

NEW APPROACH FOR BIOMASS GASIFICATION TO HYDROGEN

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ABSTRACT: In this contribution a wood gasification process is presented to continuously produce a raw gas with nearly 70 mol% hydrogen, suitable for downstream fuel synthesis or electricity production. The approach is the AER (Absorption Enhanced Reforming, [1-4]) process in which the CO₂ produced during steam gasification or steam reforming is separated from the reactor by an absorbent, so that the resulting product gas contains a high hydrogen concentration and low concentrations of carbon oxides. The CO₂ absorption not only shifts the reaction equilibrium towards the desired products, but also delivers heat for the endothermic reactions. A gas with increased CO₂ concentration is produced when the sorbent is regenerated in a subsequent process step, which simplifies CO₂ separation (e.g. for CO₂ disposal).

During the absorption-enhanced steam reforming of model components like methane in a laboratory fixed bed reactor, hydrogen concentrations > 95 mol% were measured in the dry product gas. In the fluidised bed (FB) reactor with a sorbent (calcined dolomite or calcite) for the reactive bed material, the product gas from wood gasification in batch mode contained > 70 mol% hydrogen. Tar formation is suppressed as a result of CO₂ absorption, so that the tar concentration of the raw producer gas of less than 5 g/Nm³ - and < 0.5 g/Nm³ during the beginning of the AER phase - was comparably low, despite the low gasification temperature of ca. 650°C. Two FB reactors were coupled to realise continuous operation. In this case, the reactive bed material circulates between the AER gasification reactor and the residual coke combustion reactor for sorbent regeneration.

Keywords: hydrogen, bio-syngas, atmospheric fluidised bed

1 INTRODUCTION AND MOTIVATION

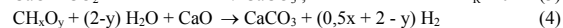
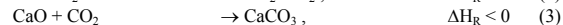
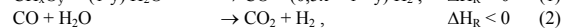
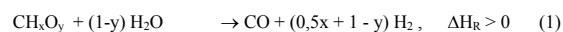
Fermentation or extraction processes, combustion, or gasification are suitable for the energetic use of solid biomass, depending on the fuel properties. The gasification processes available today generally produce a gas which could be used e.g. in combustion engines. New gasification methods are being developed, like hydrothermal gasification [5] or the AER process, which yield high-quality product gas, characterised by low inert and tar concentrations and a high hydrogen concentration. Common to both techniques is the *in situ* conditioning of the product gas which promises to simplify the subsequent gas processing, e.g. for electricity production, or fuel synthesis. Considering the renewable production of fuels, the generation of synthesis gas takes on a key role, since various fuels (e.g. Fischer-Tropsch gasoline/Diesel, methanol, di-methyl-ether, methane) can be produced from it.

2 FUNDAMENTALS OF THE AER PROCESS

Already in 1868, H₂ was produced by the steam reforming of hydrocarbons in the presence of a calcium oxide [6]. More recent activities by Curran et al. [7] utilised the high-temperature CO₂ separation with calcined dolomite in the so-called "CO₂ Acceptor Gasification Process". In the course of reducing CO₂ emissions, high-temperature CO₂ absorption has again been taken up over the last decade. Current activities in the USA, as a part of the ZECA (Zero Emission Coal Alliance) process, concern the absorption-enhanced reforming of a CH₄-containing product gas from coal gasification [8-10], while in Japan Lin et al. [11] are developing the HyPr-Ring (Hydrogen Production by Integrated Novel Gasification) process for the pressure

gasification of coal with simultaneous separation of CO₂ by CaO. In contrast, the high-temperature separation of CO₂ from the exhaust gases from combustion processes is studied in [12-13].

As a part of the European research project AER-GAS, the AER technique is being utilised for the unpressurised steam gasification of biomass (Eq. 1). Through simultaneous CO₂ absorption (with CaO as the sorbent in the example, Eq. 3), the equilibrium of the homogenous water gas shift reaction (Eq. 2) is shifted towards H₂ and CO₂ and all of the parallel reforming/gasification reactions are also influenced in favour of the desired products. Accordingly, a hydrogen-rich product gas results with reduced CO and CO₂ concentration. Eq. 4 represents the idealised sum reaction for AER gasification – the formation of secondary products (like methane, coke, and tars) are neglected here.



