

Gasification of biomass with CO₂ and H₂O mixtures in a catalytic fluidised bed

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Highlights

- Different mixtures of biomass gasifying agents were compared (H₂O+O₂, CO₂+H₂O+O₂, CO₂+O₂ and N₂+O₂).
- 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 CO₂ and H₂O as the gasifying agent.
- Use of the combination of CO₂ and H₂O leads to a higher degree of tar decomposition.

Abstract

Steam can be fully or partially substituted by CO₂ 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 CO₂ and H₂O was compared to the use of CO₂ or H₂O alone. It was found that mixtures of CO₂ and H₂O 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.

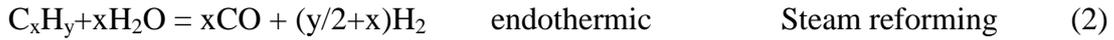
Keywords: Fluidised bed; Gasification; Catalyst; Dolomite; Limestone; Synergistic effect

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, CO₂ and H₂O, which are subsequently partially reacted in the process. However, N₂ 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 H₂, (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 CO₂ and H₂ in the syngas [4].





Steam as the gasifying agent can be fully or partially substituted by CO₂. The use of CO₂ instead of steam is of practical interest for various reasons; for example, (i) the possible reuse of CO₂ from carbon capture technologies or from the recycling of flue gas from oxyfuel combustion (composed of a mixture of CO₂ and H₂O) [5–8]; (ii) the use of CO₂ instead of N₂ as an inert gas (for example in fuel dosing trains), as CO₂ behaves as an inert at lower temperatures [6, 9, 10]; (iii) adjustment of the H₂/CO ratio in the syngas for various synthesis technologies [9, 11–13]; or (iv) because thermal processing via CO₂ rather than steam avoids the use of large quantities of water, which has a large latent heat of vapourisation [14].

CO₂ has both higher volumetric heat capacity and different radiative properties from steam [15]. Given the higher partial pressure of CO₂ in the reactor, the chemistry of the process is also altered. CO₂ 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 H₂ concentrations in the producer gas [4].



Therefore, the difference between gasification with steam, CO₂ 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 H₂O, CO₂ and their mixtures, most of it coming from thermogravimetric analysis (TGA). Thus, Bai et al. [16] found a synergistic effect between H₂O and CO₂ for the gasification of coal char. In particular, the addition of CO₂ improved the char reactivity, which was higher than the sum of the individual reactivities using either CO₂ or H₂O below 900°C. Similar results were found by Butterman et al. [14, 17] for biomass char. Carbon conversion was complete with 25% CO₂/75% steam compared to 90% conversion with pure steam in a temperature range of 800–1000°C. The strongest effect was seen upon addition of 0–5% CO₂ [14]. However, other researchers [18–21] suggested that the char reactivity was simply due to the sum of the individual reactivities using either CO₂ or H₂O. Still other researchers [22–26] have suggested that H₂O and CO₂ compete for the same active carbon sites and, therefore, the addition of CO₂ 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 H₂O/CO₂ 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 H₂O and CO₂ diffuse mainly in macropores and that the differences between H₂O and CO₂ 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 CO₂/H₂O 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 CaO [32].

Data relating to the effect of the gasifying agent composed both of CO₂ and H₂O 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 CO₂, H₂O 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 H₂O and CO₂ 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 CO₂-oxygen mixture. Silica sand in a spouting FB was used in their work, and they reported that the heating values of dry, N₂-free producer gas are lower using CO₂/O₂ in comparison with gasification by steam-O₂ mixtures at comparable conditions due to the high content of diluting CO₂ [10]. Valin et al. [9] describe a gradual replacement of H₂O by CO₂ 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 CO₂ (instead of H₂O) 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 H₂O and CO₂ 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 CO₂ and H₂O as gasifying

agent was not reported [4]. Pinto et al. [34] concluded that CO₂-blown gasification is extremely complex and more investigation is still needed to determine the best composition of CO₂, oxygen and steam mixtures. It can be hypothesised that the fluidised bed material plays a crucial role in determining whether the combined use of CO₂ and H₂O 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 H₂O/CO₂ gasification media.

