H2-Rich Syngas from Renewable Sources by Dual Fluidized Bed Steam Gasification of Solid Biomass

Christoph Pfeifer[*]   Tobias Pröll[†]

Bernhard Puchner[‡]   Hermann Hofbauer[**]

[*]Vienna University of Technology, Austria, cpfeifer@mail.zserv.tuwien.ac.at

[†]Vienna University of Technology

[‡]Vienna University of Technology

[**]Vienna University of Technology

H₂-RICH SYNGAS FROM RENEWABLE SOURCES BY DUAL FLUIDIZED BED STEAM GASIFICATION OF SOLID BIOMASS

Christoph Pfeifer, Tobias Pröll, Bernhard Puchner, Hermann Hofbauer
Vienna University of Technology, Institute of Chemical Engineering,
Getreidemarkt 9, 1060 Wien, Austria\

ABSTRACT

Steam gasification of solid biomass yields high quality producer gases that can be used for efficient combined heat and power production (CHP) and as a renewable resource for chemical syntheses. The dual fluidized bed steam gasification technology provides the necessary heat for steam gasification by circulating hot bed material that is heated in a second fluidized bed reactor by combustion of residual biomass char. The hydrogen content in producer gas of such gasifiers is about 40 vol% (dry basis). Addition of carbonates to the bed material and adequate adjustment of operation temperatures in the reactors allow selective transport of CO_2 from gasification to combustion zone (Adsorption Enhanced Reforming – AER concept). An 8 MW (fuel power) CHP plant successfully demonstrates gasification in Guessing, Austria since 2002. A pilot plant (100 kW fuel power) has been recently operated to investigate the potential of the selective CO_2 transport achieving a H_2 content of 75 vol% (dry basis) in the producer gas. No significant increase in tar formation occurs despite the low gasification temperatures (600-700 °C). It can be shown, that the selective transport of CO_2 yields high hydrogen contents in the producer gas and the possibility of operating at lower temperatures increases the efficiency of energy conversion.

INTRODUCTION

Dual fluidized bed steam gasification

Biomass steam gasification allows the conversion of solid biomass to medium calorific gas consisting mainly of hydrogen, carbon monoxide, methane, carbon dioxide, and water. The gas may either be used for electricity production (turbines, engines, fuel cells), or it may be used as renewable resource for chemical syntheses (liquid hydrocarbon fuels, pure hydrogen, synthetic natural gas, etc.).

At the Vienna University of Technology in cooperation with Repotec, the dual fluidized bed steam gasification technology has been developed to provide the heat for the gasification reactor by circulating bed material. This system is a further development of the so called FICFB technology (fast internally circulating fluidized bed) ([1]), ([2]), ([3]), ([4]). According to Figure 1, the biomass enters a bubbling fluidized bed gasifier where drying, thermal degasification, and partially heterogeneous char gasification take place at bed temperatures of about 850-900 °C. Residual biomass char leaves the gasifier together with the bed material through an inclined, steam