The CO₂ absorption is exothermal so that the gasification is nearly energetically self-sufficient. Loaded sorbent is regenerated in a subsequent process step by adding heat. For continuous gas production, unloaded sorbent and solid fuels are converted in the reactor at temperatures < 700°C. The carbonated bed material, together with the biomass coke, is removed and regenerated in a separate reactor at 750 – 900°C under air supply (with additional fuel if necessary). Thus, a low-inert-gas product gas flow and a CO₂-rich exhaust gas flow are generated in two separate process steps. In the technical realisation, two fluidised bed reactors with circulating absorbent bed material are coupled. The connection between two fluidised bed reactors is

sketched in Fig. 1, representing the FICFB (Fast Internally Circulating Fluidised Bed) process developed at the Technical University in Vienna [14] or the Battelle method [15].

An efficient and economic operation of the AER process is determined significantly by the sorbent properties. For the gasification of biomass in a FB process, the sorbent must not only be mechanically and thermally stable, but also cycle a minimum of ca. 200 absorption/desorption cycles for a purge rate of e.g. $50 \text{ kg}_{\text{raw calcite}}/t_{\text{biomass}}$, and have an average absorption capacity of ca. $0.15 \text{ g}_{\text{CO}_2}/\text{g}_{\text{oxide}}$.

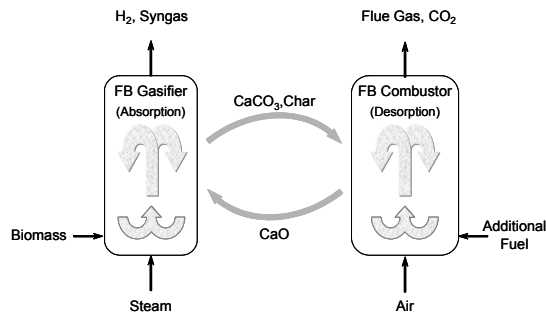


Figure 1: Coupling of two fluidised bed (FB) reactors for the continuous production of a H₂-rich gas flow from biomass. The absorbent bed material circulates between the AER reactor (absorption) and the regenerator (desorption).

The rate of the sorption reactions must be fast enough that the available dwell time in both reactors is sufficient for the required conversion. Furthermore, the sorbent should be a cost-efficient natural product which can be disposed with the ash or recycled afterwards. Additives in the sorbent like Mg- or Fe-oxides are advantageous for the internal catalytic tar decomposition [16].

The requirements for an AER fluidised bed in the FICFB process primarily affect the longer dwell times in both reactors and the larger temperature difference between gasification and the combustion of about 200 K, as compared to the use of inert bed material like quartz sand or olivine. Whereas the inert bed material during the gasification process serves as the heat transfer medium for the endothermic gasification reaction, the reactive bed material in the AER process also transports CO₂ ("pumping" CO₂ from the gasifier to the combustor).

3 METHODS, EXPERIMENT, AND RESULTS

Since the sorbent assumes a key role in the AER method, one focus of the process development was the screening of natural materials and their characterisation by thermogravimetry, TGA [17]. Substances with good absorption properties were further selected according to their mechanical stability in the laboratory FB reactor, and finally tested with biomass gasification. Fundamental studies of the AER process were first carried out in the laboratory fixed bed reactor, using methane as a model component. The biomass gasification was studied both in a FB in batch operation (without internal sorbent regeneration) and in a continuous FICFB process.

3.1 Characterisation of CO₂ Sorbents by Thermogravimetric Analysis

In thermogravimetry, the mass of a sorbent sample is measured as a function of the temperature and the composition of the surrounding gas atmosphere. Temperature cycling experiments in a constant gas atmosphere enable statements about the CO₂ absorption capacity C (Eq. 5, n = number of cycles) and about the cyclic stability CS (CO₂ uptake / release, Eq. 6).

$$\text{CO}_2 \text{ absorption capacity: } C(n) = m_{\text{CO}_2, \text{abs}}(n) / m_{\text{oxid}}(n) \quad (5)$$

$$\text{Cyclic stability: } CS = C(n) / C(n=1) \quad (6)$$

It is possible to determine the absorption and desorption reaction rates during isothermal operation in a changing gas atmosphere. Table 1 indicates the selected experimental conditions for both operating methods.

