AER-Gas II

“Biomass Fluidised Bed Gasification with *in-situ* Hot Gas Cleaning”

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Project coordinator organisation name	ZSW
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Content

1 Abstract

Project work dealt with the development of the absorption enhanced reforming (AER) process for the efficient and decentralised poly-generation of heat, power, and fuel from biomass. Main focus was on the transfer of the AER technology into commercial scale. Therefore, the 8 MW_{th} biomass gasifier in Güssing, Austria, was operated in AER mode.

The steam gasification of solid biomass by means of the AER process yields a high quality product gas with an increased H_2 concentration and a reduced content of CO, CO_2, and tars. On the basis of allothermal steam gasification in a dual fluidised bed reactor, the biomass conversion reactions are coupled with *in situ* CO_2 removal by using a CaO-containing sorbent bed material. This bed material takes-up CO_2 in the gasification zone and is regenerated in a second fluidised bed reactor by calcination of the formed $CaCO_3$. The product gas is suitable for a wide range of applications, which covers combined heat and power (CHP) production as well as the generation of liquid or gaseous fuels (e.g., substitute natural gas (SNG), H_2). Process specific advantages refer not only to *in situ* gas conditioning (including hot gas cleaning) for downstream product gas applications, but also to its flexibility in terms of biomass feedstock. Besides wood also mineral rich biomass resources appeared to be suitable fuels for the AER process for two reasons: (i) the issue of ash melting (leading to bed material agglomeration) is reduced at low gasification temperatures and (ii) the ash melting temperature is increased by the Ca-based bed material. This flexibility towards different fuels is a major advantage with view to the limited resources of biomass and the competing demands placed on this resource by the food and heat sectors.

Projects results have proven the promising potential of AER-DFB gasification. Therefore, an AER demonstration plant is currently designed. Start-up is scheduled in 2011/2012 in Geislingen, Southern Germany.

2 Overview of the project AER-GAS II

2.1 Objectives

The project work concentrates on the development and demonstration of a new, efficient, and low-cost steam gasification process for clean conversion of solid biomass. By *in situ* gas cleaning / conditioning, a product gas with a high H_2 content (> 70 Vol.%), high heating value ($\geq$ 15 MJ/Nm^3; due to low CO_2 and negligible N_2 contents), and low tar/alkali/sulphur concentration is generated. Due to the high product gas quality, it is suitable for various applications like CHP (Combined Heat and Power) generation, SNG (Substitute Natural Gas), hydrogen or synthesis gas production. Besides the delivery of an improved catalytic CO_2 sorbent bed material, the project aims to open-up new biomass potentials like humid and mineral-rich resources. The over-all goal is the operation of the 8 MW_{th} power plant at Güssing in AER mode.

→ Transfer of AER process in commercial scale

→ Development and delivery of CO_2 sorbent bed material with catalytic activity

→ Suitability of woody biomass with high humidity

→ Suitability of mineral-rich biomass resources

2.2 Project Structure

Fig. 2.1 shows the structure of the project with its 5 work packages (WP) and the contributing partners. Main outcomes of single WPs are added to show the networking.

