

## Gasification of biomass with CO<sub>2</sub> and H<sub>2</sub>O mixtures in a catalytic fluidised bed

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### Highlights

- Different mixtures of biomass gasifying agents were compared (H<sub>2</sub>O+O<sub>2</sub>, CO<sub>2</sub>+H<sub>2</sub>O+O<sub>2</sub>, CO<sub>2</sub>+O<sub>2</sub> and N<sub>2</sub>+O<sub>2</sub>).
- Mixtures of dolomitic limestone and silica sand (1:1 or 1:3 by vol.) were used as fluidised bed material.
- The highest fuel carbon conversion was observed for mixtures of CO<sub>2</sub> and H<sub>2</sub>O as the gasifying agent.
- Use of the combination of CO<sub>2</sub> and H<sub>2</sub>O leads to a higher degree of tar decomposition.

### Abstract

Steam can be fully or partially substituted by CO<sub>2</sub> as a gasification agent. This substitution affects producer gas composition, char conversion and in-situ tar reforming. Here, wood chips were gasified in a spouting fluidised bed using silica sand and catalytic dolomitic lime as the bed material at 850°C. The use of a gasifying agent composed of CO<sub>2</sub> and H<sub>2</sub>O was compared to the use of CO<sub>2</sub> or H<sub>2</sub>O alone. It was found that mixtures of CO<sub>2</sub> and H<sub>2</sub>O as the gasifying agent improve char conversion, and that the combined gasification agents are very effective in ensuring the

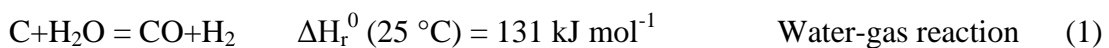
decomposition/destruction of tars when lime based materials are used in the fluidised bed.

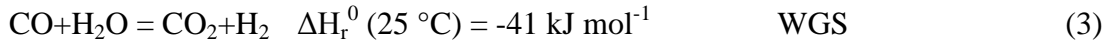
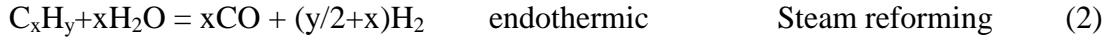
**Keywords:** Fluidised bed; Gasification; Catalyst; Dolomite; Limestone; Synergistic effect

## 1 Introduction

When a solid organic fuel is heated, it decomposes pyrolytically into three products: gases, vapourised liquids and char. A gasifying agent is required to maximise the conversion of the fuel to gas and (optionally) to provide the necessary process heat. The simplest gasification technologies use sub-stoichiometric amounts of air as the gasifying agent. Oxygen from the air oxidises the pyrolytic products while generating heat and producing CO, CO<sub>2</sub> and H<sub>2</sub>O, which are subsequently partially reacted in the process. However, N<sub>2</sub> from the air dilutes the produced gas, while considerably decreasing its heating value and potential uses. [1, 2] To avoid dilution of the produced gas by nitrogen, either oxygen mixed with a moderator (typically steam) can be used as gasifying agent, or the heat can be supplied from an external source and only steam is used for gasification, as for example in the case of gasification in a dual fluidised bed reactor [3].

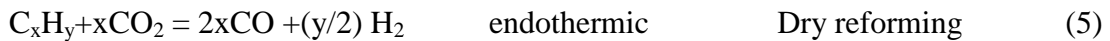
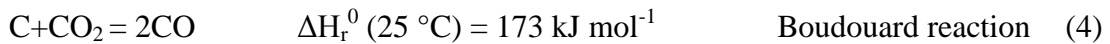
Steam, during gasification, (i) reacts endothermically with char via the water-gas heterogeneous reaction (rx. 1) to produce CO and H<sub>2</sub>, (ii) and it also decomposes the organic pyrolytic vapours (tars) by steam reforming (rx. 2), and (iii) it shifts the thermodynamic equilibrium of the water-gas shift (WGS) reaction (rx. 3) to produce higher concentrations of CO<sub>2</sub> and H<sub>2</sub> in the syngas [4].





Steam as the gasifying agent can be fully or partially substituted by CO<sub>2</sub>. The use of CO<sub>2</sub> instead of steam is of practical interest for various reasons; for example, (i) the possible reuse of CO<sub>2</sub> from carbon capture technologies or from the recycling of flue gas from oxyfuel combustion (composed of a mixture of CO<sub>2</sub> and H<sub>2</sub>O) [5–8]; (ii) the use of CO<sub>2</sub> instead of N<sub>2</sub> as an inert gas (for example in fuel dosing trains), as CO<sub>2</sub> behaves as an inert at lower temperatures [6, 9, 10]; (iii) adjustment of the H<sub>2</sub>/CO ratio in the syngas for various synthesis technologies [9, 11–13]; or (iv) because thermal processing via CO<sub>2</sub> rather than steam avoids the use of large quantities of water, which has a large latent heat of vapourisation [14].

CO<sub>2</sub> has both higher volumetric heat capacity and different radiative properties from steam [15]. Given the higher partial pressure of CO<sub>2</sub> in the reactor, the chemistry of the process is also altered. CO<sub>2</sub> reacts with char from the pyrolytic step via the Boudouard reaction (rx. 4), it decomposes organic gas and vapours (tars) via dry reforming (rx. 5) and its high partial pressure shifts the equilibrium of the WGS reaction (rx. 3) to produce higher CO and lower H<sub>2</sub> concentrations in the producer gas [4].



Therefore, the difference between gasification with steam, CO<sub>2</sub> or their mixtures should be seen mainly in gas composition, carbon (char) conversion and tar reforming.

There is limited literature dealing with the kinetics of the reaction of char with  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and their mixtures, most of it coming from thermogravimetric analysis (TGA). Thus, Bai et al. [16] found a synergistic effect between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  for the gasification of coal char. In particular, the addition of  $\text{CO}_2$  improved the char reactivity, which was higher than the sum of the individual reactivities using either  $\text{CO}_2$  or  $\text{H}_2\text{O}$  below  $900^\circ\text{C}$ . Similar results were found by Buttermann et al. [14, 17] for biomass char. Carbon conversion was complete with 25%  $\text{CO}_2$ /75% steam compared to 90% conversion with pure steam in a temperature range of  $800\text{--}1000^\circ\text{C}$ . The strongest effect was seen upon addition of 0–5%  $\text{CO}_2$  [14]. However, other researchers [18–21] suggested that the char reactivity was simply due to the sum of the individual reactivities using either  $\text{CO}_2$  or  $\text{H}_2\text{O}$ . Still other researchers [22–26] have suggested that  $\text{H}_2\text{O}$  and  $\text{CO}_2$  compete for the same active carbon sites and, therefore, the addition of  $\text{CO}_2$  decreased the rate of the water gas reaction (rx. 1). One of the reasons for the varying influence (synergy, addition or inhibition) of the combined  $\text{H}_2\text{O}/\text{CO}_2$  atmosphere can be specific pore surface area (SSA) of char. As reported by Zhang et al. [27], the gasification mechanism of large-SSA char is close to the separate active sites assumption, while the gasification mechanism of small-SSA char is close to the common active sites assumption. Guizani et al. [28, 29] report that both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  diffuse mainly in macropores and that the differences between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  should not have a substantial effect on the diffusion process as they are mainly related to micro- and meso-porosity. Further research into the causes of the improved char reactivity under mixed  $\text{CO}_2/\text{H}_2\text{O}$  atmosphere revealed that the critical factor is the catalytic activity of Na [27] and Ca species in char [16, 30, 31], mainly in the form of  $\text{CaO}$  [32].