Table 1: TGA conditions for determining the cyclic stability, the CO₂ capacity (a), and the kinetics (b)

	Method	
	(a) T cycling	(b) Isothermal
T _{min} [°C]	480	T _{abs}
T _{max} [°C]	820	T _{des}
ΔT/Δt [K/min]	10	0
y _{CO₂} [mol%]	10	10
y _{H₂O} [mol%]	20	20
y _{N₂} [mol%]	70	70
d _{particles} [μm]	< 20	355 – 710
m _{start} [mg]	ca. 50	ca. 5

Fig. 2 shows the CO₂ capacity of various natural absorbents from the dolomite and calcite groups after several cycles (n = 1, 10, 20, 30). After an initial drop, the CO₂ capacity of some substances stabilised to a value of ca. $0.3 \text{ g}_{\text{CO}_2}/\text{g}_{\text{oxide}}$. Substances with good absorption properties were further characterised by additional measurements such as the reaction rate (change in CO₂ mass per mass of oxide) as a function of the temperature, see Fig. 3. While only a small influence of the temperature is apparent for the absorption in the observed temperature range, the desorption rate clearly increases for higher temperatures. Sintering effects are to be expected for high regeneration temperatures, causing a rapid loss of CO₂ capacity over the following cycles.

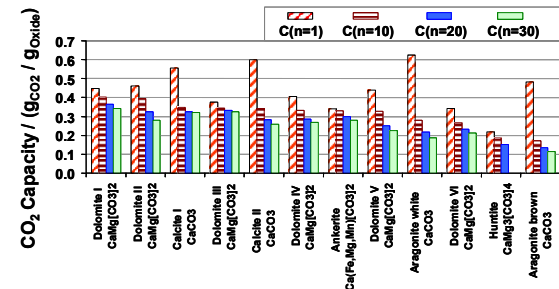


Figure 2: CO₂ capacity of selected absorbents after various numbers of cycles, see Table 1 for the conditions.

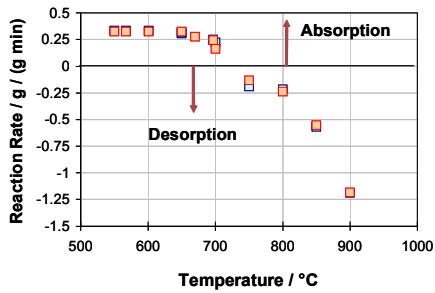


Figure 3: Absorption / desorption rates for a dolomite sample from isothermal TGA experiments, see Table 1 for the conditions.

Due to the sample mounting in the TGA, the particles are not in ideal contact with the gas. The measured reaction rates are therefore lower than those which can be achieved in a FB with good contact between the gas and the solids. Under the selected conditions ($T_{\text{abs}} = 650^{\circ}\text{C}$, $T_{\text{des}} = 850^{\circ}\text{C}$), the average particle dwell times in both reactors of the FICFB process (gasification ≥ 5 min; regeneration ≥ 1 min) are long enough for the required minimum conversion.

3.2 Laboratory Fixed Bed Reactor for the Steam Reforming of Gaseous Fuels

An electrically heated reactor with a ring-shaped fixed bed was constructed for characterising the AER method and the tested substances. Online gas analysis (NDIR spectrometry, thermal conductivity) and reactant and product gas flow measurements enable analysis of the process. Besides calcined dolomite (CaOMgO), a commercially available Ni catalyst (homogeneous mixed fixed bed) was also employed for methane reforming.

The dry product gas composition is plotted against the experimental time period in Fig. 4. Since the reactor, together with the gas analysis equipment, was previously flushed with N_2 , the individual measured values initially increase. During the first 15 minutes of the experiment, the hydrogen concentration was ca. 95 mol%, while only small amounts of CO and CO_2 (both < 1 mol%) and residual methane were measured. With increasing CO_2 sorbent load, the CO_x values increased until after ca. 40 min the influence of the CO_2 absorption was no longer apparent and the process resembled "conventional" CH_4 steam reforming at a comparably low temperature level of about 600°C .

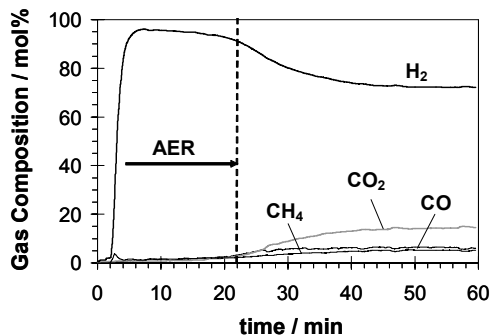


Figure 4: Product gas composition (dry) for CH_4 reforming in the AER fixed bed reactor ($T \approx 630^{\circ}\text{C}$; $\text{S/C} = 3.5$; $\text{GHSV} = 1400 \text{ h}^{-1}$).