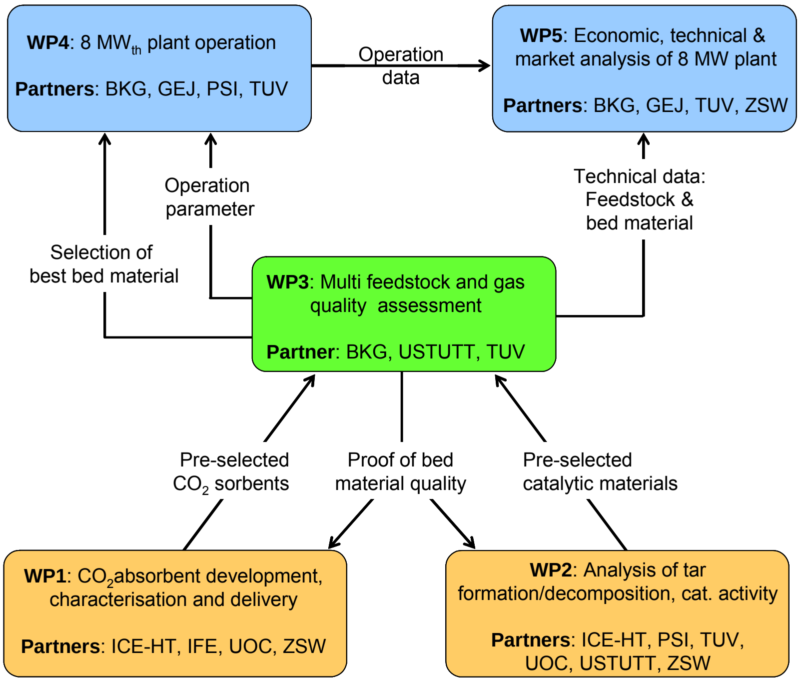

Fig.2.1: Definition, the main outcomes, and partners involved in the 5 Work Packages.

2.3 List of partners

-	ZSW	Center for Solar Energy and Hydrogen Research (D)
-	TUV	Technical University of Vienna (A)
-	BKG	Biomasse-Kraftwerk Güssing GmbH (A)
-	USTUTT	University of Stuttgart (D)
-	PSI	Paul Scherrer Institute (CH)
-	ICE-HT	FORTH – Foundation for Research and Technology Hellas (HE)
-	UOC	University of Cyprus (CY)
-	GEJ	GE Jenbacher GmbH & Co OHG (A)
-	IFE	Institute for Energy Technology (N)

2.4 Principle of process and challenges

The main characteristic of the AER (Absorption Enhanced Reforming) process for the efficient and low-cost conversion of biomass is a CaO-containing bed material, a CO_2 sorbent. It circulates between two fluidised bed reactors, takes up CO_2 in the reaction zone of a steam gasifier and releases CO_2 in the combustor. As a result of the *in situ* CO_2 removal, the reaction equilibriums are shifted towards hydrogen production and the tar concentration is reduced. Since the CO_2 absorption is a highly exothermic reaction, the released heat is integrated directly into the endothermic gasification/reforming process. The principle of AER process is illustrated in **Fig. 2.2**, applying two fluidised bed reactors with circulating sorbent bed material.