In the experiments described in this study, we compared the influence of H₂O and CO₂ 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 H₂O and CO₂ 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 CO₂ and H₂O 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 H₂O and CO₂ 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

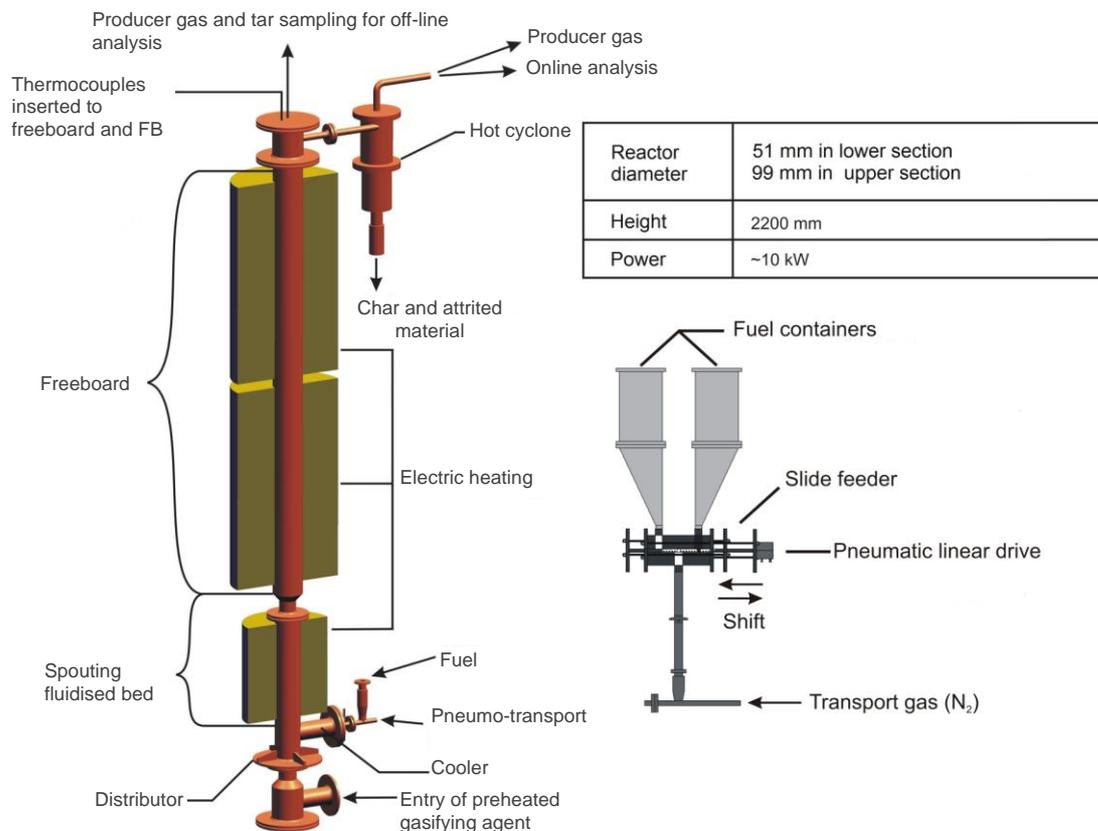


Fig. 1. Pilot-scale Spouting Fluidised Bed Reactor

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, CO₂, H₂, CH₄, C₂H₄, O₂, N₂) 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 ^a (mm)	0.25 - 0.50	0.5 - 1.25	-
Mean particle size (mm)	0.375	0.875	-
True solid density ^b (kg m ⁻³)	2530	2862	2653
Apparent density ^c (kg m ⁻³)	2530	2498	963
Particle porosity (vol %)	0	13	64
Bed voidage (vol %)	45	48	23
Loose poured bulk density (kg m ⁻³)	1394	1301	743
Specific surface area (BET) (m ² g ⁻¹)	-	-	13.8
Mesopore surface area (m ² g ⁻¹)	-	-	7.6
Micropore volume (mm ³ g ⁻¹)	-	-	3.5
Minimum fluidising velocity* (m s ⁻¹)	0.11	0.42	0.19
Minimum fluidising velocity** (m s ⁻¹)	0.05	0.25	0.10
Complete fluidising velocity* (m s ⁻¹)	0.18	0.64	0.32
Complete fluidising velocity** (m s ⁻¹)	0.09	0.48	0.20
Loss on ignition*** (wt %)	-	47	-
CaCO ₃ ^d (wt %)	< 0.03	55	-
MgCO ₃ ^d (wt %)	< 0.03	44	-
SiO ₂ ^d (wt %)	98	0.20	-

$\text{Al}_2\text{O}_3^{\text{d}}$ (wt %)	1.4	0.16	-
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Determined by: ^asieving, ^bhelium displacement, ^cmercury displacement, ^dXRF;