fluidized chute towards the combustion reactor. The combustion reactor serves for heating up the bed material and is designed as highly expanded fluidized bed (riser). Air is used as fluidization agent in the riser. The circulation rate (during standard operation) can be adjusted easily by changing the amount of primary and secondary air in the combustion chamber. After particle separation from the flue gas in a cyclone, the hot bed material flows back to the gasifier via a loop seal. Both connections, the loop seal and the chute are fluidized with steam, which effectively prevents gas leakage between gasification and combustion zone and also allows high solid throughput. The temperature difference between the combustion and the gasification reactor is determined by the energy needed for gasification as well as the bed material circulation rate. Further parameters with energetic significance are the amount of residual char that leaves the gasifier with the bed material and the gasification temperature. The system is inherently auto-stabilizing since a decrease of the gasification temperature leads to higher amounts of residual char which results in more fuel for the combustion reactor. This, in turn, transports more energy into the gasification zone and thereby stabilizes the temperature. At standard conditions about 10 wt% of the biomass input (waf) is partitioned to the combustion chamber. This char (see Figure 2) consists mainly of carbon (about 80 wt%). In practical operation, the gasification temperature can be influenced by addition of fuel (e.g. recycled producer gas, saw dust, etc.) into the combustion reactor. The pressure in both gasifier and combustion reactor is close to atmospheric conditions. The process yields two separate gas streams, a high quality producer gas and a conventional flue gas, at high temperatures. The producer gas is generally characterized by a relatively low content of condensable higher hydrocarbons (2-10 g/m^3_N of so called tars, heavier than toluene), low N_2 (< 1 vol%), and a high H_2 content of 35-40 vol% (dry basis). For practical use, Olivine, a natural mineral, has proven to be a suitable bed material with enough resistance to attrition and moderate tar cracking activity (5), (6).
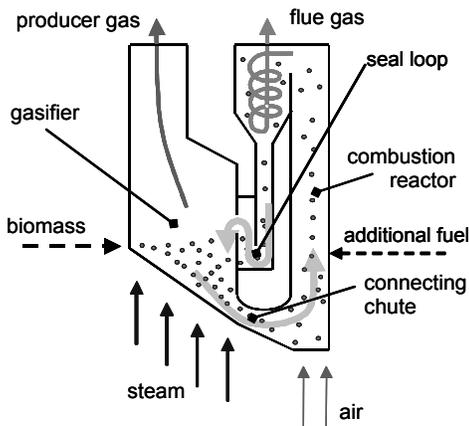

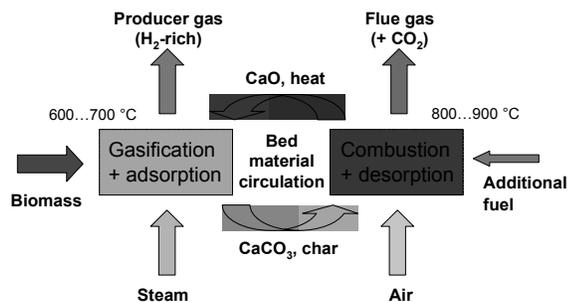
Figure 1: dual fluidized bed gasification process

Figure 2: The adsorption enhanced reforming (AER) principle

An 8 MW (fuel power) CHP plant, coupling a dual fluidized bed biomass steam gasifier and a 2 MW_{el} gas engine, has been realized in Guessing, Austria and is in operation since 2002. The plant uses wood chips from forestry as fuel and 6500 hours of CHP operation could be achieved for the year 2005. Gas cleaning is necessary in order to remove particles and high molecular organic compounds (tars)

from the producer gas before gas utilization in the engine. The CHP plant is
described in detail by Hofbauer et al. (7).

The adsorption enhanced reforming process (AER)

The bed material used for the AER-Process has apart from its function as a heat
carrier another main task. It acts as a CO_2 adsorbent material and selectively
transfers CO_2 from the gasification to the combustion reactor (Figure 2). Practically,
the bed material allows repeated cycles of carbonation and calcination of CaO
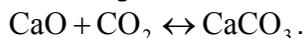according to