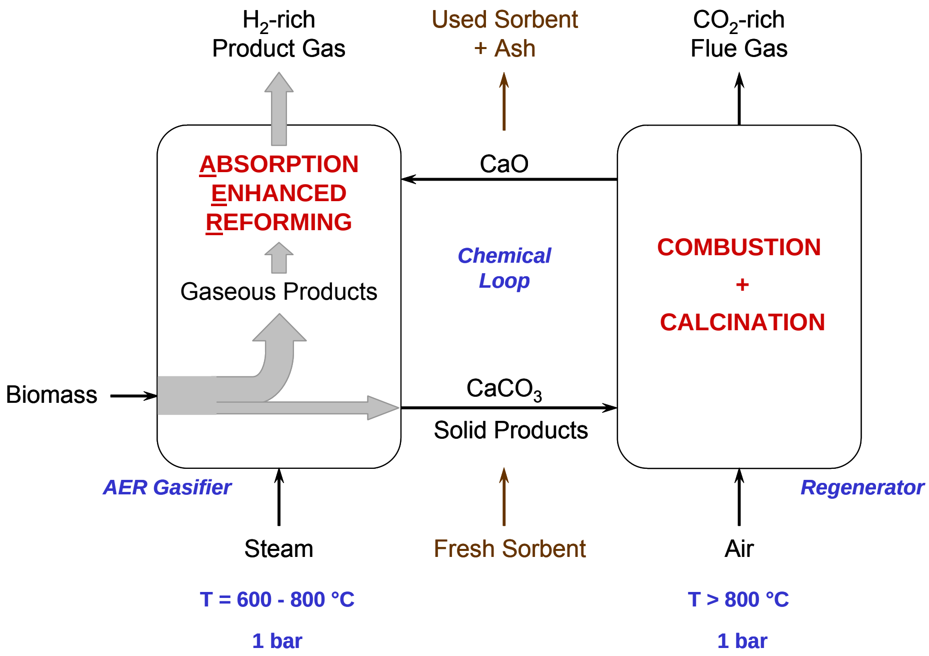

Fig. 2.2: Principle of AER process: Coupling of two fluidised bed reactors for the continuous production of a H_2-rich gas from biomass. The sorbent bed material circulates between the AER gasifier (CO_2 absorption) and the combustor (CO_2 desorption).

While biomass is gasified with steam in the first fluidised bed reactor at 650 to 700°C (1 bar), the loaded sorbent material is transported – together with gasification residues - into a second fluidised bed reactor for regeneration. This calcination reaction at ca. 800°C is enabled by combustion of biomass residuals. Additional fuel (e.g. product gas) is needed, allowing the adjustment of the process temperature. Two gas streams are obtained, a H_2-rich product gas as well as a CO_2-enriched flue gas.

The requirements on appropriate CO_2 sorbent bed materials are high: sufficient mechanical stability, suitable sorption properties, and preferably also catalytic activity towards tar removal.

Further challenges consider mineral-rich biomass resources like straw as fuel for gasification. Due to ash melting, leading to bed material agglomeration, these fuels are difficult to handle in fluidised bed gasifiers. In case of AER conditions, low gasification temperatures (< 750°C) and the CaO containing bed material are supposed to prevent agglomeration.

The comparable low AER gasification temperature has further interesting effects. The methane content of the raw gas increases and tars mainly consist of primary and secondary tar components (like phenol and toluene) instead of poly-cyclic compounds being problematic in subsequent process steps. Even though the low temperature level, the tar content is still small due to the CO_2 sorbent. Considering commercial realisation, the downstream gas cleaning unit can be simplified, because the product gas quality is increased by implementing *in situ* hot gas cleaning, thereby reducing plant complexity and costs.

2.5 Advantages of AER - results of AER-GAS

Important advantages of the AER process were demonstrated in the previous European project AER-GAS. They are briefly summarised as follows:

- product gas with high hydrogen content (up to 80 vol.-%),
- low CO_x content, and
- low tar content (< 500 mg/m³) by *in situ* hot gas cleaning
- *in situ* heat supply for endothermic biomass conversion.

The following figure shows a typical composition of the raw product gas and of the lower heating value (LHV) obtained during continuous wood gasification in the AER-DFB gasifier.

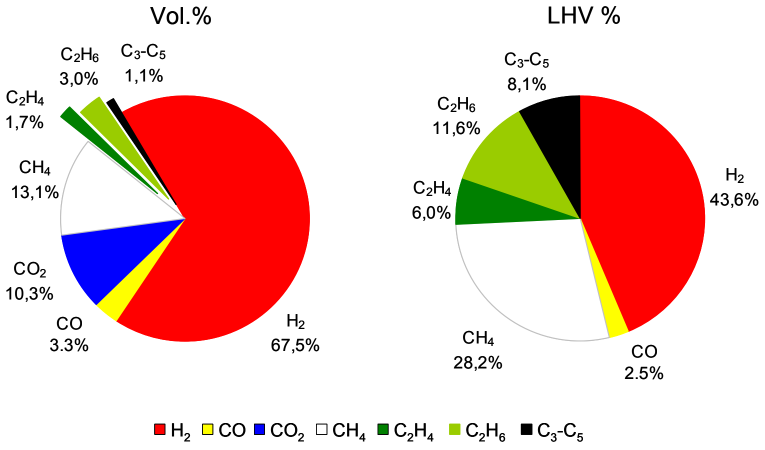

Fig. 2.3: Yielded product gas from AER-DFB gasification of biomass: gas composition (dry basis) and contribution of gas components to overall Lower Heating Value (LHV).