Data relating to the effect of the gasifying agent composed both of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on the yield of tar and its composition are scarce. Only one relevant study was found, namely that of Simell et al. [33] who compared the effect of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and their mixtures on the reforming of a model tar compound (toluene) employing a simulated producer gas at a pressure of 2 MPa, 900°C, in the presence of different catalysts. They report that, with both dolomite and nickel catalysts, steam reforming (rx. 2) and dry reforming (rx. 5) reactions took place at a high rate, with dry reforming being faster than steam reforming. Moreover, dry reforming was inhibited by the presence of steam.

Some literature comparing gasification with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in a fluidised bed (FB) can also be found. Svoboda et al. [10] compared the gasification of coal slurries with steam-oxygen mixture to gasification with  $\text{CO}_2$ -oxygen mixture. Silica sand in a spouting FB was used in their work, and they reported that the heating values of dry,  $\text{N}_2$ -free producer gas are lower using  $\text{CO}_2/\text{O}_2$  in comparison with gasification by steam- $\text{O}_2$  mixtures at comparable conditions due to the high content of diluting  $\text{CO}_2$  [10]. Valin et al. [9] describe a gradual replacement of  $\text{H}_2\text{O}$  by  $\text{CO}_2$  during allothermal gasification of biomass with SiC and olivine as bed materials in a bubbling FB. They report that the hydrocarbon and tar yields are not significantly influenced by this substitution, nor are the net conversion of carbon into gas and the cold gas efficiency [9]. However, Pohořelý et al. [4] report that the use of  $\text{CO}_2$  (instead of  $\text{H}_2\text{O}$ ) substantially increased the carbon and energy conversion efficiency and decreased the yield of tar when gasifying wood chips in a spouting FB with dolomitic limestone as the bed material. They suggest that balanced partial pressures of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the gasification reactor (with dolomitic limestone in the FB at 850°C) are beneficial for tar decomposition reactions via steam and dry reforming; however, the combined use of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as gasifying

agent was not reported [4]. Pinto et al. [34] concluded that CO<sub>2</sub>-blown gasification is extremely complex and more investigation is still needed to determine the best composition of CO<sub>2</sub>, oxygen and steam mixtures. It can be hypothesised that the fluidised bed material plays a crucial role in determining whether the combined use of CO<sub>2</sub> and H<sub>2</sub>O will have a beneficial effect on char gasification and tar reforming. In this work, we hypothesize that a fluidised-bed material containing CaO will cause a synergy in the combined use of H<sub>2</sub>O/CO<sub>2</sub> gasification media.

In the experiments described in this study, we compared the influence of H<sub>2</sub>O and CO<sub>2</sub> and their mixtures on the gasification of wood chips in a catalytic FB composed of 1:1 or 1:3 (by volume) of dolomitic limestone (DL) and silica sand (SS). The aim was (i) to explore the possible synergy of using a mixture of H<sub>2</sub>O and CO<sub>2</sub> as gasifying agent for carbon and tar conversion into producer gas and (ii) to examine the influence of the concentration of DL in a SS FB (50% or 25% by vol.) with the combined use of CO<sub>2</sub> and H<sub>2</sub>O as gasifying agent. To the best of our knowledge, no such investigation has been made before in a pilot plant with dolomitic limestone (or limestone) mixed with an inert material in the FB. Moreover, the literature about the influence of the combination of H<sub>2</sub>O and CO<sub>2</sub> as gasifying agent is often contradictory (char reactivity) or extremely limited (reactions with tars). This work aims to clarify this situation.

## 2 Materials and Methods

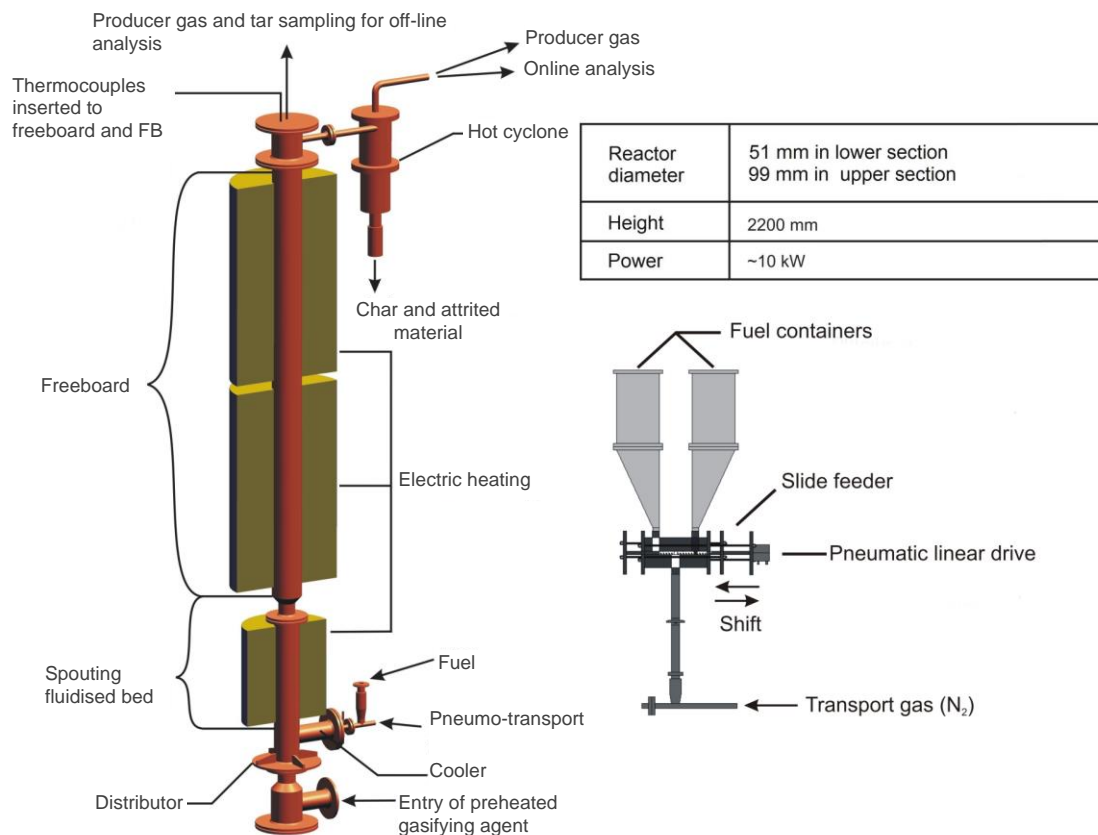


Fig. 1. Pilot-scale Spouting Fluidised Bed Reactor

The experiments described here were performed in a spouting FB reactor shown in Fig. 1, which is described in detail elsewhere [35]. The producer gas leaves the reactor, passes through the hot cyclone and then is sampled on-line by means of nondispersive infrared (NDIR) and thermal conductivity (TC) analysers. The gas is also sampled regularly, using gas sampling bottles connected directly to the top of the reactor (before the hot cyclone) for subsequent off-line analysis by a two-channel gas chromatograph (GC HP 6890). The tars are also sampled directly from the outlet of the reactor before entering the cyclone to prevent any possible condensation of heavy compounds. The tar sampling was performed in accordance with an established tar protocol [36] and the