* 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 H_2O by 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 ⁻¹)	1300			
Raw fuel feeding rate (g h ⁻¹)	1440			
Experimental label	H ₂ O+O ₂	CO ₂ +H ₂ O+O ₂	CO ₂ +O ₂	N ₂ +O ₂
Gas inlet*				
Steam (m ³ h ⁻¹)	1.36	0.41	0.00	0.00
O ₂ (m ³ h ⁻¹)	0.27	0.27	0.27	0.27
CO ₂ (m ³ h ⁻¹)	0.00	0.95	1.36	0.00
N ₂ (m ³ h ⁻¹)	0.37	0.37	0.37	1.73
N ₂ pneumatic transport (m ³ h ⁻¹)	1.50	1.50	1.50	1.50
Total gas inlet (m ³ h ⁻¹)	3.50	3.50	3.50	3.50
Parameters				
ER (m ³ m ⁻³) ^a	0.20	0.20	0.20	0.20
H ₂ O/C (mol mol ⁻¹) ^b	1.2	0.46	0.14	0.13
CO ₂ /C (mol mol ⁻¹) ^c	0.00	0.70	1.05	0.00
CO ₂ /(H ₂ O+CO ₂) (mol mol ⁻¹)	0	0.70	1.00	-
O/C (mol mol ⁻¹) ^d	2.31	1.75	1.64	1.25
H ₂ O/F (kg kg ⁻¹) ^e	0.88	0.34	0.11	0.11
CO ₂ /F (kg kg ⁻¹) ^f	0.00	1.31	1.88	0.00
O ₂ /F (kg kg ⁻¹) ^g	0.27	0.27	0.27	0.27

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

^a Equivalence ratio – available O₂ related to the O₂ needed for stoichiometric combustion of fuel (F).

^b H₂O from the gasifying agent and fuel moisture related to the C bound in fuel.

^c CO₂ from the gasifying agent related to the C bound in fuel.

^d O bound in fuel, fuel moisture and H₂O and CO₂ in the gasifying agent related to the C bound in fuel and CO₂ input.

^e H₂O in gasifying agent and fuel moisture related to the input of dry fuel.

^f CO₂ in gasifying agent related to the input of dry fuel.

^g O₂ 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 CO₂ and H₂O, 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 H₂O+O₂ mixture, a large yield of H₂ and CO₂ and low yield of H₂O and CO were observed and vice versa when gasifying the fuel with the mixture of CO₂+O₂. 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.