2.6 Main achievements of AER-GAS II (all partners)

Whereas in the former AER-GAS project the feasibility of the AER process was proven with very good results (e.g. high product gas quality), this follow-up project concentrates on the transfer of the technology in industrial scale. Therefore, important know-how with view to future AER gasification plants was obtained from operating the 8 MW_{th} biomass gasifier at Güssing in AER mode. Project work concentrated also on new aspects like multi-fuel compatibility, material research, and tar formation / removal mechanisms.

The main achievements are summarised in brief in the following. Details are described in section 3.

- Proof of scale-up by adaptation of the existing power plant at Güssing (8 MW_{th} biomass gasifier) to the AER technology / proof of scale up of AER gasification by operating the commercial power plant in Güssing in AER mode
- Fundamental knowledge of the process for future design of AER gasifcation plants
- Proof of power generation from H_2-rich AER product gas by adaptation of the existing gas engine at Güssing

- Production of a raw product gas from biomass with high quality: low tar (< 1 g/Nm³), low sulphur (< 50ppm H_2S), and alkali content, increased H_2 concentration (up-to 75 vol.%), and high calorific value (14-15 MJ/Nm^3)
- Availability of CO_2 sorbent with high mechanical and chemical cycle stability as well as catalytic activity to enhance homogeneous conversion reactions in the gasifier, especially tar removal. Promising materials were identified by screening method with focus on mechanical stability, CO_2 capacity, and catalytic activity toward phenol steam reforming. Calcite sorbents appear to be more active than olivine in primary tar reforming.
- Development of thermal pre-treatment method to improve the mechanical stability of lime without destroying the CO_2 reactivity. Industrial production for tests in Güssing.
- Feasibility of new methods to improve CO_2 sorbents (coating, agglomeration, etc.) applicable in industrial scale.
- Availability of low cost bed material (lime) for fluidised bed applications: 8 different limestone-based bed materials were successfully used in AER DFB gasification
- A comprehensive tar investigation was conducted under continuous AER conditions in DFB mode. The influences of different process parameters were recognized and the best process conditions are identified.
- A commercially available tar catalyst was tested under AER conditions in batch mode.
- Proof of the multi-fuel compatibility of the technology by using different fuels, in particular straw and wood, the latter with various moisture
- A comprehensive experimental and theoretical alkali and sulphur investigation was conducted under AER conditions.
- Proof of economical and energetic advantages of the innovative technology

In summer 2007, the 1st test campaign in a commercial power plant, in the 8 MW_{th} biomass gasifier at Güssing, took place, at which the transfer of the AER technology in commercial scale could be proven. Even though the gasifier is not designed for AER operation, it could be operated in AER mode without any constructive changes. The AER technology enables further improvement of the Güssing concept with view to efficiency increase and product gas quality (H_2 rich product gas with less pollutants like tars or impurities – compared to standard operation). The thermally pre-treated sorbent bed material, based on limestone, showed a very high mechanical stability at good reactivity in terms of CO_2 absorption, resulting at decreased CO_2 content of the product gas, see **Fig. 2.4**.

Concluding, the project has delivered important outcomes, which resulted in concrete plans to construct the first AER gasification plant. In this issue, the operator and investor consortium was formed, which will start operation early 2011. Thus, the break-through of the AER technology on R&D level was reached.

