

## Experimental Investigation of the Absorption Enhanced Reforming of Biomass in a 20 kW<sub>th</sub> Dual Fluidized Bed System\*

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### Abstract

A gasification product gas with a hydrogen content over 75 vol-%<sub>db</sub> and a heating value of 15 MJ/m<sup>3</sup><sub>STP,db</sub> has been obtained through the absorption enhanced reforming of biomass. The Absorption Enhanced Reforming (AER) process involves a Dual Fluidized Bed (DFB) system consisting of a gasifier and a regenerator (calciner). In the DFB system, the Ca - looping ratio is an important parameter defined as the ratio of the molar flow rate of regenerated sorbent (F<sub>Ca</sub>) and carbon (F<sub>C</sub>) which enters the gasifier as fuel. A special feature of the 20 kW<sub>th</sub> DFB test facility at IFK is the Ca - looping rate control through a cone valve. Therefore, the Ca - looping ratio (F<sub>Ca</sub>/F<sub>C</sub>) was varied between a value of 2 and 12 mol<sub>Ca</sub>/mol<sub>C</sub> to investigate its influence on the cold gas efficiency, product gas yield, yield of gas components and gravimetric tar concentration during the AER of biomass. The experiments were carried out with wood pellets and a Greek limestone as CO<sub>2</sub> sorbent. The experimental work shows a clear influence of the Ca - looping ratio on the AER process. It shows also that beyond a certain value of this parameter, the tar and gas composition is stabilized.

**Keywords:** Steam gasification; biomass; tar; dual fluidized bed gasifier; CO<sub>2</sub> capture; hydrogen.

### 1. Introduction

#### 1.1. Dual Fluidized Bed Biomass Steam Gasification

The main biomass steam gasification reactions are listed in Table 1. These reactions are mainly endothermic, therefore heat is required to sustain the gasification process. This heat can be provided through two different approaches: by partial fuel oxidation (autothermal gasification), or externally via heat carrier or heat exchanger (allothermal gasification). Absorption enhanced reforming is an allothermal gasification process.

During allothermal gasification pure steam can be used as the gasification agent leading to a medium calorific value product gas (12-14 MJ/m<sup>3</sup><sub>STP</sub>) with a hydrogen content of 40-60 vol-%<sub>db</sub> (Corella, et. al., 2008; Soukup, et. al., 2009). The required heat to the gasifier can be provided by the following steps: (i) transportation of the char generated in the gasifier into a combustion chamber; (ii) combustion of the generated char in the combustion chamber; and (iii) transfer of the generated heat from the combustion chamber

to the gasifier through solid circulation (Corella et. al., 2007).

This leads to a gasifier system, consisting of a biomass steam gasifier and a char combustion chamber. Additionally, a transport pipe is needed to transfer the heat carrier solids between the reactors. The transport pipe has to ensure gas sealing between the gasifier and the combustor. Such gasifier systems can be realized by a Dual Fluidized Bed (DFB) system consisting of a Bubbling Fluidized Bed (BFB) as the gasifier and a Circulating Fluidized Bed (CFB) as the combustor. The acronym DFB used to describe these systems, is well established (Corella et. al., 2007).

An 8 MW<sub>th</sub> DFB steam gasifier with combined heat and power (CHP) has been operating in Güssing since 2002 with Olivine as the circulating bed material (Hofbauer et al., 2002). Based on this principle a 9 MW<sub>th</sub> CHP DFB gasifier was constructed in 2009 in Oberwart (Neues Biomassekraftwerk Oberwart, 2009).

Table 1. Excerpt of main biomass steam gasification reactions (Florin, Harris, 2008; Higman, van der Burgt, 2003).

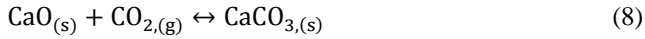
Name of reaction	Chemical equation	$\Delta H_{923}^0$ kJ/mol	Eq.
Biomass reforming	$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{m}{2} + n\right)H_2$	$+\Delta H$	(1)
Water-gas-shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	-36	(2)
Water-gas (i)	$C + H_2O \leftrightarrow CO + H_2$	+136	(3)
Water-gas (ii)	$C + 2H_2O \leftrightarrow CO_2 + 2H_2$	+100	(4)
Boudouard	$C + CO_2 \leftrightarrow 2CO$	+171	(5)
CO methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-224	(6)
CO <sub>2</sub> methanation	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-188	(7)

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### 1.2. Absorption Enhanced Reforming (AER)

The hydrogen concentration of the product gas, during allothermal biomass gasification with pure steam, can be enhanced by using a CO<sub>2</sub> absorbing sorbent, e.g. CaO. Thereby, the CO<sub>2</sub> is captured in situ Eq. (8) after it is produced in Eqn. (2) and Eqn. (4). This exothermic removal of the CO<sub>2</sub> leads to a shifting of the water-gas-shift reaction to the product side in Eqn. (2). Therefore, all parallel reforming reactions are influenced, resulting in an enhanced H<sub>2</sub> output.