tarry compounds were analysed by a GC (HP 6890) coupled with a mass-selective detector (MSD 5973). A detailed description of the analyses can be found elsewhere [37–39]. The methodology of sampling and determination of gas composition and tar content was validated on a number of experiments conducted in the same experimental facility under the same conditions. The content of the major gas components (CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>) was detected off-line using the GC-TCD/FID method using a multipoint calibration, with a relative measurement error of  $\pm 1\%$ . Content of minor gaseous components (e.g., benzene, toluene, xylene) was calculated using one-point calibration with a relative error of  $\pm 4\%$  due to the higher uncertainty of the used gaseous reference materials. Tar protocol used for sampling and subsequent GC-MS analysis for the determination of the content of individual components of tar in combination with the long-established method of processing of the liquid samples obtained allowed the determination of the contents of the individual groups with a relative measurement error up to  $\pm 7\%$ .

Wood chips (proximate and ultimate analyses are presented in Table 1) were supplied by J. Rettenmaier & Sohne GmbH, from a commercially available product trademarked ‘Räuchergold HBK 750–2000’.

Table 1. Proximate and ultimate analysis of wood fuel

Proximate analysis (% wt.)	
Moisture	9.0
Ash	0.89
Volatiles	75
Fixed carbon	15
HHV (MJ/kg)	18
LHV (MJ/kg)	16
Ultimate analysis (% wt.)	
C	49
H	6.1



N	0.19
O (by difference)	45

DL was used as the catalytic material in the FB diluted by silica sand (the volumetric concentration of DL in the FB was 50% or 25%). The properties of the materials are summarised in Table 2 and presented in detail in our previous article [40]. The specific fractions of the two materials (silica sand and dolomitic limestone) were carefully selected in order to ensure complete fluidisation of the mixture on the one hand, and to prevent excessive loss of the lime due to attrition and carry-over from the reactor on the other hand. The particles of limestone appear to easily attrite during the experiment and thus their minimal fluidising velocity can decrease substantially. [40]

Table 2. Properties of the FB bed materials

Materials	Silica sand	Dolomitic limestone	
		raw	calcined
Particle size <sup>a</sup> (mm)	0.25 - 0.50	0.5 - 1.25	-
Mean particle size (mm)	0.375	0.875	-
True solid density <sup>b</sup> (kg m <sup>-3</sup> )	2530	2862	2653
Apparent density <sup>c</sup> (kg m <sup>-3</sup> )	2530	2498	963
Particle porosity (vol %)	0	13	64
Bed voidage (vol %)	45	48	23
Loose poured bulk density (kg m <sup>-3</sup> )	1394	1301	743
Specific surface area (BET) (m <sup>2</sup> g <sup>-1</sup> )	-	-	13.8
Mesopore surface area (m <sup>2</sup> g <sup>-1</sup> )	-	-	7.6
Micropore volume (mm <sup>3</sup> g <sup>-1</sup> )	-	-	3.5
Minimum fluidising velocity* (m s <sup>-1</sup> )	0.11	0.42	0.19
Minimum fluidising velocity** (m s <sup>-1</sup> )	0.05	0.25	0.10
Complete fluidising velocity* (m s <sup>-1</sup> )	0.18	0.64	0.32
Complete fluidising velocity** (m s <sup>-1</sup> )	0.09	0.48	0.20
Loss on ignition*** (wt %)	-	47	-
CaCO <sub>3</sub> <sup>d</sup> (wt %)	< 0.03	55	-
MgCO <sub>3</sub> <sup>d</sup> (wt %)	< 0.03	44	-
SiO <sub>2</sub> <sup>d</sup> (wt %)	98	0.20	-

$\text{Al}_2\text{O}_3^{\text{d}}$ (wt %)	1.4	0.16	-
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Determined by: <sup>a</sup>sieving, <sup>b</sup>helium displacement, <sup>c</sup>mercury displacement, <sup>d</sup>XRF;  
\* at 25°C, \*\* at 850°C, \*\*\* at 900°C and 101.325 kPa

Experimental conditions are summarised in Table 3. Two experimental runs were performed with different mixtures of the fluidised bed materials (50% or 25% vol. of DL in SS; 1.5 L of bed material in total). During each experiment, the reactor was heated up to 500°C; then, the appropriate amount of silica sand was added to the reactor and heated to the desired temperature of 850°C by three electrical furnaces, shown in Fig. 1. Initially, the appropriate amount of DL was added in one batch, and allowed to calcine and to heat up to 850°C. Once the desired temperature in the FB was reached, fuel dosing and gasification started with  $\text{H}_2\text{O}+\text{O}_2$  as the gasifying agent (second column in Table 3). The DL was periodically replenished to replace the attrited mass carried over from the reactor. The proper mass necessary to maintain bed height was computed from a previously published model [41] and the time interval needed to add additional bed material was short enough not to significantly alter the composition of the gas [40]. Steady state gasification proceeded for 1.5 h and then the gas and tar samples were collected for off-line analysis (the tars were collected over a 40-min period and two gas samples were collected during this period). After that, the composition of the gasifying agent was changed, the composition of the gas was allowed to stabilise and again the samples for off-line analysis were collected for each steady state described in Table 3. During the experiment with 50% vol. of DL in the FB, the transition states when replacing  $\text{H}_2\text{O}$  by  $\text{CO}_2$  were monitored by off-line gas analysis as well. The correctness of the analyses was checked by performing a C, H and O elemental balances (Fig. S2–S4 in the Supplemental Information file).