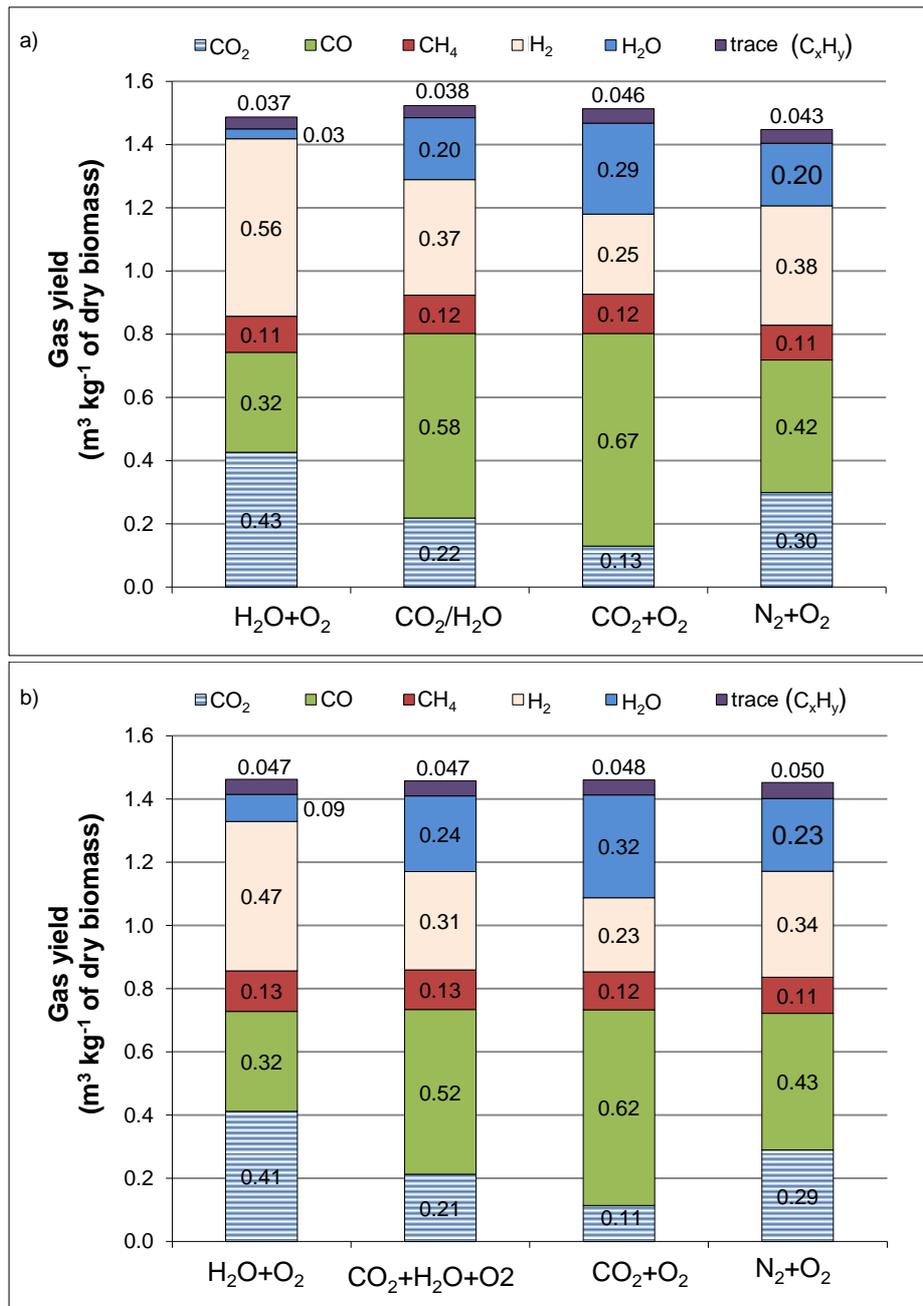


Fig. 2. Yield of major gases. a) 50% vol. limestone in the FB; b) 25% vol. limestone in the FB; inputs of H₂O, N₂ and CO₂ are subtracted (only gases arising in the reactor are shown). All volume units are expressed at 25°C and 101.325 kPa

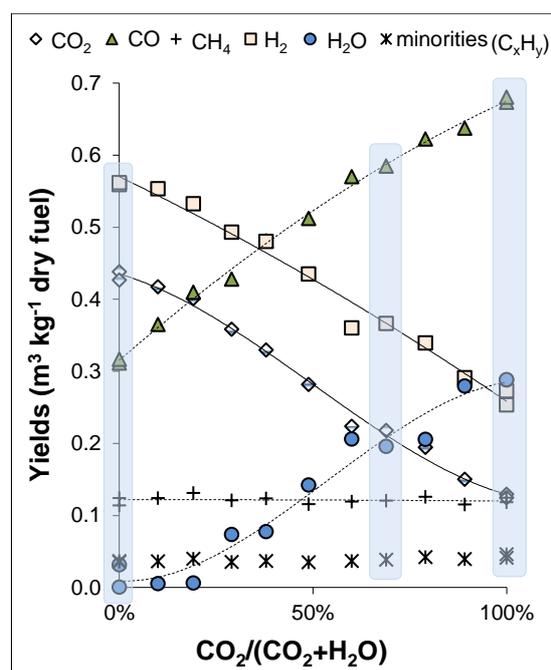


Fig. 3. Yield of gases produced in the reactor at transition states (50% vol. DL in the FB); corresponding steady states depicted in the first three columns (from the left) of Fig. 2a are highlighted by the light-blue fields; inputs of H₂O, N₂ and CO₂ are subtracted (only gases arising in the reactor are shown); H₂O 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 ₂ O+O ₂	CO ₂ +H ₂ O+O ₂	CO ₂ +O ₂	N ₂ +O ₂
CO ₂	11 (10)	23 (24)	29 (29)	7.7 (7.3)
H ₂	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 ₄	2.9 (3.2)	3.1 (3.2)	3.1 (3.0)	2.8 (2.9)
N ₂	36 (37)	36 (37)	36 (37)	63 (63)
H ₂ 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 _x H _y	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 CO₂+H₂O+O₂ with 50% DL in the FB and was the highest when compared to the use of H₂O+O₂ and CO₂+O₂ with 25% DL in FB. This finding suggests that the

calcined DL plays a crucial role in the gasification of char by CO₂ and that the combined use of CO₂ and H₂O is more effective in the conversion of char compared to the use of H₂O 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 H₂O/CO₂ mixture and promotes a synergistic effect. Gao et al. [32] suggest that the H₂O 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 H₂O/CO₂ with the lower concentration of CaO (Fig. 4b). The H₂O can promote the generation of honeycomb pores on the char surface, and CO₂ 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.