The CO<sub>2</sub>/CaO-equilibrium in Eqn. (8) strongly depends on the process temperature at atmospheric conditions. The CO<sub>2</sub> capture takes place between 450 °C to 750 °C (Florin and Harris, 2008). Above 750 °C, CO<sub>2</sub> can not be captured whereas at a temperature above 800 °C CaCO<sub>3</sub> is regenerated to CaO, while CO<sub>2</sub> is released. The gasification temperature should be as high as possible from the view of carbon conversion and tar formation. However, the thermodynamic boundary conditions from the CO<sub>2</sub>/CaO-equilibrium for CO<sub>2</sub> capture leads to an operating window between 650 °C and 725 °C.

Additionally, by using CaO, the CO<sub>2</sub> capture releases heat in the gasifier which decreases the need for heat, transported by the circulating bed material (Soukup et al., 2009; Pfeifer et al., 2007). The endothermic regeneration takes place in the combustion chamber at 850 °C to 900 °C. The necessary heat for regeneration is supplied by the combustion of the unconverted char, which is transferred together with the bed material (mixture of CaO, CaCO<sub>3</sub> and ash). The principle of the absorption enhanced reforming with circulating Ca - based bed material in a dual reactor system is shown in Figure 1.

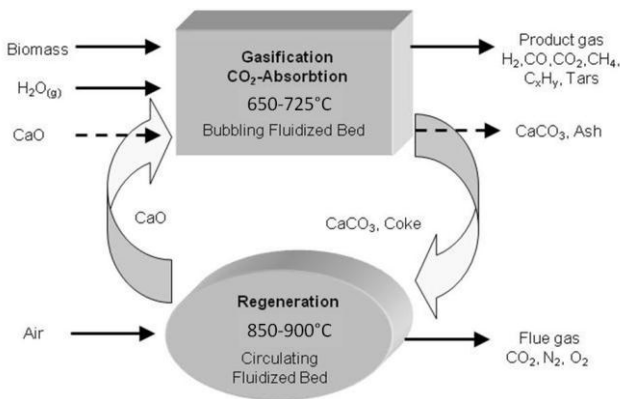


Figure 1. Principle of the absorption enhanced reforming (AER).

In the literature, there are a number of different criteria in order to assess the efficiency of a gasification process. Recommended criteria are carbon conversion and cold gas efficiency (CGE), also found in literature as chemical efficiency (Higman and van der Burgt, 2003). The efficiency of a H<sub>2</sub> - production process via gasification, by calculating the thermal efficiency, was analyzed in (Florin and Harris, 2008). The thermal efficiency is based on the chemical efficiency and is defined as the ratio of the energy output obtained from the H<sub>2</sub> produced (deducting the heat necessary to drive the reaction process) and the biomass energy input to the system. In addition to the CGE criteria,

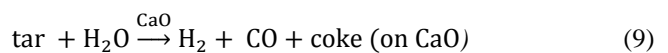
the gas composition and quality (tar loading and trace pollutants) are necessary to determine the gas cleaning and utilization requirements in order to evaluate the effectiveness of the AER process. In this paper the effectiveness of the AER process is evaluated based on the CGE, the gas composition (especially H<sub>2</sub> concentration) gas yield, and the gravimetric tar concentration in the product gas.

The quality of the gas and the efficiency of the process are affected by a variety of process parameters, e.g. gasification temperature, biomass and bed composition, steam to biomass-carbon ratio (S/C), weight hourly space velocity (WHSV). Regarding to parameter variation, extensive research was conducted in the past. However, this research focused on conventional biomass steam gasification (gasification without in situ CO<sub>2</sub> capture). A summary, regarding 12 variables that influence the effectiveness of the conventional biomass gasifier, was published in (Corella et. al., 2008).

One of the key parameters for the DFB AER process is the Ca-looping rate of the sorbent material between the gasifier and the combustor. The influences of this parameter on the cold gas efficiency (CGE), the product gas composition, product gas yield, and the tar concentration are analyzed in this work.