Table 3. Experimental conditions

Bed Material in the FB	DL and SS (1:1 vol. or 1:3)			
Reactor temperature (°C)	850 ± 5			
Dry fuel feeding rate (g h <sup>-1</sup> )	1300			
Raw fuel feeding rate (g h <sup>-1</sup> )	1440			
Experimental label	H <sub>2</sub> O+O <sub>2</sub>	CO <sub>2</sub> +H <sub>2</sub> O+O <sub>2</sub>	CO <sub>2</sub> +O <sub>2</sub>	N <sub>2</sub> +O <sub>2</sub>
<b>Gas inlet*</b>				
Steam (m <sup>3</sup> h <sup>-1</sup> )	1.36	0.41	0.00	0.00
O <sub>2</sub> (m <sup>3</sup> h <sup>-1</sup> )	0.27	0.27	0.27	0.27
CO <sub>2</sub> (m <sup>3</sup> h <sup>-1</sup> )	0.00	0.95	1.36	0.00
N <sub>2</sub> (m <sup>3</sup> h <sup>-1</sup> )	0.37	0.37	0.37	1.73
N <sub>2</sub> pneumatic transport (m <sup>3</sup> h <sup>-1</sup> )	1.50	1.50	1.50	1.50
Total gas inlet (m <sup>3</sup> h <sup>-1</sup> )	3.50	3.50	3.50	3.50
<b>Parameters</b>				
ER (m <sup>3</sup> m <sup>-3</sup> ) <sup>a</sup>	0.20	0.20	0.20	0.20
H <sub>2</sub> O/C (mol mol <sup>-1</sup> ) <sup>b</sup>	1.2	0.46	0.14	0.13
CO <sub>2</sub> /C (mol mol <sup>-1</sup> ) <sup>c</sup>	0.00	0.70	1.05	0.00
CO <sub>2</sub> /(H <sub>2</sub> O+CO <sub>2</sub> ) (mol mol <sup>-1</sup> )	0	0.70	1.00	-
O/C (mol mol <sup>-1</sup> ) <sup>d</sup>	2.31	1.75	1.64	1.25
H <sub>2</sub> O/F (kg kg <sup>-1</sup> ) <sup>e</sup>	0.88	0.34	0.11	0.11
CO <sub>2</sub> /F (kg kg <sup>-1</sup> ) <sup>f</sup>	0.00	1.31	1.88	0.00
O <sub>2</sub> /F (kg kg <sup>-1</sup> ) <sup>g</sup>	0.27	0.27	0.27	0.27

\*All volume units are expressed at 25°C and 101.325 kPa.

<sup>a</sup> Equivalence ratio – available O<sub>2</sub> related to the O<sub>2</sub> needed for stoichiometric combustion of fuel (F).

<sup>b</sup> H<sub>2</sub>O from the gasifying agent and fuel moisture related to the C bound in fuel.

<sup>c</sup> CO<sub>2</sub> from the gasifying agent related to the C bound in fuel.

<sup>d</sup> O bound in fuel, fuel moisture and H<sub>2</sub>O and CO<sub>2</sub> in the gasifying agent related to the C bound in fuel and CO<sub>2</sub> input.

<sup>e</sup> H<sub>2</sub>O in gasifying agent and fuel moisture related to the input of dry fuel.

<sup>f</sup> CO<sub>2</sub> in gasifying agent related to the input of dry fuel.

<sup>g</sup> O<sub>2</sub> in gasifying agent related to the input of dry fuel.

### 3 Results and Discussion

When gasifying the wood with gasifying agent with different shares of CO<sub>2</sub> and H<sub>2</sub>O, the yield of gases generated in the reactor (Fig. 2 and Fig. 3, Table 4) changed mainly due to the water-gas-shift reaction (rx. 3). Namely, when gasifying with the H<sub>2</sub>O+O<sub>2</sub> mixture, a large yield of H<sub>2</sub> and CO<sub>2</sub> and low yield of H<sub>2</sub>O and CO were observed and vice versa when gasifying the fuel with the mixture of CO<sub>2</sub>+O<sub>2</sub>. Slight differences in the

producer gas composition can be observed by comparing the gasification with 50 % vol. DL in FB (Fig. 2a) and 25% vol. DL in FB (Fig. 2b). This can be attributed to variations in effectiveness of the catalyst on the gasification due to its different concentration in the FB. A detailed insight into the yield of minor organic compounds (trace  $C_xH_y$ ) is depicted in supplemental information, Fig. S5.

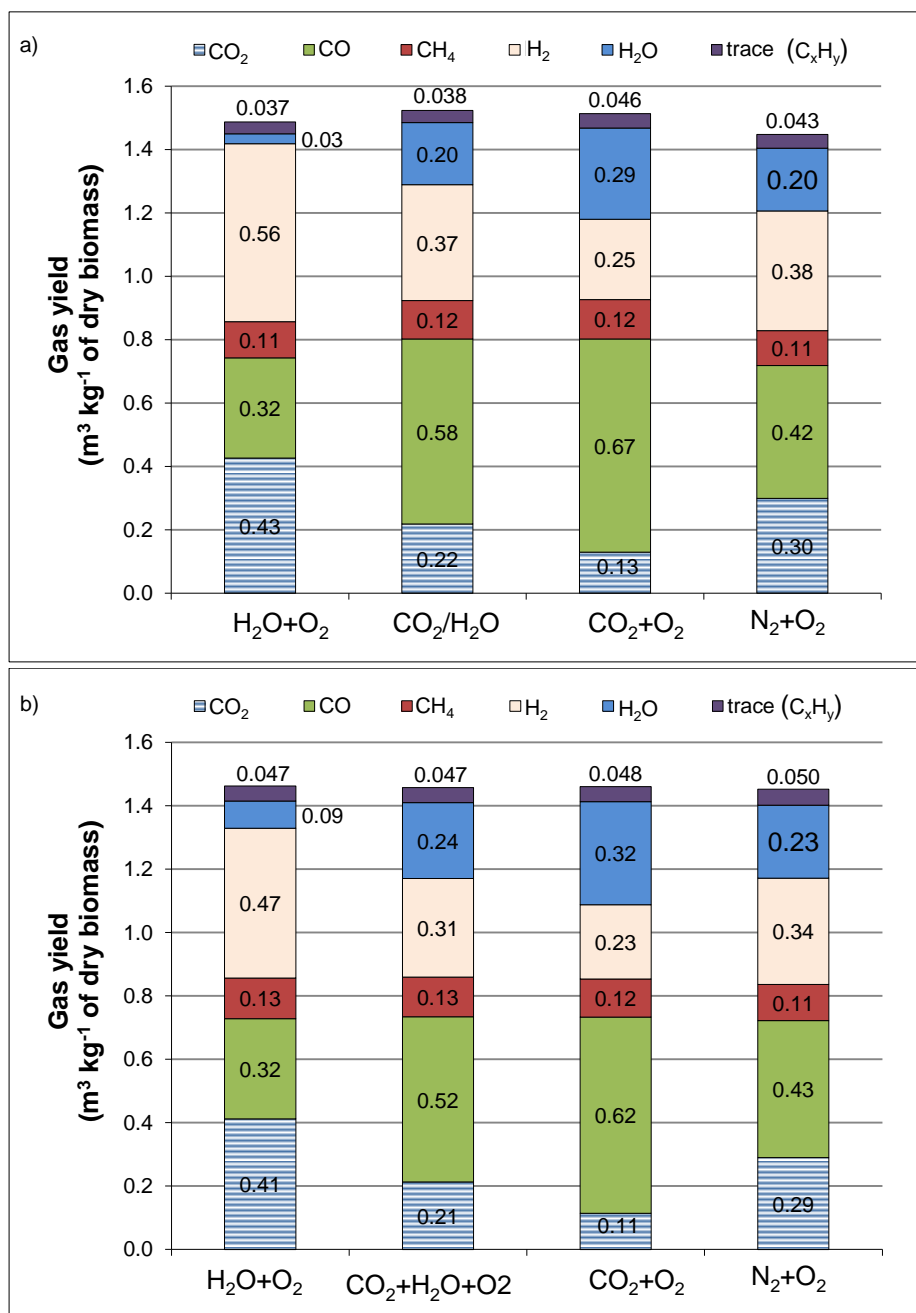


Fig. 2. Yield of major gases. a) 50% vol. limestone in the FB; b) 25% vol. limestone in the FB; inputs of H<sub>2</sub>O, N<sub>2</sub> and CO<sub>2</sub> are subtracted (only gases arising in the reactor are shown). All volume units are expressed at 25°C and 101.325 kPa