$$CaO + CO_2 \leftrightarrow CaCO_3 .$$

Figure 3 shows the equilibrium partial pressure of CO_2 for both CaO and MgO. The
relevant partial pressures in both the gasification and the combustion reactor are in
the range of 0.1 bar. Magnesium oxide remains always calcinated at temperatures
above 300°C in atmospheric gasifiers and therefore cannot be considered for CO_2
transport. The transition temperature for $CaCO_3$ towards CaO in the relevant
pressure range is between 700 and 800°C, which allows significant CO_2 transfer
from gasifier to combustion reactor for properly adjusted temperatures in the two
reactors (gasification: 600-700°C, combustion: > 800°C). Both calcite ($CaCO_3$) and
dolomite ($CaMg(CO_3)_2$) are proposed as active bed materials (8). In the case of
dolomite, only the Ca-fraction is active, while the Mg-fraction remains MgO. Within
the present study, calcite is considered as bed material because of its acceptable
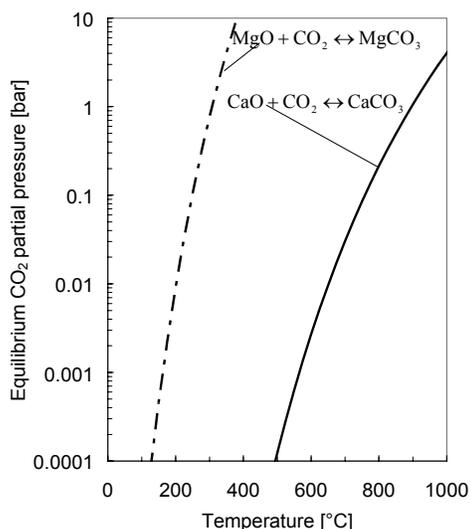transport capacity and sufficient mechanical strength.

Figure 3: Equilibrium partial pressure of CO_2 for the calcinations of MgO and CaO

Component	Conventional process[a]	AER-process[b]
H_2O, vol%	30…45	51...65
CH_4, vol% (dry)	10…11	10…14
C_2H_4, vol% (dry)	2…2.5	1…2
C_3-Fract. , vol% (dry)	0.5…0.7	0.5…0.8
CO, vol% (dry)	24…26	4…8
CO_2, vol% (dry)	20…22	6…13
H_2, vol% (dry)	38…40	65…75
H_2S, v-ppm (dry)	130…170	11…37
NH_3, v-ppm (dry)	1100…1700	840…965
Tar g/m^3_N (dry)	2…5	0.5…3.5
LHV MJ/m^3_N (dry)	12.9…13.6	13.1…16.5

[a] 8MW$_{th}$ demonstration plant in Güssing, Austria according to Pröll et. al. (9)
[b] 100kWth pilot plant at the Vienna University of Technology, Austria

Table 1: Typical producer gas composition ranges for conventional dual fluidized bed steam gasification and AER process

Through simultaneous CO_2-adsorption during the gasification process the CO-shift
reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
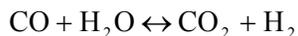
proceeds towards H_2 and CO_2 and all of the parallel reforming/gasification reactions
are also influenced in favor of the desired product H_2 (cracking and reforming of
hydrocarbons). Furthermore, the adsorption process releases heat in the gasification
reactor, which decreases the need for heat transport by the circulating bed material.
For continuous gas production, unloaded adsorbent and solid fuels are converted in

the reactor at temperatures of 600-700°C. The carbonated bed material, together with the ungasified biomass, is regenerated by endothermic calcination in the combustion reactor at 800-900°C.

Table 1 shows typical measured producer gas compositions for both the conventional dual fluidized bed steam gasification and the AER process if untreated wood is used as fuel (demo plant: wood chips, pilot plant: wood pellets). However, it should be mentioned that hydrogen fractions up to 75 vol% were obtained depending on the gasification temperature and on the steam-to-fuel ratio. The hydrocarbon concentrations remain largely unchanged despite the significant difference of reaction conditions. The CO, CO_2, H_2, and H_2O concentrations are significantly influenced by selective CO_2 removal and the shift-equilibrium. The reversible reforming and water-gas shift reactions are shifted beyond their thermodynamic limits by adding a CO_2 acceptor ([14]). The different concentrations of N- and S- species can be explained by lower N and S content in the pellets compared to the wood chips. The dry gas energy content is only a little higher for the AER process. The chemical efficiency is higher than in the conventional case since energy transported as sensible heat in the gas streams is lower. An increase of 4 percentage points (e.g. from about 70 to 74 % at a fuel water content of 20 wt%) can be achieved.