### 1.3. The Ca-looping Rate and the Role of CaO in the AER Gasifier

As has been shown in many studies, the carbonation reaction is not fully reversible and a sorbent particle exhibits a maximum carbonation conversion X<sub>max</sub> which decays with increasing carbonation-calcination cycles (Grasa and Abanades, 2006). Moreover, the actual carbonation conversion of a sorbent particle X<sub>carb</sub> during the AER process is always smaller than X<sub>max</sub>. The difference between the maximum carbonation conversion X<sub>max</sub> and the actual carbonation conversion X<sub>carb</sub> of a sorbent particle is termed as the free active CaO (f<sub>a</sub>) (Abanades et al., 2004). The f<sub>a</sub> has been shown to be the key factor in influencing the carbonation reaction rate and hence CO<sub>2</sub> capture efficiency (Abanades et al., 2004; Charitos et al., 2010). It has also been shown that the Ca - looping ratio is inversely proportional to the actual carbonation conversion X<sub>carb</sub> (Charitos, et al., 2010). This means, that increased Ca - looping ratio leads to higher CO<sub>2</sub> conversion and therefore, in theory, to higher H<sub>2</sub> concentration through the water-gas-shift reaction. Post-combustion CO<sub>2</sub> capture experimentation conducted in the same DFB system as used here has shown that a minimum molar Ca - looping ratio of F<sub>Ca</sub>/F<sub>C</sub> = 6 mol<sub>CaO</sub>/mol<sub>C</sub> is needed to achieve a CO<sub>2</sub> capture efficiency of over 80 % (Charitos et al., 2010). Additionally, unreacted CaO is a catalyst in steam reforming reactions of tar as generally described in Eqn. (9) (Corella et. al., 2006). During these reactions different types of tar, which are created at 650 °C (standard AER conditions), are catalytically cracked and steam reformed to H<sub>2</sub> and coke. The created coke covers the surface of the CaO, which leads to a deactivation of the ongoing tar catalysis and prevents CO<sub>2</sub> absorption.



Summarizing, the information above suggests that the Ca-looping ratio in a DFB system effects CO<sub>2</sub> capture, H<sub>2</sub> production and tar cracking.

A very important variable is also the turnover time of the bed material. The turnover time  $\tau_{\text{Bed}}$ , shown in Eqn. (10), is interconnected with the Ca-looping rate  $G_{\text{CaO}}$  (mass flow of CaO to the gasifier, kg/h) and the total mass of bed material in the gasifier.

$$\tau_{\text{Bed}} = \frac{W_{\text{Bed}}}{G_{\text{CaO}}} \quad (10)$$

A high Ca-looping rate between the beds and therefore a small turnover time could lead to a low residence time of the biomass char in the gasifier. The char and unconverted biomass is transported out of the gasifier together with the bed material. This may result in a low carbon conversion and low CGE. Moreover, a high Ca-looping rate would lead to a high demand of energy in the reactor to heat up the solids to calcination temperature (approx. 850 °C). Therefore, a high amount of char or extra fuel would be needed. The aim of this experimental work is to determine the minimum Ca-looping ratio required to ensure sufficient CO<sub>2</sub> capture for maximum hydrogen yield in the product gas and minimum tar concentration during the AER process in a DFB. The dimensionless calcium looping ratio was therefore varied in this work in the range of 2 to 12 mol<sub>CaO</sub>/mol<sub>C</sub>, resulting in a turnover time of the bed material between 1 and 10 minutes.

## 2. Experimental

### 2.1. Description of the 20 kW<sub>th</sub> DFB Gasifier at IFK

A DFB facility has been built at IFK, consisting of a CFB regenerator with 12.4 m height and 7.0 cm diameter and a BFB gasifier with 3.5 m height and 11.4 cm diameter. The DFB facility is shown schematically in Figure 2. The design and hydrodynamic suitability of the facility is based on fundamental research regarding post-combustion CO<sub>2</sub> capture with CaO as the sorbent bed material (Charitos et al., 2009; Hawthorne et al., 2008). Therefore, the reactor design is easily transferable to the AER process. The feeding system of biomass and of steam as fluidization agent as well as the measurement techniques had to be adapted. The BFB is used as the gasifier (a) and the riser as the CFB regenerator (b). Both reactors, standpipes and loop seals are electrically heated.

The CaO bed material is transported between the gasifier and combustor-regenerator, allowing for continuous operation of the AER process. The Ca-looping rate is controlled by varying the cone valve (d) opening and the BFB absolute pressure through a pressure control valve (e) in the range of 0 to 100 mbar. By closing the cone valve completely, the bed material is only circulating within the internal loop of the regenerator and no regenerated bed material is provided to the gasifier.

Preheated steam and carrier nitrogen gas from the biomass dosing unit, together with the regenerated CaO, coming from the double exit loop seal (c) through the cone valve (d) enter the BFB gasifier. The maximum height of the bed in the gasifier is limited by an overflow, located 50.0 cm above the BFB distributor (f). The char and partially carbonated CaO exits the gasifier through this overflow, enters the lower standpipe (g) and subsequently the lower loop seal (h), through which the sorbent flow proceeds to the CFB regenerator. The regenerator off-gas proceeds to the stack while the riser entrainment is separated in a cyclone (i), proceeds to the upper standpipe (j) and reaches the double exit loop seal (c). The desired

Ca-looping rate proceeds to the BFB gasifier and the rest of the flow goes through the loop seal weir (k) into the internal loop and returns to the regenerator.

The product gas from the gasifier is stripped from particles via a cyclone and candle filter. It is analyzed and afterwards burned.