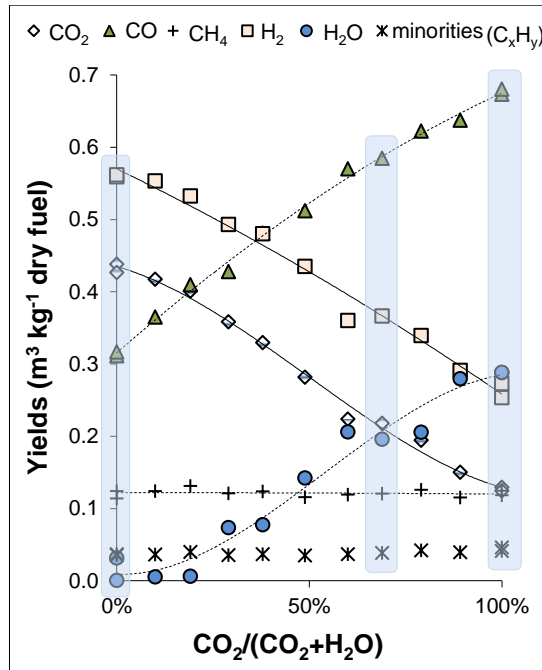


Fig. 3. Yield of gases produced in the reactor at transition states (50% vol. DL in the FB); corresponding steady states depicted in the first three columns (from the left) of Fig. 2a are highlighted by the light-blue fields; inputs of H<sub>2</sub>O, N<sub>2</sub> and CO<sub>2</sub> are subtracted (only gases arising in the reactor are shown); H<sub>2</sub>O yield is computed as an average from H and O elemental balance. All volume units are expressed at 25°C and 101.325 kPa.

Table 4. Concentration of individual gases in the producer gas with 1:1 DL and SS (and 1:3 DL and SS) in the FB.

vol. %	H <sub>2</sub> O+O <sub>2</sub>	CO <sub>2</sub> +H <sub>2</sub> O+O <sub>2</sub>	CO <sub>2</sub> +O <sub>2</sub>	N <sub>2</sub> +O <sub>2</sub>
CO <sub>2</sub>	11 (10)	23 (24)	29 (29)	7.7 (7.3)
H <sub>2</sub>	14 (12)	9.3 (7.8)	6.4 (5.9)	9.7 (8.5)
CO	8.1 (8)	15 (13)	17 (16)	11 (11)
CH <sub>4</sub>	2.9 (3.2)	3.1 (3.2)	3.1 (3.0)	2.8 (2.9)
N <sub>2</sub>	36 (37)	36 (37)	36 (37)	63 (63)
H <sub>2</sub> O	27 (29)	13 (14)	7.3 (8.2)	5.1 (5.8)
Ethylene	0.73 (0.89)	0.75 (0.89)	0.87 (0.88)	0.82 (0.91)
other C <sub>x</sub> H <sub>y</sub>	0.21 (0.29)	0.22 (0.31)	0.28 (0.33)	0.27 (0.36)

Carbon conversion efficiency (Fig. 4) was almost complete when gasifying with the mixture of CO<sub>2</sub>+H<sub>2</sub>O+O<sub>2</sub> with 50% DL in the FB and was the highest when compared to the use of H<sub>2</sub>O+O<sub>2</sub> and CO<sub>2</sub>+O<sub>2</sub> with 25% DL in FB. This finding suggests that the

calcined DL plays a crucial role in the gasification of char by  $\text{CO}_2$  and that the combined use of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is more effective in the conversion of char compared to the use of  $\text{H}_2\text{O}$  alone. The gasification of char occurs via reactions (rx. 1) and (rx. 4). From the current perspective, the two reactions combined are seen to be able to convert a higher percentage of fuel carbon (char) into gaseous compounds. Although the results reported by Gao et al. [32] are related to CaO inherent in the char, they can be partially applied to char gasification in a fluidised bed containing CaO. The CaO plays a remarkable catalytic role during char gasification with  $\text{H}_2\text{O}/\text{CO}_2$  mixture and promotes a synergistic effect. Gao et al. [32] suggest that the  $\text{H}_2\text{O}$  can decrease the size of CaO particles and increase its dispersion so that the catalytic effect of calcium can be much more effective. This would explain the highest carbon conversion when using the mixture of  $\text{H}_2\text{O}/\text{CO}_2$  with the lower concentration of CaO (Fig. 4b). The  $\text{H}_2\text{O}$  can promote the generation of honeycomb pores on the char surface, and  $\text{CO}_2$  can enlarge the honeycomb pores, thus facilitating entry of the gasifying agents. [32] The carbon conversion efficiency is closely connected with cold gas efficiency reported in supplemental information file Fig. S1.

