lignocellulosic chars. Prog Energy Combust Sci 2009;35:121–40. https://doi.org/10.1016/j.pecs.2008.08.001.
[32] Gupta A, Thengane SK, Mahajani S. CO2 gasification of char from lignocellulosic garden waste: Experimental and kinetic study. Bioresour Technol 2018;263:180–91. https://doi.org/10.1016/j.biortech.2018.04.097.
[33] Dupont C, Nocquet T, Da Costa JA, Verne-Tournon C. Kinetic modelling of steam gasification of various woody biomass chars: Influence of inorganic elements. Bioresour Technol 2011;102:9743–8. https://doi.org/10.1016/j.biortech.2011.07.016.
[34] González-Vázquez MP, García R, Gil MV, Pevida C, Rubiera F. Unconventional biomass fuels for steam gasification: Kinetic analysis and effect of ash composition on reactivity. Energy 2018;155:426–37. https://doi.org/10.1016/j.energy.2018.04.188.
[35] Hognon C, Dupont C, Grateau M, Delrue F. Comparison of steam gasification reactivity of algal and lignocellulosic biomass: Influence of inorganic elements. Bioresour Technol 2014;164:347–53. https://doi.org/10.1016/j.biortech.2014.04.111.

[36] López-González D, Fernandez-Lopez M, Valverde JL, Sanchez-Silva L. Gasification of lignocellulosic biomass char obtained from pyrolysis: Kinetic and evolved gas analyses. Energy 2014;71:456–67. https://doi.org/10.1016/j.energy.2014.04.105.
[37] Romero Millán LM, Sierra Vargas FE, Nzihou A. Steam gasification behavior of tropical agrowaste: A new modeling approach based on the inorganic composition. Fuel 2019;235:45–53. https://doi.org/10.1016/j.fuel.2018.07.053.
[38] DeGroot WF, Kannan MP, Richards GN, Theander O. Gasification of agricultural residues (biomass): influence of inorganic constituents. J Agric Food Chem 1990;38:320–3. https://doi.org/10.1021/jf00091a070.
[39] Kannan MP, Richards GN. Gasification of biomass chars in carbon dioxide: dependence of gasification rate on the indigenous metal content. Fuel 1990;69:747–53. https://doi.org/10.1016/0016-2361(90)90041-N.
[40] Link S, Arvelakis S, Hupa M, Yrjas P, Külaots I, Paist A. Reactivity of the Biomass Chars Originating from Reed, Douglas Fir, and Pine. Energy Fuels 2010;24:6533–9. https://doi.org/10.1021/ef100926v.
[41] Strandberg A, Holmgren P, Wagner DR, Molinder R, Wiinikka H, Umeki K, et al. Effects of Pyrolysis Conditions and Ash Formation on Gasification Rates of Biomass Char. Energy Fuels 2017;31:6507–14. https://doi.org/10.1021/acs.energyfuels.7b00688.
[42] Umeki K, Moilanen A, Gómez-Barea A, Konttinen J. A model of biomass char gasification describing the change in catalytic activity of ash. Chem Eng J 2012;207–208:616–24. https://doi.org/10.1016/j.cej.2012.07.025.
[43] Jiang L, Hu S, Xu K, Wang Y, Syed-Hassan SSA, Su S, et al. Formation, fates and roles of catalytic precursors generated from the K2CO3-carbon interactions in the K2CO3-catalyzed CO2 gasification of coal char. J Anal Appl Pyrolysis 2017;124:384–92. https://doi.org/10.1016/j.jaap.2016.11.006.
[44] Kramb J, Gómez-Barea A, DeMartini N, Romar H, Doddapaneni TRKC, Konttinen J. The effects of calcium and potassium on CO2 gasification of birch wood in a fluidized bed. Fuel 2017;196:398–407. https://doi.org/10.1016/j.fuel.2017.01.101.
[45] Zahara ZF, Kudo S, Daniyanto, Ashik UPM, Norinaga K, Budiman A, et al. CO2 Gasification of Sugar Cane Bagasse: Quantitative Understanding of Kinetics and Catalytic Roles of Inherent Metallic Species. Energy Fuels 2018;32:4255–68. https://doi.org/10.1021/acs.energyfuels.7b03147.