The upper and lower loop seal are fluidized with nitrogen gas. Nitrogen gas flows in the loop seals as well as the carrier gas in the feeding system leads to a dilution of the product gas. Because of the danger of plugging in the quartz glass standpipe segments (g), it was not possible to perform fluidization of the loop seals with steam. In a commercial DFB the loop seals will be fluidized with steam to avoid this dilution. Moreover, the commercial feeding system is designed as plug screw to avoid back flushing. Therefore, reporting the nitrogen free product gas concentration in this work is appropriate.

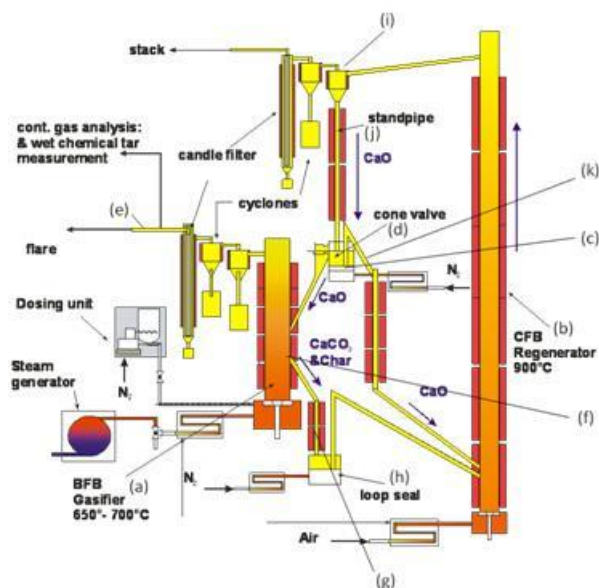


Figure 2. Scheme of IFK DFB gasifier facility: (a) BFB gasifier, (b) CFB riser regenerator, (c) double exit loop seal, (d) cone valve, (e) pressure control valve, (f) BFB overflow, (g) lower quartz glass standpipe segments, (h) lower loop seal, (i) CFB cyclone, (j) upper standpipe, (k) loop seal weir.

### 2.2. Measurement Technique

All operational and measurement parameters, namely temperature, pressure, opening of the cone valve and gas concentrations are displayed and recorded by a data logging program Labview®. Pressure and temperature are measured at five positions along the gasifier.

A by-pass of the product gas is analyzed, regarding non-condensable and condensable gas components as well as tars. The non-condensable gas compounds CO, CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and H<sub>2</sub> are measured by the online-measurement device Advance Optima of the Swiss company ABB. The non-condensable hydrocarbons (C<sub>1</sub> till C<sub>6</sub>) in the product gas can be measured discontinuously by a micro gas chromatograph. The non-condensable gas compounds CO, CO<sub>2</sub>, O<sub>2</sub> of the regenerator off gas are measured also by an online-measurement device Advance Optima of the Swiss company ABB.

The total gas flow rate of the product gas is measured via a gas meter for 5 minutes. In this time the condensed water is collected to calculate the steam content in the product gas.

The Ca-looping rate of the bed material between the gasifier and the regenerator is measured manually. Therefore, the fluidization of the lower loop seal has to be interrupted for the measuring period. When the fluidization of the lower loop seal is interrupted, the quartz glass segment of the lower standpipe fills with bed material, exiting the gasifier. The dimensions of the quartz glass segment and the density of the bed material are known. Hence, by measuring the time until the bed material increases to a certain height in the standpipe, the calcium looping rate  $G_{CaO}$  between gasifier and regenerator can be calculated.

The European Committee for Standardization (CEN) provides the most suitable analyzing methods for the investigation of tar during biomass gasification. These methods are a guideline to assure a quantitatively and qualitatively high standard of measurement as well as international comparability. The tar sampling method during the experimental work at IFK, presented in this paper, follows the recommendation of this Tar Guideline (Tar Guideline, CEN/BT/TF 143, 2004).

### 2.3. Procedure

The experiment starts with pre-calcination of the bed material in batch mode at 875 °C. Approximately 15 kg of the pre-calcined bed material are filled into the DFB system for start-up. After fluidizing the regenerator with air, the gasifier with steam, and the upper and lower loop seals with nitrogen, the Ca-looping rate between the reactors is initiated by opening the cone valve. The Ca-looping rate between the beds is then measured and adjusted. Next, the fuel feeding is started. A steady-state operation is reached as soon as the product gas composition is constant. Subsequently, the product gas flow rate is measured. Before the tar measurement starts, a gas probe for the GC is taken in a gas probe bag. After tar sampling, the product gas flow rate is measured again. The Ca-looping rate is measured again to verify the existence of constant conditions throughout the experimental phase. After every experimental phase, the fuel dosing is stopped and the bed material is regenerated by burning the char in the gasifier by changing gasifier fluidization from steam and nitrogen to air. This method is important to provide equivalent conditions, in regard to the bed material, for the subsequent experimental phase.

For the final experimental phase the cone valve was totally closed; the bed material was only circulating in the internal loop of the regenerator and no regenerated bed material was provided to the gasifier. In this case, the bed material was continuously laden with CO<sub>2</sub> which leads to a batch mode gasification. Each experimental phase lasted approximately one hour.