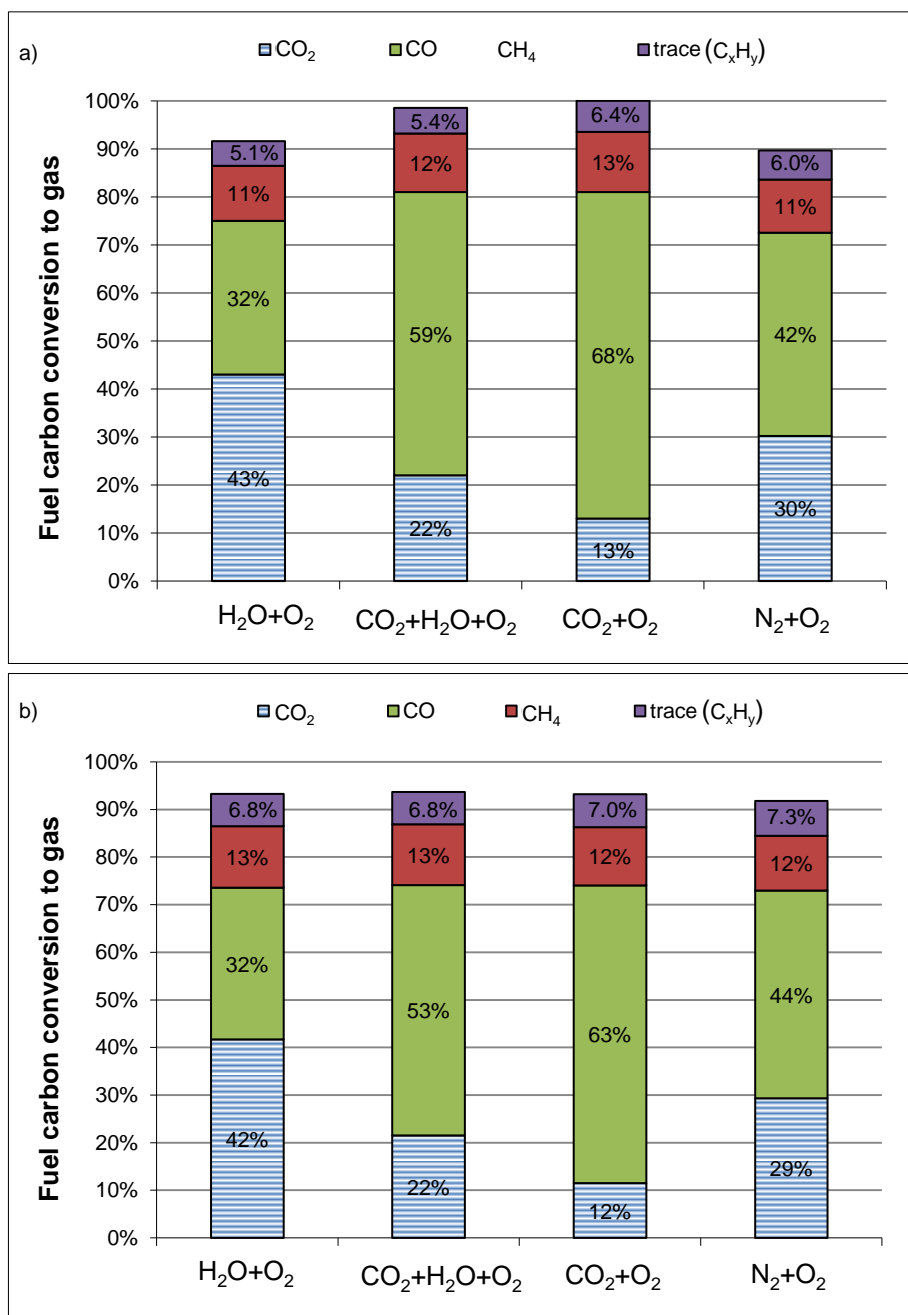


Fig. 4. Fuel-carbon-to-gas conversion efficiency a) 50% vol. limestone in the FB b) 25% vol. limestone in the FB.

Tar compounds (produced mainly by the pyrolysis of the fuel) are decomposed through steam and dry reforming reactions (rx. 2 and rx. 5). These processes were clearly more effective when higher concentrations of DL in the FB were used. With 50% dolomitic lime in the FB (Fig. 5a), the steam reforming reaction (rx. 2), which is predominant



when gasifying with high partial pressure of  $\text{H}_2\text{O}$ , was more effective than the dry reforming reaction (rx. 5), which is predominant with the high  $\text{CO}_2$  partial pressure in the reactor. The combined use of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the gasifying agent led to a significant decrease in tar yield when compared to gasification with  $\text{CO}_2+\text{O}_2$ , but a slight increase in the yield of tars when compared to gasification with  $\text{H}_2\text{O}+\text{O}_2$ . The situation is different when using lower amounts of DL in the FB (Fig. 5b). Overall, higher yields of tars were measured for all cases and the lowest tar yield was measured when  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were used together as the gasifying agent. Therefore, in this case, the combined use of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the gasifying agent had a synergistic effect on the tar reforming reactions. A detailed analysis of the tar compounds is depicted in Supplemental Information file (Table S1) and their yield is compared with the yield of minor organic compounds present in the gas (Fig. S5).

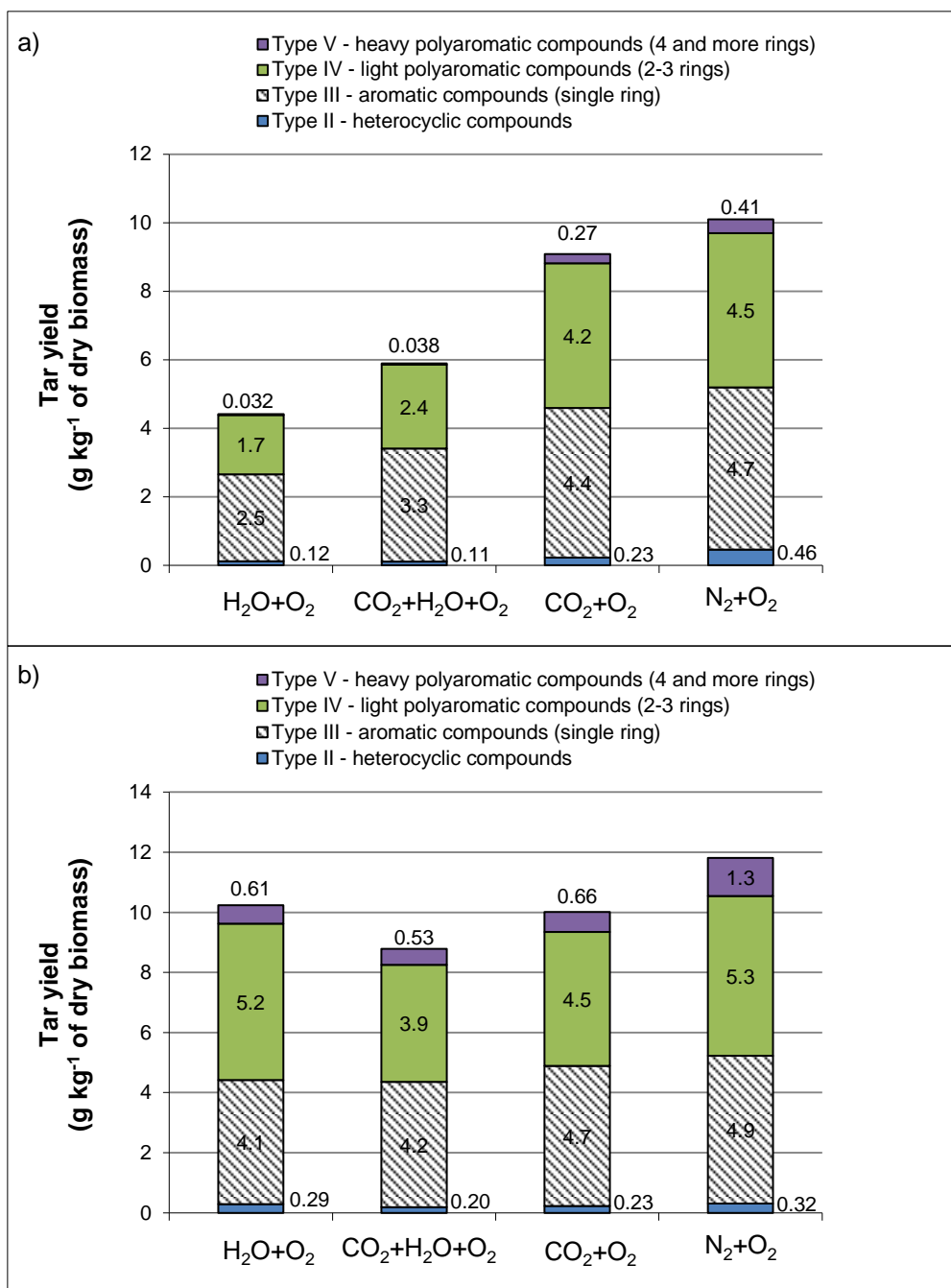


Fig. 5. Tar yield: a) 50% vol. limestone in the FB; b) 25% vol. limestone in the FB; the tars are divided into 4 groups according to ECN classification [42].