Previous experiments on the 100 kW pilot plant gasifier showed that the tar content strongly depends on the gasification temperature. Because of the low gasification temperatures required in the AER-process, a high amount of tar could be expected ([5]). To reduce tars already inside the gasifier, a cracking and reforming catalyst can be added to the bed material. For the experiments presented here, Ni-olivine ([10]), ([11]) has been used as additional catalyst which is described in detail in Pfeifer et al. ([12]). No deactivation due to the repeated high temperature processing could be observed during all experiments lasting up to 40 h. Similar findings were published by Mattison and coworkers ([13]) who tested Ni based catalysts as bed material in a chemical-looping combustion reactor for approx. 150 h without any signs of deactivation. For all displayed experiments 10 wt% of Ni-olivine was used. However, results from experiments without any additional catalyst permit the presumption that long-termed addition of catalysts to the bed material can be omitted.

EXPERIMENTAL

Experimental Setup
The pilot plant represents the third generation of 100 kW (fuel power) dual fluidized bed gasifiers at Vienna University of Technology and started operation in January 2003. Biomass is fed directly into the gasifier bed from a gas-proof daily hopper using an arrangement of two screw feeders (slow metering screw and fast feeding screw).To allow long-term experiments, a smaller hopper for bed material is available to provide bed material for covering attrition losses during the experiment. The bed material is fed into the reactor by an electric powered screw conveyor with variable speed. In order to reach the required combustion temperature additional fuel is needed to be fed to the combustion reactor. In the pilot plant, light fuel oil is added to the combustion reactor by a speed-controlled pump via a nozzle tube. The flow rate of fuel oil is determined by a control loop aiming at a constant combustion section temperature. The combustion reactor is fluidized with air added at different heights of the reactor. The primary air is used to create a stationary (bubbling)

fluidized bed in the bottom zone of the combustion reactor. At a higher level, secondary air is fed to the combustion zone through three nozzles and creates a highly expanded (transporting) fluidized bed. The entrained solids are captured through a disengaging chamber with a separation efficiency of more than 99.9%. Auxiliary air is used for the combustion of the producer gas in the cyclone combustor. The gasification reactor and both siphons are fluidized with steam during gasification operation. By variation of the steam volume flows to the siphons the solid flow rate is adapted. During start up, air is also used for gasifier and siphon fluidization. The feed lines of the siphons and the gasifier are electrically heated. This is necessary in order to heat the air during the heating up period and to superheat the steam during gasification operation. In order to control the temperature in the gasification reactor, a water-cooled heat exchanger with three independent bundles allows effective cooling of the stationary fluidized bed in the gasifier. After exiting the freeboard of the ga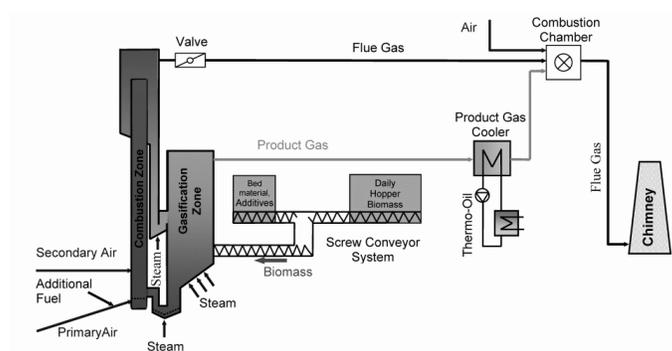sifier the raw producer gas is cooled down to 150–350°C in an oil-cooled heat exchanger. Downstream of the heat exchanger the producer gas samples are taken. The producer gas composition is measured by an online gas chromatograph. Finally, the producer gas of the pilot plant is combusted in a cyclone combustion chamber with additional air. The hot flue gas is also added to the

Figure 4: Simplified flow sheet of the 100kW$_{th}$ pilot plant

cyclone combustor, where the discharged particles are separated. The combustion cyclone exhaust gas is then led to the chimney. Figure 4 shows a simplified flow sheet of the pilot plant. Key operation conditions of the gasifier are listed in Table 2.