### 2.4. Used Feedstock and Bed Material

To avoid ash accumulation during continuous AER experiments a biomass with very low ash content was used as feedstock. Therefore, the experimental work was carried out with wood pellets as fuel certificated as EN 14961-2. The composition of this feedstock is shown in the following Table 2. The feeding system consists of two dosing screws: (i) a metric screw feeder to control the biomass flow rate, (ii) a rapidly rotating screw feeder, to avoid pyrolysis, which introduces the biomass into the gasifier above the distributor in the lower third of the bed height.

Table 2. Main characteristics of the feedstock.

Elemental analysis	Unit	Wood pellets
C	[wt-% <sub>a.r.</sub> ]	48.0
H	[wt-% <sub>a.r.</sub> ]	5.5
O	[wt-% <sub>a.r.</sub> ]	42.6
N	[wt-% <sub>a.r.</sub> ]	< 0.3
S	[wt-% <sub>a.r.</sub> ]	< 0.3
Ash	[wt-% <sub>a.r.</sub> ]	0.2
H <sub>2</sub> O	[wt-% <sub>a.r.</sub> ]	3.7
LHV	[MJ/kg <sub>daf</sub> ]	18.8

As bed material, a limestone from Greece has been used with characteristics shown in Table 3. To ensure the tendencies obtained from the 1<sup>st</sup> experiment, a 2<sup>nd</sup> experiment was conducted. The same sorbent type was used for the 2<sup>nd</sup> experiment, however, the bed material used for the 2<sup>nd</sup> experiment was originally pre-calcined and re-carbonated in a rotary kiln. This bed material was abbreviated as bed material B.

Table 3. Main characteristics of the bed material A and pre-calcined bed material B.\*

Elemental analysis	Unit	Bed material
CaO	[wt-% <sub>Bed</sub> ]	95.53
MgO	[wt-% <sub>Bed</sub> ]	0.94
SiO	[wt-% <sub>Bed</sub> ]	2.30
$\rho_{Solid}$	[kg/m <sup>3</sup> ]	1800
Dp	[ $\mu$ m]	300-600

\*Minor components (>>1 wt-%): Fe<sub>2</sub>O<sub>3</sub>; K<sub>2</sub>O; Na<sub>2</sub>O; P<sub>2</sub>O<sub>5</sub>; C; SO<sub>3</sub>;  $\Sigma = 1.23$  wt-%<sub>Bed</sub>

### 2.5. DFB Operating Conditions

The boundary conditions for the gasifier are set to standard AER conditions at 650 °C. The average temperature in the regenerator was approximately 850 °C to ensure complete char combustion and calcination of the bed material. For the experimental phase with bed material A, the Ca-looping ratio was set at seven different levels, as shown in Table 4. Furthermore, Table 4 lists the most important experimental conditions during each experiment, abbreviated as A-1 to A-7.

A problem during these experiments was that the fuel rate increased slightly. This leads to slightly different WHSV and TR as well as S/C-ratio which can influence the CGE, tar and gas composition (Corella et al., 2008). The experimental conditions for the experiments with bed material B are shown in Table 5, abbreviated as B-1 to B-3.

## 3. Results and Discussion

### 3.1. Effect of the Ca - Looping Ratio on the Gas Composition

Figure 3 and Figure 4 show the results of the non-condensable gas composition over the molar Ca-looping ratio ( $F_{Ca}/F_C$ ) for the experiments with bed material A and B.

The gas concentrations show obvious tendencies as a function of the molar Ca-looping ratio ( $F_{Ca}/F_C$ ) for both experiments with bed material A and B. Above a Ca-looping ratio value of 6 mol<sub>CaO</sub>/mol<sub>C</sub>, the gas concentrations tend to reach a constant level. A Ca - looping ratio below 4 mol<sub>CaO</sub>/mol<sub>C</sub> leads to a rapid decrease of H<sub>2</sub> and to an increase of CO<sub>2</sub> and CO. This is in accordance with the fundamental CO<sub>2</sub> capture experiments, presented in 1.3, (Charitos et al., 2010).

Table 4. Conditions of the experiments with bed material A.

Operational parameter	A-1	A-2	A-3	A-4	A-5	A-6	A-7
Fuel rate [kg <sub>a,r</sub> /h]	3.3	3.4	3.6	3.9	4.0	4.0	4.1
S/C [mol <sub>H2O</sub> /mol <sub>Fuel,C</sub> ]	1.5	1.5	1.4	1.3	1.3	1.3	1.3
WHSV [kg <sub>Fuel,a,r</sub> .h <sup>-1</sup> /kg <sub>Bed</sub> ]	1.4	1.3	1.5	1.4	1.6	1.7	2.0
TR [kg <sub>Fuel,a,r</sub> .h <sup>-1</sup> /m <sup>2</sup> <sub>Gasifier</sub> ]	326	332	351	379	389	393	397
F <sub>Ca</sub> /F <sub>C</sub> [mol <sub>CaO</sub> /mol <sub>Fuel,C</sub> ]	7.6	7.4	1.9	11.5	4.7	2.7	0.0
τ <sub>Bed</sub> [min]	2.5	2.5	9.3	1.5	3.5	6.1	∞

Table 5. Conditions of the experiments with bed material B.