## 4 Conclusions

Wood chips were gasified in a fluidised bed composed of silica sand and dolomitic lime at volume ratios of 1:1 or 3:1 at temperature of 850°C. Gasifying agents composed of CO<sub>2</sub> and H<sub>2</sub>O led to high conversion of char to gas. Tar was effectively decomposed by the combined effect of steam and dry reforming. A higher concentration of catalytic lime (mainly CaO) in the fluidised bed led to higher carbon conversion when using CO<sub>2</sub>+H<sub>2</sub>O in the gasifying agent. Tar reforming reactions were more effective with a higher lime concentration in the fluidised bed; however, the combined effect of steam and dry reforming was more pronounced with a lower lime concentration in the fluidised bed. The combined use of CO<sub>2</sub> and H<sub>2</sub>O as gasifying agent is clearly beneficial in achieving higher char conversions and for more effective tar reforming in an environment catalysed by CaO.

## 5 Acknowledgements

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## 6 References

- [1] V. S. Sikarwar, M. Zhao, P. Clough, J. Yao, X. Zhong, M. Z. Memon, N. Shah, E. J. Anthony and P. S. Fennell, "An overview of advances in biomass gasification", *Energy Environ. Sci.*, vol. 9, no. 10, pp. 2939–2977, 2016.
- [2] M. Pohořelý, M. Jeremiáš, P. Kameníková, S. Skoblia, K. Svoboda and M. Punčochář, "Biomass Gasification", *Chem. List.*, vol. 106, pp. 264–274, 2012.
- [3] K. Göransson, U. Söderlind, J. He and W. Zhang, "Review of syngas production via biomass DFBGs", *Renew. Sustain. Energy Rev.*, vol. 15, no. 1, pp. 482–492, 2011.
- [4] M. Pohořelý, M. Jeremiáš, K. Svoboda, P. Kameníková, S. Skoblia and Z. Beňo, "CO<sub>2</sub> as moderator for biomass gasification", *Fuel*, vol. 117, pp. 198–205, 2014.
- [5] P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber and T. E. Müller, "Worldwide innovations in the development of carbon capture technologies and the utilization of CO<sub>2</sub>", *Energy Environ. Sci.*,

- vol. 5, no. 6, p. 7281, 2012.
- [6] N. Spiegl, A. Sivena, E. Lorente, N. Paterson and M. Millan, "Investigation of the Oxy-fuel Gasification of Coal in a Laboratory-Scale Spouted-Bed Reactor: Reactor Modifications and Initial Results", *Energy & Fuels*, vol. 24, no. 9, pp. 5281–5288, 2010.
- [7] B. Prabowo, M. Aziz, K. Umeki, H. Susanto, M. Yan and K. Yoshikawa, "CO<sub>2</sub>-recycling biomass gasification system for highly efficient and carbon-negative power generation", *Appl. Energy*, vol. 158, pp. 97–106, 2015.
- [8] H. Yu, G. Chen, Y. Xu and D. Chen, "Experimental Study on the Gasification Characteristics of Biomass with CO<sub>2</sub> /Air in an Entrained-flow Gasifier", *BioResources*, vol. 11, no. 3, pp. 6085–6096, 2016.
- [9] S. Valin, L. Bedel, J. Guillaudeau, S. Thiery and S. Ravel, "CO<sub>2</sub> as a substitute of steam or inert transport gas in a fluidised bed for biomass gasification", *Fuel*, vol. 177, pp. 288–295, 2016.
- [10] K. Svoboda, M. Pohořelý, M. Jeremiáš, P. Kameníková, M. Hartman, S. Skoblia and M. Šyc, "Fluidized bed gasification of coal–oil and coal–water–oil slurries by oxygen–steam and oxygen–CO<sub>2</sub> mixtures", *Fuel Process. Technol.*, vol. 95, pp. 16–26, 2012.
- [11] G. W. Huber, S. Iborra and A. Corma, "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering", *Chem. Rev.*, vol. 106, no. 9, pp. 4044–4098, 2006.
- [12] K. Svoboda, M. Hartman, M. Pohořelý, M. Šyc, P. Kameníková, M. Jeremiáš and L.-W. W. Huang, "Thermodynamic Possibilities and Limits for Producer Gas Desulfurization and HCL Related Interferences for Zn, Mn, Ce and La Based Sorbents of Sulfur Compounds", *Key Eng. Mater.*, vol. 656–657, pp. 101–106, 2015.
- [13] A. M. Parvez, I. M. Mujtaba and T. Wu, "Energy, exergy and environmental analyses of conventional, steam and CO<sub>2</sub>-enhanced rice straw gasification", *Energy*, vol. 94, pp. 579–588, 2016.
- [14] H. C. Butterman and M. J. Castaldi, "CO<sub>2</sub> as a carbon neutral fuel source via enhanced biomass gasification", *Environ. Sci. Technol.*, vol. 43, no. 23, pp. 9030–9037, 2009.
- [15] B. J. P. Buhre, L. K. Elliott, C. D. Sheng, R. P. Gupta and T. F. Wall, "Oxy-fuel combustion technology for coal-fired power generation", *Prog. Energy Combust. Sci.*, vol. 31, no. 4, pp. 283–307, 2005.
- [16] Y. Bai, Y. Wang, S. Zhu, L. Yan, F. Li and K. Xie, "Synergistic effect between CO<sub>2</sub> and H<sub>2</sub>O on reactivity during coal chars gasification", *Fuel*, vol. 126, pp. 1–7, 2014.
- [17] H. C. Butterman and M. Castaldi, "Influence of CO<sub>2</sub> Injection on Biomass Gasification", *Ind. Eng. Chem. Res.*, vol. 46, pp. 8875–8886, 2007.
- [18] C. Guizani, F. J. Escudero Sanz and S. Salvador, "The gasification reactivity of high-heating-rate chars in single and mixed atmospheres of H<sub>2</sub>O and CO<sub>2</sub>", *Fuel*, vol. 108, pp. 812–823, 2013.
- [19] R. C. Everson, H. W. J. P. Neomagus, H. Kasaini and D. Njapha, "Reaction kinetics of pulverized coal-chars derived from inertinite-rich coal discards: Gasification with carbon dioxide and steam", *Fuel*, vol. 85, no. 7–8, pp. 1076–1082, 2006.
- [20] S. Nilsson, A. Gómez-Barea and P. Ollero, "Gasification of char from dried