Table 2: Key operation conditions of the gasifier.

Operating conditions	Gasification zone	Combustion zone
Particle density, kg/m³	2700	
Particle mean size*, mm	0.573	
Cross-section geometry	square	circular
Side length/diameter, mm	285	100
Superficial gas velocity, m/s	1-0.4	12
Ratio U/U$_{mf}$ $^{\#}$	6-2.6	-
Ratio U/U$_t$	-	4.7
Net circulation flux of solids, kg/m²s	-	12.2

* see Figure 5 $^{\#}$ decreasing with height due to the conical shape

Experimental results

Four different bed materials were tested for this work, two dolomites, one calcites, and one carolith. Best results in regard to attrition resistance combined with activity were obtained by using a calcite originating from Greece (in the following termed Greek calcite). Thus, results of one typical experiment (accomplished on the 24th of March 2004 – called experiment 040324) with this bed material are presented exemplarily. Previously to the experiments in the pilot plant the possible bed materials were screened in a laboratory scale fluidized bed reactor to identify their attrition resistance. Additionally thermo gravimetric analysis (TGA) experiments

where accomplished to test the activity of the samples after repeated absorption/desorption cycles. These tests showed that all 4 bed materials should have a sufficient adsorption capacity, also after a high number of cycles. As known from appropriate literature limestone and dolomite CO_2 sorbents tend to lose activity with repeated cycles of absorption/desorption (14). However, the activity stabilizes at lower levels and a reduced CO_2 adsorption capacity can be compensated to some extent by increasing the circulation rate of the bed material
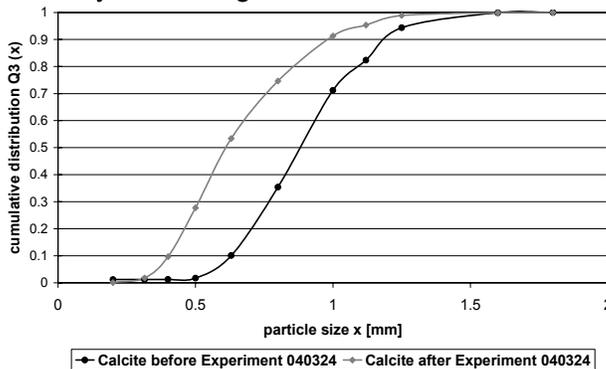

Figure 5: Cumulative distribution of the Greek calcite before and after experiment 040324

Figure 5 shows the cumulative particle size distribution before and after this experiment. It is easy to recognize that all of the distribution curves are shifted to smaller particle sizes. The average shift for all experiments was about 0.3 mm. However, from these graphs it is not possible to say if the crushing takes place during the initial calcination step before gasification takes place or during gasifying operation conditions.

This experiment was carried out to show that the AER-process also works at gasification temperatures near to 700°C. The average gasification and combustion temperature as well as the pressure drop during this experiment are shown in Figure 6. The combustion temperature was around 900°C during the whole experiment. Starting at 700 °C the gasification
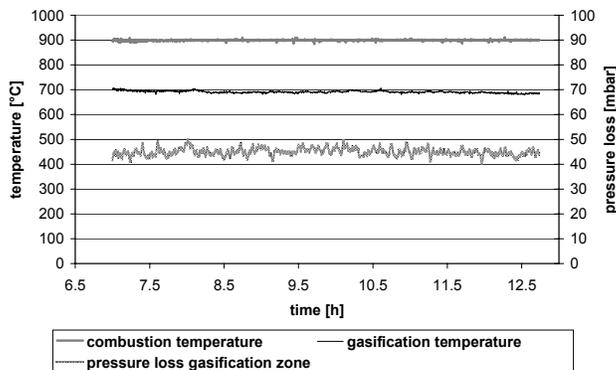