3.3 Fluidised Bed for the Steam Gasification of Biomass (Batch Mode)

The absorption-enhanced steam gasification of wood pellets was studied in an electrically heated, circulating fluidised bed in batch mode (see Table II). Whereas calcined dolomite (CaOMgO) was already present as the bed material in the reactor before the beginning of the experiment, the biomass was continuously metered with a screw feeder in the lower part of the reactor. The fluidising occurred with superheated process steam at 450°C . Online gas analysis, a micro-GC, online tar measurement (flame ionisation detector, FID), gravimetric tar analysis, and a GC-MS were available to analyse the product flows. Table III lists the conditions for the AER gasification experiment shown in Fig. 5.

Table II: FB Reactor geometry and bed material

Reactor		
Height	[m]	3
Diameter _{reactor}	[mm]	108
Diameter _{freeboard}	[mm]	135
Heater _{el.}	[kW]	5 x 3.6
Temperature _{cyclone}	[°C]	400
Bed material		
Calcined dolomite	[kg]	5
Particle diameter	[mm]	0.7 – 1.2
Catalyst	--	--

Table III: Experimental conditions for wood gasification in the FB reactor, batch mode ($\text{S/C} = n_{\text{H}_2\text{O}}/n_{\text{C}}$)

Mode	T_{oven}	T_{measured}	Gas	\dot{m}_{wood}	S/C
	[°C]	[°C]		[kg/h]	--
AER	650	630 - 680	H_2O	3	~ 3
Regen.	870	850	air	0	--

Along with the product gas composition (H_2 , CO_2 , CO and CH_4), the tar concentration (FID measurement) is plotted against the experimental time period. Also in this case the test facility was flushed with nitrogen before the experiment, which explains the initial increase in the measured values. The CO_2 bonding was at a maximum during the first 15 minutes of the experiment, so that a H_2 concentration greater than 75 Vol.% (dry basis) was achieved. Similar to the fixed bed reactor, the CO_x values increased gradually with increased CO_2 loading of the bed material, while the H_2 values sank. The influence of the CO_2 absorption on the tar concentration is also readily apparent. Whereas little tar ($< 0.5 \text{ g}_\text{C}/\text{Nm}^3$) was detected during the initial phase, the tar concentration increased to the same degree as the CO_2 uptake weakened until the tar concentration amounted to ca. $1.5 \text{ g}_\text{C}/\text{Nm}^3$ as the end of the experiment.

Parallel to the online tar measurement with the FID, tar samples were also taken during the AER reaction and analysed both gravimetrically and with GC-MS. The sample was taken during the first 45 minutes of the experiment (H_2 concentration > 70 Vol.%). The results from the tar analysis are given in Table IV.

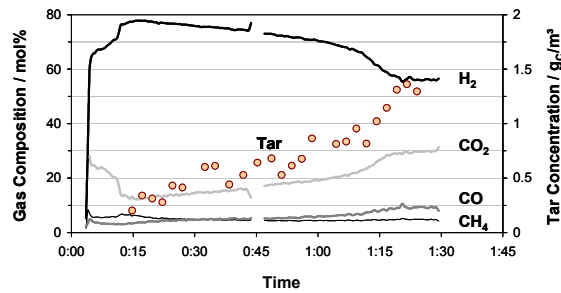


Figure 5: Product gas composition and tar concentration (FID) during the absorption-enhanced steam gasification of wood, see Table III for the experimental conditions.

Table IV: Tar measurement during the AER phase (45 min) of the FB gasification experiment

Tar _{gravimetric} [g/Nm ³ _{dry}]	
total	2,62
Tar measurements with GC-MS [g/Nm ³ _{dry}]	
total	3.13
phenol	1.56
toluene	1.02
indene	0.16
naphthalene	0.28
phenantrene	0.11

Since there are tar components which are detected both by gravimetry and by GC-MS, it is necessary to subtract the doubly detected tar components from the sum when calculating the total tar concentration [18]. According to this method, an average total tar concentration of 4.6 g/Nm³ was determined for the experiment. The main tar components like phenol and toluene can e.g. be easily removed in a subsequent reforming step.