Operational parameter	B-1	B-2	B-3
Fuel rate [kg <sub>a,r</sub> /h]	3.5	3.5	3.5
S/C [mol <sub>H2O</sub> /mol <sub>Fuel,C</sub> ]	1.7	1.7	1.7
WHSV [kg <sub>Fuel,a,r</sub> .h <sup>-1</sup> /kg <sub>Bed</sub> ]	1.4	1.4	1.4
TR [kg <sub>Fuel,a,r</sub> .h <sup>-1</sup> /m <sup>2</sup> <sub>Gasifier</sub> ]	342	343	344
F <sub>Ca</sub> /F <sub>C</sub> [mol <sub>CaO</sub> /mol <sub>Fuel,C</sub> ]	6.3	4.3	2.5
τ <sub>Bed</sub> [min]	3.1	4.5	7.6

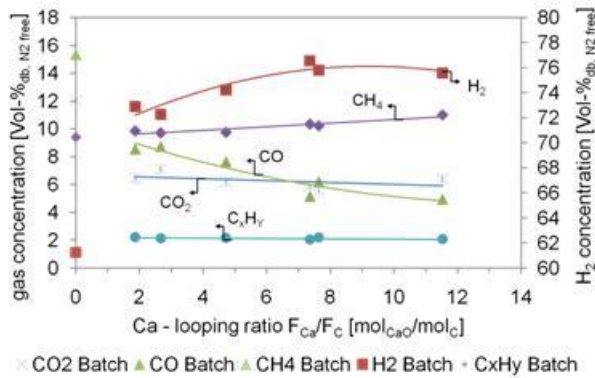


Figure 3. Gas composition vs. the Ca-looping ratio for experiments with bed material A.

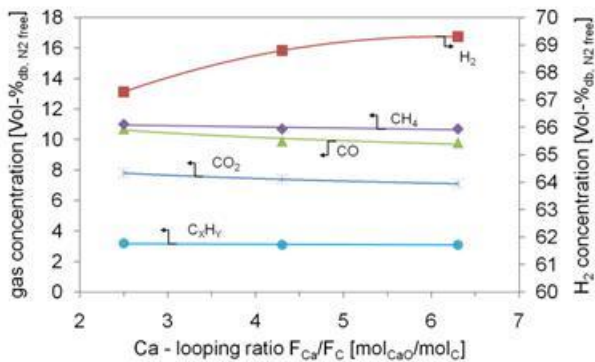


Figure 4. Gas composition vs. the Ca-looping ratio for experiments with bed material B.

Between the two experiments with bed material A and B a slight difference was noted in regard to H<sub>2</sub>, CO<sub>2</sub> and CO concentrations. The worse results obtained for the experiments with bed material B, shown in Figure 4, can be attributed to the sorbent pre-treatment. Due to the pre-treatment, the material is initially in a higher carbonation-calcination cycle while the material of the experiments with bed material A is initially in the first carbonation-calcination cycle. Hence, the “older” bed material of the experiments with bed material B can be responsible for the worse concentrations of Figure 4 in comparison to those of Figure 3.

### 3.2. Effect of the Ca-Looping Ratio on the CGE and Gas Yield

The influence of the Ca-looping ratio on the CGE and the product gas yield for both experiments with bed material A and B are shown in Figure 5. The tendencies for both experiments are similar. With increasing Ca-looping ratio the product gas yield and the CGE are decreasing. This trend can be explained on the basis of the turnover time (τ<sub>Bed</sub>). With increasing Ca-looping ratio the turnover time becomes less and therefore the time available for biomass conversion is also reduced. As a result, larger quantities of not fully gasified biomass feedstock are transported together with outgoing sorbent flow out of the gasifier.

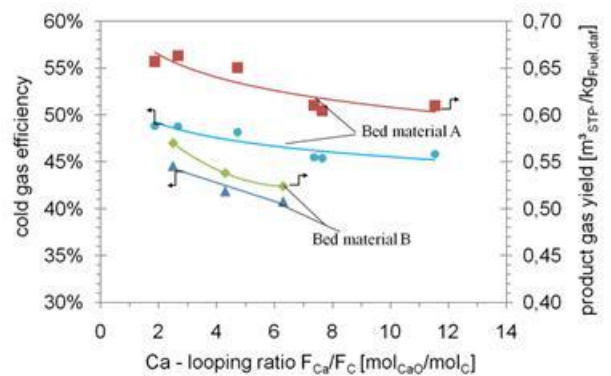


Figure 5. CGE and product gas yield vs. the Ca-looping ratio for experiments with bed material A and B.