Figure 6: Temperatures and pressure drop over gasification zone during experiment 040324

temperature slightly decreases down to 680 °C during operation time. The decrease of the pressure drop over the experiment is very low as well, which indicates a nearly constant amount of bed material in the reactor over the whole experiment. Therefore, there was no need for feeding bed material to the reactor during the experiment.
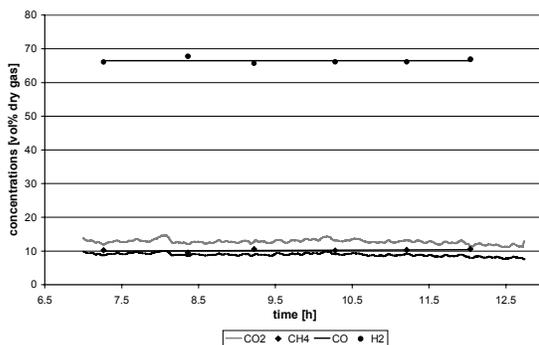

Figure 7: gas composition during experiment 040324

As shown in Figure 7 the gas composition was also very constant over the experimental time. The average hydrogen concentration obtained was 66.5 vol%. This value is relatively low compared to the other experiments accomplished with this bed material because of the increased gasification temperature, which shifts the equilibrium of the adsorption reaction partial towards desorption. This is verified by a CO_2 concentration

of 13 vol% in this experiment. The other concentrations of the product gas components are within the variations obtained during the other experiments. Hydrogen concentrations up to 75 vol% were obtained at gasification temperatures of about 600 °C.

Summary
Generally the performance of the Greek Calcite was good. The obtained average hydrogen concentration varied between 66 and 75 vol%. The amount of tars in the product gas was strongly dependent on the experimental settings, such as gasification and combustion temperature, steam-to-fuel ratio, addition of catalytic bed material and of course circulation rate of the bed material (14). The last effect is already described by Orio et al. (15). The amount of tars in the product gas was for all experiments in the range of 2 g/Nm³, which is in the same magnitude as for gasification with olivine alone at 850 °C. The reason for the relatively low tar levels despite low gasification temperatures is the catalytic activeness of dolomite respectively calcite. Concentrations of ammonia were measured at levels between 800 and 1000 ppm, which corresponds to results with olivine as bed material.

CONCLUSION

Apart from the significantly higher H_2 content in the producer gas, the AER concept is more efficient in converting primary fuel energy into producer gas than conventional dual fluidized bed steam gasification because of the lower operating temperature. Summarizing the current work, the AER concept is a highly promising variation of the dual fluidized bed steam gasification technology. As one of the next steps, large scale (in the 8 MW$_{th}$ demonstration plant in Güssing, Austria) and long term demonstration of the AER concept are considered. Further work will also focus on the mechanisms of tar destruction inside the gasifier and on the optimization of bed materials with respect to transport capacity and to attrition resistance.

ACKNOWLEDGEMENT

NOMENCLATURE
U   superficial gas velocity, m/s

Subscripts
mf   minimum fluidization
t   terminal settling of single particles

REFERENCES

[1] Hofbauer, H.; Veronik, G.; Fleck, T.; Rauch, R. The FICFB gasification process. In *Developments in thermochemical biomass conversion*; Bridgwater, A.V., Boocock, D., Eds.; Blackie Academic & Professional: Glasgow, U.K., **1997**; Vol. 2, pp 1016-1025
[2] Hofbauer, H.; Rauch, R.; Loeffler, G.; Kaiser, S.; Fercher, E.; Tremmel, H. Six years experience with the FICFB-Gasification process. In *Twelfth European Biomass*

Conference; Palz, W., Spitzer, J., Maniatis, K., Kwant, K., Helm, P., Grassi, A., Eds.; *The 12th International Conference on Fluidization - New Horizons in Fluidization Engineering, Art. 109 [2007]*
ETA: Florence, Italy, **2002**; pp 982-985