[46] Hüttinger KJ, Minges R. Influence of the catalyst precursor anion in catalysis of water vapour gasification of carbon by potassium: 1. Activation of the catalyst precursors. Fuel 1986;65:1112–21. https://doi.org/10.1016/0016-2361(86)90179-1.
[74] Hüttinger KJ, Minges R. The influence of the catalyst precursor anion in catalysis of water vapour gasification of carbon by potassium: 2. Catalytic activity as influenced by activation and deactivation reactions. Fuel 1986;65:1122–8.https://doi.org/10.1016/0016-2361(86)90180-8.
[48] Wen W-Y. Mechanisms of Alkali Metal Catalysis in the Gasification of Coal, Char, or Graphite. Catal Rev 1980;22:1–28. https://doi.org/10.1080/03602458008066528.
[49] Arnold RA, Habibi R, Kopyscinski J, Hill JM. Interaction of Potassium and Calcium in the Catalytic Gasification of Biosolids and Switchgrass. Energy Fuels 2017;31:6240–7. https://doi.org/10.1021/acs.energyfuels.7b00972.
[50] Bach-Oller A, Fursujo E, Umeki K. Effect of potassium impregnation on the emission of tar and soot from biomass gasification. Energy Procedia 2019;158:619–24. https://doi.org/10.1016/j.egypro.2019.01.164.

[56] Feng D, Zhao Y, Zhang Y, Sun S, Gao J. Steam Gasification of Sawdust Biochar Influenced by Chemical Speciation of Alkali and Alkaline Earth Metallic Species. Energies 2018;11:205-221. https://doi.org/10.3390/en11010205.
[52] Lv X, Xiao J, Shen L, Zhou Y. Experimental study on the optimization of parameters during biomass pyrolysis and char gasification for hydrogen-rich gas. Int J Hydrog Energy 2016;41:21913–25. https://doi.org/10.1016/j.ijhydene.2016.09.200.
[50] Yip K, Tian F, Hayashi J, Wu H. Effect of Alkali and Alkaline Earth Metallic Species on Biochar Reactivity and Syngas Compositions during Steam Gasification. Energy Fuels 2009;24:173–181. https://doi.org/10.1021/ef900534n
[54] Zhang Y, Ashizawa M, Kajitani S, Miura K. Proposal of a semi-empirical kinetic model to reconcile with gasification reactivity profiles of biomass chars. Fuel 2008;87:475–81. https://doi.org/10.1016/j.fuel.2007.04.026.
[55] Delannay F, Tysoe WT, Heinemann H, Somorjai GA. The role of KOH in the steam gasification of graphite: Identification of the reaction steps. Carbon 1984;22:401–7. https://doi.org/10.1016/0008-6223(84)90012-5.
[56] Meijer R, Kapteijn F, Moulijn JA. Kinetics of the alkali-carbonate catalysed gasification of carbon: 3. H2O gasification. Fuel 1994;73:723–30. https://doi.org/10.1016/0016-2361(94)90015-9.
[57] Bennici S, Jeguirim M, Limousy L, Haddad K, Vaulot C, Michelin L, et al. Influence of CO2 Concentration and Inorganic Species on the Gasification of Lignocellulosic Biomass Derived Chars. Waste Biomass Valorization 2019. https://doi.org/10.1007/s12649-019-00658-1.
[58] Bouraoui Z, Dupont C, Jeguirim M, Limousy L, Gadiou R. CO2 gasification of woody biomass chars: The influence of K and Si on char reactivity. Comptes Rendus Chim 2016;19:457–65. https://doi.org/10.1016/j.crci.2015.08.012.
[59] DeGroot WF, Shafizadeh F. Kinetics of gasification of Douglas Fir and Cottonwood chars by carbon dioxide. Fuel 1984;63:210–6. https://doi.org/10.1016/0016-2361(84)90039-5.
[60] Feng D, Zhao Y, Zhang Y, Xu H, Zhang L, Sun S. Catalytic mechanism of ion-exchanging alkali and alkaline earth metallic species on biochar reactivity during CO2/H2O gasification. Fuel 2018;212:523–32. https://doi.org/10.1016/j.fuel.2017.10.045.