The yields for the gas components H<sub>2</sub>, CO<sub>2</sub> and CO for the experiments with bed material A are shown in Figure 6. The tendencies follow the same trends as those in Figure 3. At a Ca-looping ratio of 8 mol<sub>CaO</sub>/mol<sub>C</sub> the H<sub>2</sub>, CO and CO<sub>2</sub> yields reach a nearly constant level. At semi-batch mode conditions (cone valve closed) the H<sub>2</sub> yield is less than at continuous conditions and equal to 0.370 m<sup>3</sup><sub>STP</sub>/kg<sub>Fuel,daf</sub>. The CO and CO<sub>2</sub> concentrations at semi batch conditions,

shown in Figure 1, are, as expected, much larger than at continuous conditions and the gas yield is equal to  $93 \cdot 10^{-3}$  and  $73 \cdot 10^{-3} \text{ m}^3_{\text{STP}}/\text{kg}_{\text{Fuel,daf}}$ , respectively. The CO yield decreases faster than the H<sub>2</sub> yield increases with increasing Ca-looping ratio, thus leading to a small decrease of the overall product gas yield, as shown in Figure 5. The decreasing CO yield leads to a reduction of the CGE because of the higher LHV of CO compared to H<sub>2</sub>, as shown in Figure 5.

At the same gasification conditions, the CGE and the product gas yield are clearly lower than in comparison to the experiments with bed material A. This is an unexpected result which may be caused by less fuel conversion for the experiments with bed material B compared to the experiments with bed material A.

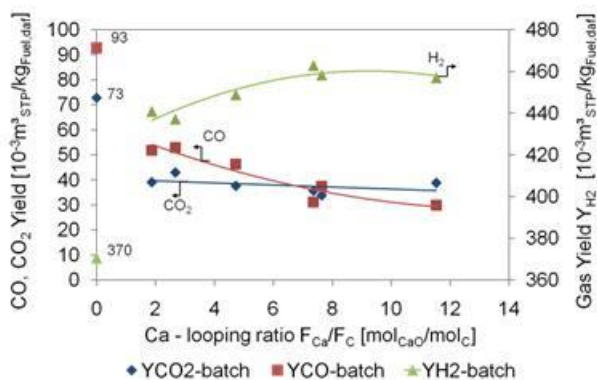


Figure 6. Yield of H<sub>2</sub>, CO, and CO<sub>2</sub> vs. the Ca-looping ratio for experiments with bed material A.

### 3.3. Effect of the Ca-Looping Ratio on the Tar Concentration

The effect of the Ca-looping ratio on the gravimetric tar concentration for both experiments with bed material A and B are shown in Figure 7. The gravimetric tar concentration decreases significantly with increasing Ca-looping ratio. Because of heat loss in the standpipe, the regenerated bed material is cooled down to 600 to 700 °C before entering the gasifier. Therefore, the tar reduction is not influenced by thermal cracking. Above a Ca-looping ratio of approximately 8 mol<sub>CaO</sub>/mol<sub>C</sub>, the gravimetric tar concentration reaches a constant value. There is a significant difference between the pre-treated sorbent B and the untreated material A with respect to the obtained gravimetric tar concentration. The underlying reason is not fully understood and is subject of further research. However, tar concentrations as low as 13.9 g/kg<sub>Fuel,daf</sub> and 4.1 g/kg<sub>Fuel,daf</sub>, for the experiments with bed material A and bed material B, were reached, respectively.

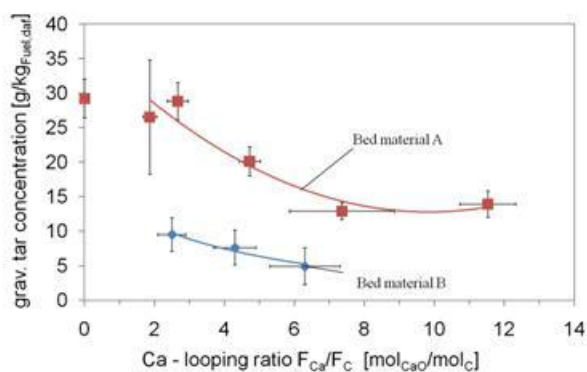


Figure 7. Gravimetric tar concentration vs. the Ca-looping ratio for experiments with bed material A and B.

## 4. Conclusions

The Ca-looping ratio is identified as a key parameter for DFB biomass steam enhanced reforming with CaO as a CO<sub>2</sub> sorbent. Increasing Ca-looping ratio leads to (i) increasing H<sub>2</sub> concentration and yield, decreasing CO and CO<sub>2</sub> concentration and yield; (ii) decreasing cold gas efficiency (CGE) and overall product gas yield, and (iii) decreasing gravimetric tar concentration. Above a molar Ca-looping ratio of 8 mol<sub>CaO</sub>/mol<sub>C</sub> there is no significant influence on the gas composition as well as on the gravimetric tar concentration. However, an increasing Ca-looping ratio leads to a decreasing turnover time of the bed material which results in reduction of the cold gas efficiency and product gas yield. Tar concentrations as low as 13.9 g/kg<sub>Fuel,daf</sub> and 4.1 g/kg<sub>Fuel,daf</sub> were measured for the experiments with bed material A and pretreated bed material B, respectively.