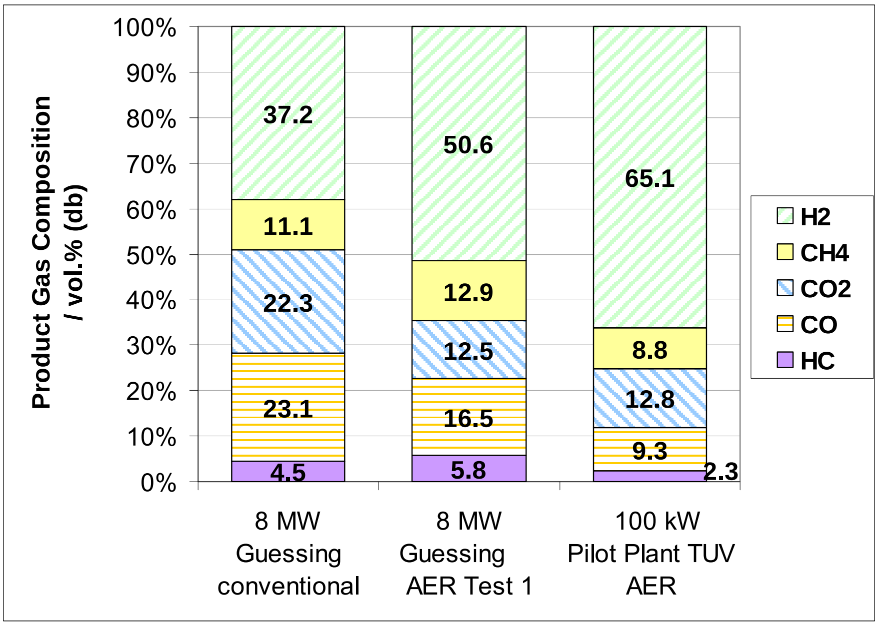

Fig. 2.4: Product gas composition during operation of the Güssing gasifier in conventional mode and AER mode – compared to test facility at Vienna University (TUV). Thermally pre-treated limestone was employed as bed material.

2.7 Process applications

Based on the promising results of AER-GAS and AER-GAS II, an AER gasification plant is currently designed by TBM (Technology Platform Biomass and Methane, GmbH and Co.KG), located in Geislingen, Germany. In the first step, wood chips will be used as fuel and the product gas will be burnt in a gas engine for combined heat and power generation. In future steps, also woody biomass from landscape conservation (bioshere reserve "Swabian Alb") will be employed as fuel; in addition, methanation of the product gas is foreseen to provide renewable SNG. The flexibility in terms of product gas application is related to the product gas composition, which can be adjusted by *in situ* gas conditioning (e.g. controlled CO_2 removal and CO shift reaction). Thus, the AER process has a high potential for decentralised efficient poly-generation of heat, power, and fuel from different biomass resources. A possible integration of the AER process in the existing infrastructure is illustrated in figure 5.

In the near future, it is expected that further utilities as well as plant constructors will be interested in the technology. The potential of AER gasifiers is high, especially with view to biomass rich areas in Eastern Europe.

An important spin-off is the high temperature CO_2 sorbent bed material, which can also be used for CO_2 separation from flue gases. Furthermore, it may also be suitable for "conventional gasification, as it is realised in Güssing and Oberwart (Austria). Thus, a new market for the lime / dolomite industry is opened-up.