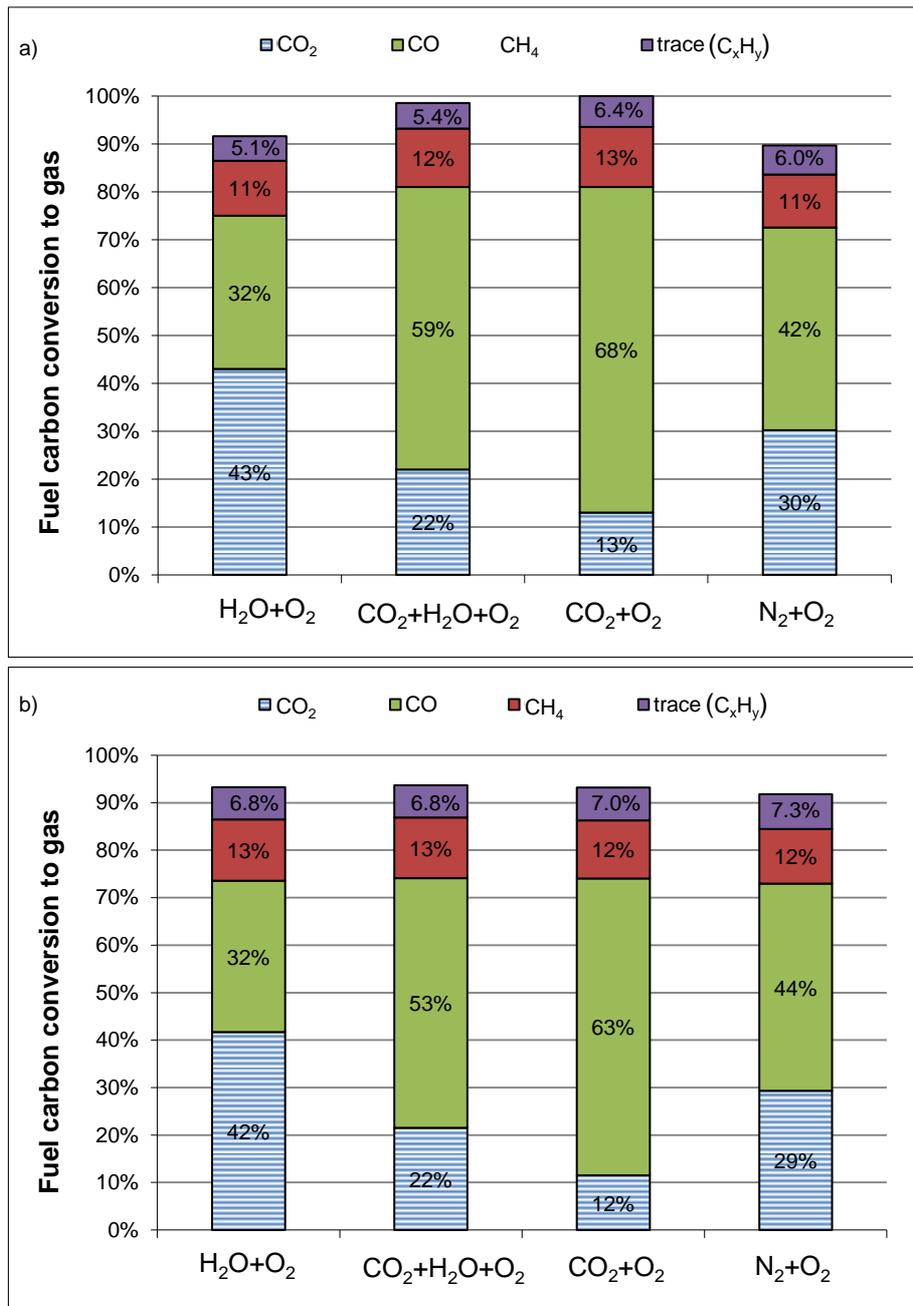


Fig. 4. Fuel-carbon-to-gas conversion efficiency a) 50% vol. limestone in the FB b) 25% vol. limestone in the FB.