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## Nomenclature

<i>db</i>	dry basis
<i>daf</i>	dry ash free
<i>a.r.</i>	as received
<i>STP</i>	Standard Temperature and Pressure (273.15 K, 1013hPa)
<i>th</i>	Thermal input
<i>LHV</i>	Lower Heating Value
<i>G<sub>CaO</sub></i>	Calcium looping rate
<i>F<sub>Ca</sub>/F<sub>C</sub></i>	Molar circ. ratio, mol <sub>CaO</sub> h <sup>-1</sup> /mol <sub>Fuel,C</sub> h <sup>-1</sup>
<i>WHSV</i>	Weight Hourly Space Velocity, kg <sub>Fuel,a.r.</sub> h <sup>-1</sup> /kg <sub>Bed</sub>
<i>TR</i>	Throughput, kg <sub>Fuel,a.r.</sub> h <sup>-1</sup> /m <sup>2</sup> <sub>Gasifier</sub>
<i>CGE</i>	Cold Gas Efficiency based on the lower heating value (LHV)

## References:

- Florin, N. H., Harris, A. T., 2008, Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents, *Chemical Engineering Science* 63, pp. 287 - 316
- Higman, C., van der Burgt, M., 2003, *Gasification*. Gulf Professional Publishing. United States of America
- Corella, J., et. al., 2008, Biomass gasification with pure steam in fluidised bed: 12 variables that affect the effectiveness of the biomass gasifier, *Int. J. Oil, Gas and Coal Technology*, Volume 1, Number 1-2, pp. 194 - 207
- Soukup, G., et. al., 2009, In situ CO<sub>2</sub> capture in a dual fluidized bed biomass steam gasifier: bed material and fuel variation, *Chem. Eng. Technol.* 32, No.3, pp. 348-354
- Corella, J., et. al., 2007, A Review on Dual Fluidized-Bed Biomass Gasifiers, *Industrial & Engineering Chemistry Research*, American Chemical Society, 46, pp. 6831-6839
- Hofbauer, H. et al., 2002, Six Years Experience with the FICFB-Gasification process, 12th European Biomass Conference, Italy, pp. 982-985

- Neues Biomassekraftwerk Oberwart, 2009, Optimierte Konzeption der Biomassevergasung aufbauend auf dem DFB-Konzept aus Güssing, Der Reaktor, Vereinszeitung des Vereins der StudentInnen und AbsolventInnen der Verfahrenstechnik an der TU Wien, Jahrgang 19, Ausgabe 88, Nr.4
- Pfeifer, C., et. al., 2007, In-Situ CO<sub>2</sub>-Absorption in a Dual Fluidized Bed Biomass Steam Gasifier to Produce a Hydrogen Rich Syngas International Journal of Chemical Reactor Engineering, Vol. 5, Article A9
- Grasa, G.S., Abanades, J.C., 2006. CO<sub>2</sub> capture capacity in long series of carbonation/ calcination cycles. Ind. Eng. Chem. Res. 45, pp. 8846-8851
- Abanades, J.C., et al., 2004, Capture of CO<sub>2</sub> from combustion flue gases in a fluidized bed of CaO, AIChE J. 50 (7), pp. 1614-1622
- Charitos, A., et al., 2010, Parametric study of the Calcium Looping process for CO<sub>2</sub> capture in a 10 kW<sub>th</sub> Dual Fluidized Bed, Int. J. of Greenhouse Gas Control, submitted for publication
- Corella, J., et. al., 2006, Steam Gasification of Coal at Low-Medium (600°C~800°C) Temperature with Simultaneous CO<sub>2</sub> Capture in Fluidized Bed at Atmospheric Pressure: The Effect of Inorganic Species. 1. Literature Review and Comments, Industrial & Engineering Chemistry Research, American Chemical Society, 45, pp. 6137-6146
- Charitos, A., et al., 2009, Hydrodynamic analysis and design of a 10 kW<sub>th</sub> Calcium Looping Dual Fluidized Bed for post-combustion CO<sub>2</sub> capture. Powder Technol., accepted for publication.
- Hawthorne, C., et al., 2008, Design of a dual fluidized bed system for the post-combustion removal of CO<sub>2</sub> using CaO. Part I: CFB carbonator reactor model, Proceedings of the CFB9 conference, Hamburg; pp. 759-764
- Tar Guidline, CEN/BT/TF 143, 2004, Biomass Gasification - Tar and Particles in Product Gases - Sampling and Analysis