- sewage sludge in fluidized bed: Reaction rate in mixtures of CO<sub>2</sub> and H<sub>2</sub>O", *Fuel*, vol. 105, pp. 764–768, 2013.
- [21] K. Jayaraman and I. Gokalp, "Effect of char generation method on steam, CO<sub>2</sub> and blended mixture gasification of high ash Turkish coals", *Fuel*, vol. 153, pp. 320–327, 2015.
- [22] D. G. Roberts and D. J. Harris, "Char gasification in mixtures of CO<sub>2</sub> and H<sub>2</sub>O: Competition and inhibition", *Fuel*, vol. 86, no. 17–18, pp. 2672–2678, 2007.
- [23] S. Umemoto, S. Kajitani and S. Hara, "Modeling of coal char gasification in coexistence of CO<sub>2</sub> and H<sub>2</sub>O considering sharing of active sites", *Fuel*, vol. 103, pp. 14–21, 2013.
- [24] C. Chen, J. Wang, W. Liu, S. Zhang, J. Yin, G. Luo and H. Yao, "Effect of pyrolysis conditions on the char gasification with mixtures of CO<sub>2</sub> and H<sub>2</sub>O", *Proc. Combust. Inst.*, vol. 34, no. 2, pp. 2453–2460, 2013.
- [25] D. G. Roberts and D. Harris, "Char Gasification Kinetics in Mixtures of CO<sub>2</sub> and H<sub>2</sub>O: The Role of Partial Pressure in Determining the Extent of Competitive Inhibition", *Energy & Fuels*, vol. 28, no. 12, pp. 7643–7648, 2014.
- [26] Y. Wang and D. A. Bell, "Competition between H<sub>2</sub>O and CO<sub>2</sub> during the gasification of Powder River Basin coal", *Fuel*, vol. 187, pp. 94–102, 2017.
- [27] R. Zhang, Y. Chen, K. Lei and D. Liu, "The effects of specific surface area and ash on char gasification mechanisms in the mixture of H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub> and CO", *Fuel*, vol. 209, no. June, pp. 109–116, 2017.
- [28] C. Guizani, F. J. Escudero Sanz, M. Jeguirim, R. Gadiou and S. Salvador, "The effects of textural modifications on beech wood-char gasification rate under alternate atmospheres of CO<sub>2</sub> and H<sub>2</sub>O", *Fuel Process. Technol.*, vol. 138, pp. 687–694, 2015.
- [29] C. Guizani, F. J. Escudero Sanz and S. Salvador, "Influence of temperature and particle size on the single and mixed atmosphere gasification of biomass char with H<sub>2</sub>O and CO<sub>2</sub>", *Fuel Process. Technol.*, vol. 134, pp. 175–188, 2015.
- [30] C. S. M. de Lecea, M. Almela-Alarcón and A. Linares-Solano, "Calcium-catalysed carbon gasification in CO<sub>2</sub> and steam", *Fuel*, vol. 69, no. 1, pp. 21–27, 1990.
- [31] Y. Wang, S. H. Zhu, M. Q. Gao, Z. R. Yang, L. J. Yan, Y. Bai and F. Li, "A study of char gasification in H<sub>2</sub>O and CO<sub>2</sub> mixtures: Role of inherent minerals in the coal", *Fuel Process. Technol.*, vol. 141, pp. 9–15, 2016.
- [32] M. Gao, Z. Yang, Y. Wang, Y. Bai, F. Li and K. Xie, "Impact of calcium on the synergistic effect for the reactivity of coal char gasification in H<sub>2</sub>O/CO<sub>2</sub> mixtures", *Fuel*, vol. 189, pp. 312–321, 2017.
- [33] P. A. Simell, J. O. Hepola and A. O. I. Krause, "Effects of gasification gas components on tar and ammonia decomposition over hot gas cleanup catalysts", *Fuel*, vol. 76, no. 12, pp. 1117–1127, 1997.
- [34] F. Pinto, R. André, M. Miranda, D. Neves, F. Varela and J. Santos, "Effect of gasification agent on co-gasification of rice production wastes mixtures", *Fuel*, vol. 180, pp. 407–416, 2016.
- [35] M. Jeremiáš, M. Pohořelý, P. Bode, S. Skoblia, Z. Beňo and K. Svoboda, "Ammonia yield from gasification of biomass and coal in fluidized bed reactor", *Fuel*, vol. 117, pp. 917–925, 2014.
- [36] CSN P CEN/TS 15430 - Biomass gasification - Tar and particles in product gases - Sampling and analysis. 2006.

- [37] M. Pohořelý, M. Vosecký, P. Hejdová, M. Punčochář, S. Skoblia, M. Staf, J. Vošta, B. Koutský and K. Svoboda, "Gasification of coal and PET in fluidized bed reactor", *Fuel*, vol. 85, no. 17–18, pp. 2458–2468, 2006.
- [38] M. Šyc, M. Pohořelý, M. Jeremiáš, M. Vosecký, P. Kameníková, S. Skoblia, K. Svoboda and M. Punčochář, "Behavior of Heavy Metals in Steam Fluidized Bed Gasification of Contaminated Biomass", *Energy & Fuels*, vol. 25, no. 5, pp. 2284–2291, 2011.
- [39] K. Svoboda, M. Pohořelý, M. Jeremiáš, P. Kameníková, S. Skoblia, Z. Beňo and M. Šyc, "Concentration of HCl, HF and sulfur compounds in fuel gas from fluidized bed gasification of coals and wood by steam-oxygen mixtures", in *CHISA 2012 - 20th International Congress of Chemical and Process Engineering and PRES 2012 - 15th Conference PRES*, 2012, no. May 2016, p. 19.
- [40] M. Pohořelý, M. Jeremiáš, S. Skoblia, Z. Beňo, M. Šyc and K. Svoboda, "Transient Catalytic Activity of Calcined Dolomitic Limestone in a Fluidized Bed during Gasification of Woody Biomass", *Energy & Fuels*, vol. 30, no. 5, pp. 4065–4071, 2016.
- [41] M. Hartman, K. Svoboda, M. Pohořelý, M. Šyc and M. Jeremiáš, "Attrition of Dolomitic Lime in a Fluidized-Bed at High Temperature", *Chem. Pap.*, vol. 67, no. 2, pp. 164–172, 2013.
- [42] L. G. Devi, K. J. Ptasinski, F. J. J. G. Janssen, S. V. B. van Paasen, P. C. Bergman and J. H. Kiel, "Catalytic decomposition of biomass tars: use of dolomite and untreated olivine", *Renew. Energy*, vol. 30, no. 4, pp. 565–587, 2005.

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