[61] Huang Y, Yin X, Wu C, Wang C, Xie J, Zhou Z, et al. Effects of metal catalysts on CO2 gasification reactivity of biomass char. Biotechnol Adv 2009;27:568–72. https://doi.org/10.1016/j.biotechadv.2009.04.013.
[62] Kirtania K, Axelsson J, Matsakas L, Christakopoulos P, Umeki K, Furusjö E. Kinetic study of catalytic gasification of wood char impregnated with different alkali salts. Energy 2017;118:1055–65. https://doi.org/10.1016/j.energy.2016.10.134.
[63] Kramb J, DeMartini N, Perander M, Moilanen A, Konttinen J. Modeling of the catalytic effects of potassium and calcium on spruce wood gasification in CO2. Fuel Process Technol 2016;148:50–9. https://doi.org/10.1016/j.fuproc.2016.01.031.
[64] Lahijani P, Zainal ZA, Mohamed AR, Mohammadi M. CO2 gasification reactivity of biomass char: Catalytic influence of alkali, alkaline earth and transition metal salts. Bioresour Technol 2013;144:288–95. https://doi.org/10.1016/j.biortech.2013.06.059.
[65] Perander M, DeMartini N, Brink A, Kramb J, Karlström O, Hemming J, et al. Catalytic effect of Ca and K on CO2 gasification of spruce wood char. Fuel 2015;150:464–72. https://doi.org/10.1016/j.fuel.2015.02.062.

[66] Struis RPWJ, von Scala C, Stucki S, Prins R. Gasification reactivity of charcoal with CO2. Part I: Conversion and structural phenomena. Chem Eng Sci 2002;57:3581–92. https://doi.org/10.1016/S0009-2509(02)00254-3.
[67] Ding L, Dai Z, Wei J, Zhou Z, Yu G. Catalytic effects of alkali carbonates on coal char gasification. J Energy Inst 2017;90:588–601. https://doi.org/10.1016/j.joei.2016.05.003.
[68] Moulijn JA, Cerfontain MB, Kapteijn F. Mechanism of the potassium catalysed gasification of carbon in CO2. Fuel 1984;63:1043–7. https://doi.org/10.1016/0016-2361(84)90185-6.
[69] Arnold RA, Hill JM. Catalysts for gasification: a review. Sustain Energy Fuels 2019;3:656–72. https://doi.org/10.1039/C8SE00614H.
[70] McKee DW. Mechanisms of the alkali metal catalysed gasification of carbon. Fuel 1983;62:170–5. https://doi.org/10.1016/0016-2361(83)90192-8.
[71] Nzihou A, Stanmore B, Sharrock P. A review of catalysts for the gasification of biomass char, with some reference to coal. Energy 2013;58:305–17. https://doi.org/10.1016/j.energy.2013.05.057.
[72] Mudge LK, Sealock LJ, Weber SL. Catalyzed steam gasification of biomass. J Anal Appl Pyrolysis 1979;1:165–75. https://doi.org/10.1016/0165-2370(79)80013-3.
[73] Elliott DC, Hallen RT, Sealock LJ. Alkali catalysis in biomass gasification. J Anal Appl Pyrolysis 1984;6:299–316. https://doi.org/10.1016/0165-2370(84)80024-8.
[74] Tromp PJJ, Cordfunke EHP. A thermochemical study of the reactive intermediate in the alkali-catalyzed carbon gasification. I. X-ray diffraction results on the alkali-carbon interaction. Thermochim Acta 1984;77:49–58. https://doi.org/10.1016/0040-6031(84)87045-8.
[75] Wang S, Wang C, Ji X. Towards understanding the salt-intercalation exfoliation of graphite into graphene. RSC Adv 2017;7:52252–60. https://doi.org/10.1039/C7RA07489A.
[76] Fermoso J, Arias B, Pevida C, Plaza MG, Rubiera F, Pis JJ. Kinetic models comparison for steam gasification of different nature fuel chars. J Therm Anal Calorim 2008;91:779–86. https://doi.org/10.1007/s10973-007-8623-5.