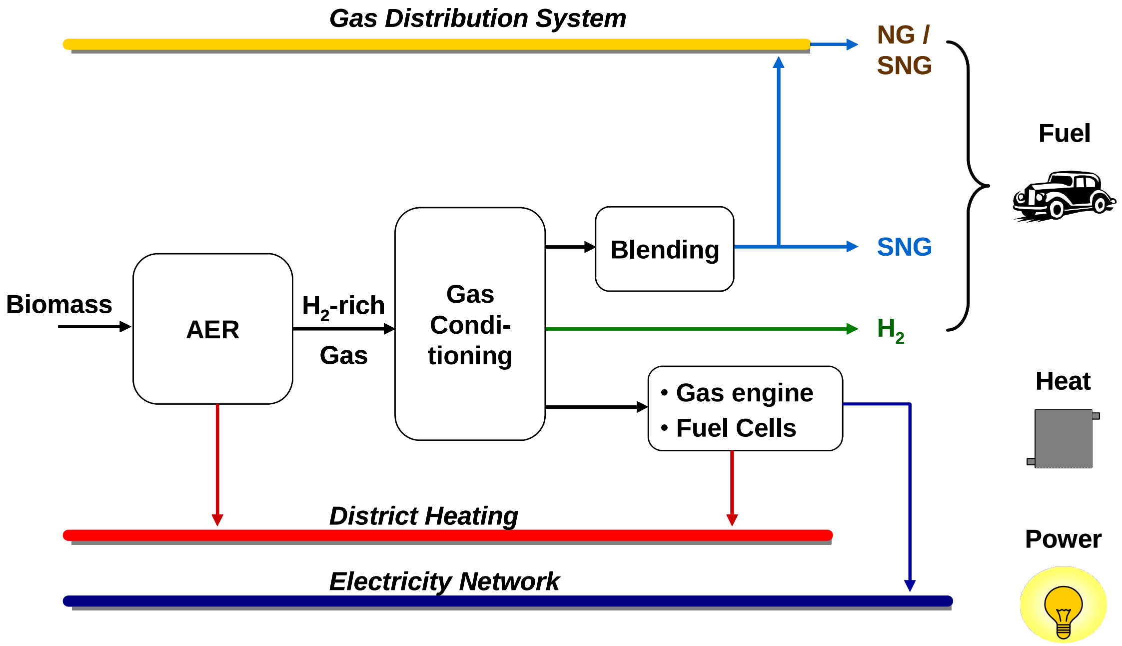

Fig. 2.5: AER process for poly-generation of heat, power, and fuel (e.g. SNG, H_2) from solid biomass.

2.8 Coordinator contact

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3 Work performed and results achieved

3.1 WP 1: CO_2 sorbent development, characterisation, delivery

Introduction / Motivation and goals

A stable and reactive CO_2 sorbent bed material has a key function within the AER process. Carbonates are suitable natural materials, because they release and absorb CO_2 at requested temperatures (gasification, combustion), because they are widely available at low cost and they are not toxic. However, not every calcite or dolomite is a suitable candidate and deactivation of the material must be considered. Detailed material screening, characterisation, and analysis are important, as the AER process is a totally new application of carbonates.

A suitable CO_2 sorbent bed material is characterised by:

- a high mechanical stability (under hot FB conditions)
- a sufficient reactivity towards CO_2 sorption reaction (especially CO_2 up-take) under multi-cycle calcination-recarbonation conditions, taking into account the CO_2-capacity (g CO_2 / g Oxide) as well as the reaction rate
- a high catalytic activity towards tar removal (steam reforming and CO shift)

This work package concentrated on the identification of promising CO_2 sorbent bed materials to be used in AER-DFB gasification and on the improvement of the mechanical stability of the sorbent.

1) Screening, characterisation, and delivery of CO_2 sorbent bed materials

Within WP 1, various natural CaO-containing materials were screened in order to select 5 promising sorbent bed materials to be used for gasification experiments in WP 2 & 3. The material, being most suitable for the DFB gasifier, was used as bed material for the test campaign in the power plant at Güssing. The material selection procedure adopted had the following steps:

1) Fast mechanical stability test (at ambient temperature) to “exclude” materials with poor mechanical stability:
    - ICE-HT: **micro fluidised bed reactor** or
    - IFE: **mechanical strength test** or
    - ZSW: **milling test**

    → Recommendation of sorbents showing promising mechanical stability

2) Detailed characterisation of pre-selected sorbent bed material:
    - **fast mechanical stability tests (ZSW, ICE-HT, IFE)**
    - **Catalytic activity towards phenol steam reforming (UOC**)
    - **TGA experiments (ZSW, ICE-HT, IFE),** and finally
    - **Fluidised bed “flash calcination” experiments** (ZSW) of selected candidates

    → Recommendation of 5 sorbent bed materials

3) Suitability of selected sorbents for DFB gasification:
   - **AER DFB gasification** in 100 kW gasifier at TUV and, if appropriate, in 8 MW_{th} gasifier at BKG

The following figure illustrates the procedure of the material selection. The material screening started with view to the mechanical stability. Then it focused on sorption properties and on catalytic activity towards tar removal. Finally, the best candidates were tested under real gasification conditions in a dual fluidised bed reactor in order to identify the most suitable ones.