3.4 Continuous Gasification with the FICFB Process with Internal Regeneration

Coupling two FB reactors by two steam fluidised siphons enables AER gasification with internal regeneration of the sorbent and thereby the continuous production of a product gas flow. A sketch of the reactor is presented in Fig. 6. The dwell time is directly dependent on the circulation rate, which can generally be adjusted through the fluidising conditions in the two beds and the two siphons, through the grain size of the bed material, and through the amount of bed material employed. Furthermore, the dwell time in the combustion region was increased by expanding the cross section of the reactor, enabling the required sorbent conversion. The biomass for gasification was introduced as wood pellets from a storage container using a screw feeder. Uncalcined calcite, containing nickel-doped olivine for tar reduction [19], was employed as the reactive bed material for the experiments. The calcium carbonate was calcined *in situ* before the AER experiment in order to avoid the formation of hydroxides from the calcined material during the process start up. The process is monitored through data acquisition with LabView, which records the temperatures and pressures in the reactor. The exact product gas composition is determined by a gas chromatograph. Gas analysers are additionally available

to record the compositions of the product gas and the exhaust gas. Table 7 indicates the conditions for the AER experiment shown here. Heating oil was chosen as the additional fuel in the combustion region for experimental reasons, but should be replaced by biomass or product gas in a technical plant.

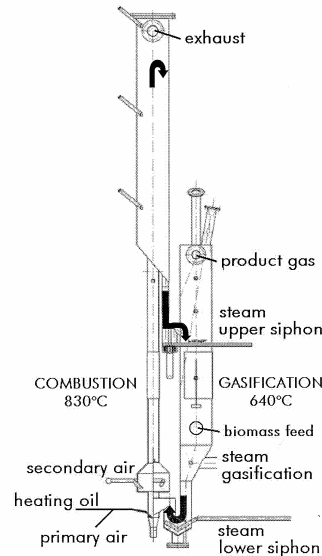


Figure 6: Schematic construction of the FICFB reactor for the continuous AER gasification of solid fuels.

Table V: Experimental conditions for the FICFB AER Process

Gasification temperature	[°C]	640
Regeneration temperature	[°C]	830
Amount of fuel (wood)	[kg/h]	15
Amount of oil	[kg/h]	2.25
Bed material: calcite	[kg]	150
Average grain size	[mm]	1
Catalyst: Ni-Olivine	[kg]	15

Table VI: Comparison of the gas composition for the standard bed material and for calcite

Bed material		Olivine	Calcite
Gasification temperature		850 °C	640 °C
H ₂	[mol%]	37.7	67.5
CO	[mol%]	29.1	3.3
CO ₂	[mol%]	19.6	10.3
CH ₄	[mol%]	10.4	13.1
C ₂ H ₄	[mol%]	2.8	1.7
C ₂ H ₆	[mol%]	0.3	3.0
HC (C ₃ -C ₅)	[mol%]	0.1	1.1

The comparison of the product gas composition in Table IV for the standard bed material olivine (gasification temperature 850°C) and for the AER process (gasification temperature 640°C) shows a clear increase in the H₂ concentration in combination with the desired reduction of the CO_x concentration. Fig. 7 demonstrates the time dependence of the reactor temperatures and the main components of the product gas. Nearly constant operation was possible over the testing period of ca. 10 h, without degradation of the gas composition or needing to add fresh sorbent.

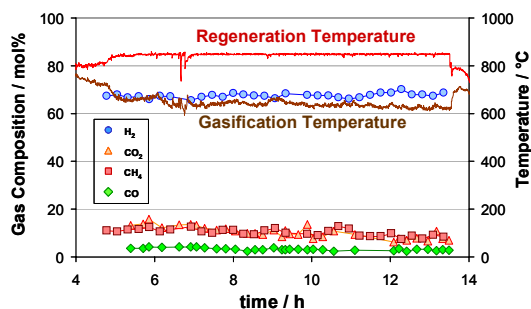


Figure 7: Product gas composition for the absorption-enhanced steam gasification of wood with the FICFB process, see Tab. V for the experimental conditions.

4 CONCLUSIONS AND OUTLOOK

In this contribution we presented a new process for the steam gasification of solid biomass which produced a continuous flow of gas with 70 mol% H₂ (dry basis). The reaction equilibria were shifted towards the desired products through the internal separation of CO₂ in the gasification reactor, resulting in a hydrogen-rich gas with a low concentration of inert gases and tars.

Current activities concentrate on both improving the sorbent properties and optimising the operational conditions with respect to C-conversion, *in situ* tar reduction, and defined product gas composition. The latter can be selectively influenced by the biomass / sorbent ratio, the temperature, and the dwell time in the reactors. Besides generating a hydrogen-rich gas, it is thus also possible to produce a synthesis gas with a defined stoichiometry factor for subsequent synthesis.

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