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 H₂O, was more effective than the dry reforming reaction (rx. 5), which is predominant with the high CO₂ partial pressure in the reactor. The combined use of H₂O and CO₂ in the gasifying agent led to a significant decrease in tar yield when compared to gasification with CO₂+O₂, but a slight increase in the yield of tars when compared to gasification with H₂O+O₂. 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 CO₂ and H₂O were used together as the gasifying agent. Therefore, in this case, the combined use of CO₂ and H₂O 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).

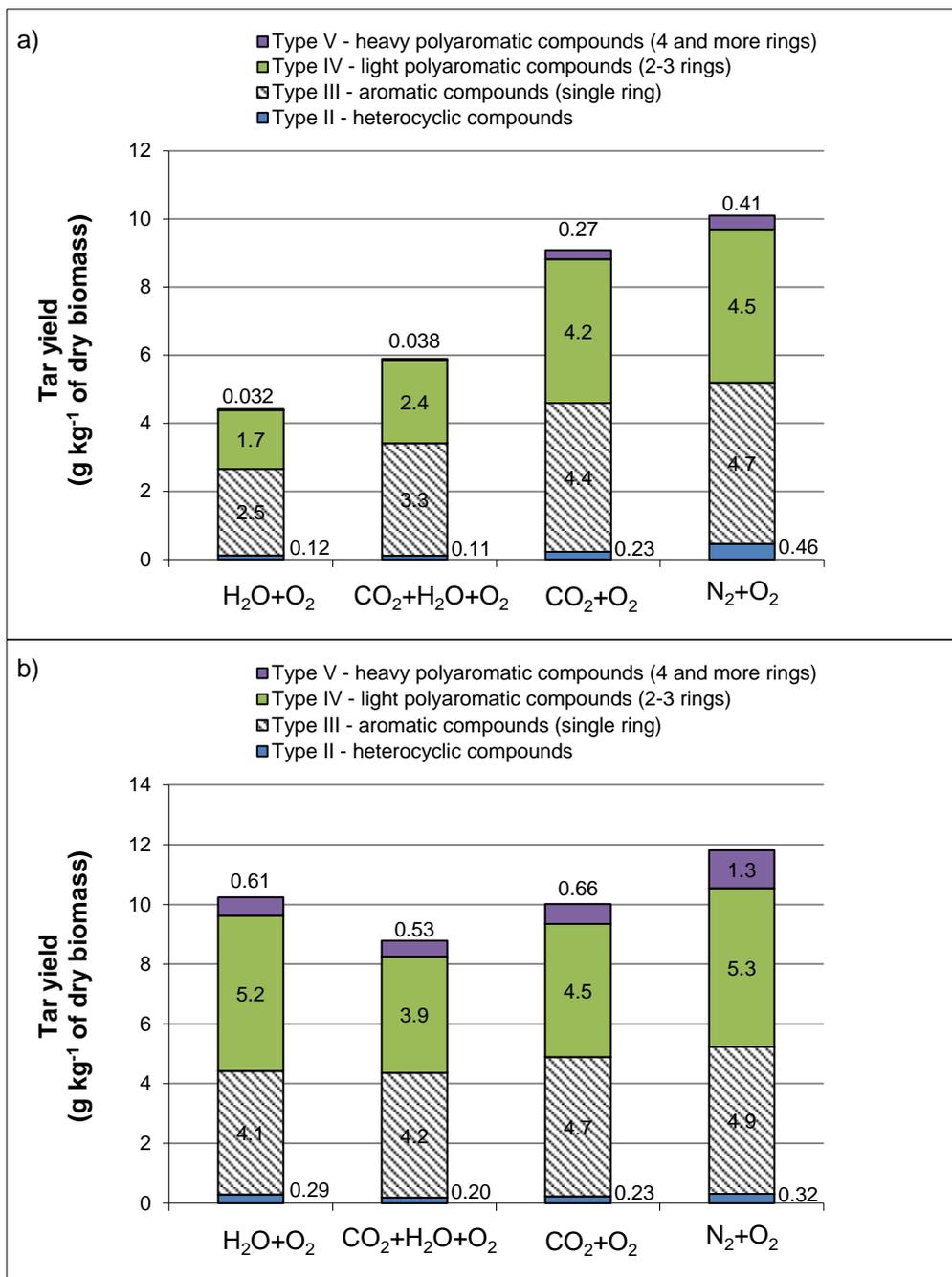


Fig. 5. Tar yield: a) 50% vol. limestone in the FB; b) 25% vol. limestone in the FB; the tars are divided into 4 groups according to ECN classification [42].

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 CO₂ and H₂O 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 CO₂+H₂O 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 CO₂ and H₂O 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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