[3] Löffler, G.; Kaiser, S.; Bosch, K.; Hofbauer, H. Hydrodynamics of a dual fluidized-bed gasifier - Part I: simulation of a riser with gas injection and diffuser. *Chem. Eng. Sci*. **2003**, 58, 4197-4213

[4] Kaiser, S.; Löffler, G.; Bosch, K.; Hofbauer, H. Hydrodynamics of a dual fluidized bed gasifier. Part II: simulation of solid circulation rate, pressure loop and stability. *Chem. Eng. Sci*. **2003**, 58, 4215-4223

[5] Hofbauer, H.; Rauch, R. Stoichiometric water consumption of steam gasification by the FICFB-gasification process. At *Progress in Thermochemical Biomass Conversion*, Innsbruck, Austria, September **2000** (http://www.ficfb.at)

[6] Rauch, R.; Pfeifer, C.; Bosch, K.; Hofbauer, H.; Swierczynski, D.; Courson, C.; Kiennemann, A. Comparison of different Olivines for Biomass Steam Gasification, Proceedings of the Conference for Science in Thermal and Chemical Biomass Conversion, Victoria, Canada, 30. Aug.-3. Sep. **2004**, Vol 1., 799-809

[7] Hofbauer, H.; Rauch, R.; Bosch, K.; Koch, R.; Aichernig, C. Biomass CHP plant Guessing – a success story. In *Pyrolysis and Gasification of Biomass and Waste*; Bridgwater, A. V.; Ed.; CPL Press: Newbury, U.K., **2003**; pp 371-383

[8] Sun, P.; Grace, J.; Lim, C.J.; Anthony, E. Simultaneous CO_2 and SO_2 Capture at Fluidized Bed Combustion Temperatures. ASME Paper FBC2005-78125, 18th International Conference on Fluidized Bed Combustion, Toronto, Canada, May 22-25, **2005**

[9] Pröll, T.; Siefert, I.; Friedl, A.; Hofbauer, H. Removal of NH3 from biomass gasification producer gas by water condensing in an organic solvent scrubber. Ind. Eng. Chem. Res. **2005**, 44, 1576-1584

[10] Courson, C.; Makaga, E.; Petit, C.; Kiennemann, A. Development of Ni Catalysts for Gas Production from Biomass Gasification. Catal. Today. **2000**, 63, 427-437

[11] Rapagná,S.; Foscolo,P.U.; Provendier,H.; Petit,C.; Kiennemann,A.; Procedimento per la gassificazione di biomasse; Italian patent No 2000A000157-24/3/**2000**

[12]Pfeifer, C.; Rauch, R.; Hofbauer, H. In-Bed Catalytic Tar Reduction in a Dual Fluidised Bed Biomass Steam Gasifier. *Ind. Eng. Chem. Res*. **2004**, 43, 1634-1640

[13] Mattison, T.; Garcia-Labiano, F.; Kronberger, B.; Lyngfelt, A.; Adanez, J.; Hofbauer, H. CO2 capture from coal combustion using chemical-looping combustion, Proceedings of the 8th International Conference on Greenhouse Gas Control Technologies, 19-22 June **2006**, Trondheim, Norway, 175-176

[14] Johnsen. K.; Ryu, H.J.; Grace, J.R.; Lim, C.J. Sorption-enhanced steam reforming of methane in a fluidized bed reactor with dolomite as CO_2-acceptor, Chemical Engineering Science 61 (**2006**) 1195-1202

[15] Luisser, M.: Calcination of Limestone in a Fluidized Bed as Part of the AER Gas Process, Diploma Thesis. Vienna University of Technology, Austria, **2004**

[16] Orio,A.; Corella,J.; Narvaez,I.; Performance of different dolomites on hot raw gas cleaning from biomass gasification with air; Industrial & Engineering Chemistry Research, **1997**, 36,3800 - 3808