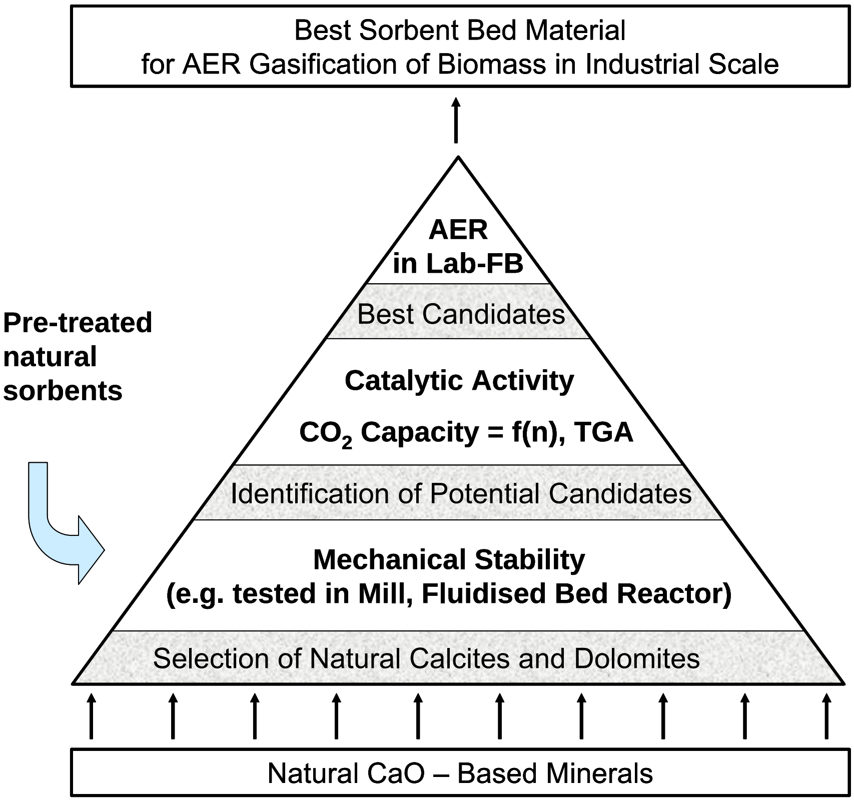


Fig. 3.1: Procedure for the selection of a promising sorbent bed material to be used in the gasifier at Güssing.

Methodology of sorbent characterisation and main achievements

In the following, the methodologies, mentioned above, are briefly described and the results achieved are presented.

A) Mechanical stability in milling test (ZSW)

The milling test was developed at ZSW in order to have a quick and simple method to assess the mechanical stability of minerals concerning the use as bed material for fluidised bed reactors. It is not a standard test (like the Hardgrove grind ability test for coals), but the results are reproducible and can be compared among each other.

During the development of the ball mill test method, it turned out to be important to use a narrow particle size fraction (600 – 710µm) as well as a defined bulk volume (32ml). Keeping both values constant allows the comparison of results, e.g., from materials with different density like $CaCO_3$ and CaO.

The mill is shown beneath and the technical parameters are listed in **Table 3.1**.

Fig. .2 Ball mill for quick and simple tests of mechanical stability (ZSW).

Tab. 3.1: Ball mill and sample parameters

Mill	
Type	Frietsch pulverisette 6
Grinding beaker	80 ml, steel
Transmission ratio	$i_{relative}$ 1 : -1.82
Balls	5 Achate (d=20mm)
Turns	440
Time	5 min
Sample	
32	ml (volumetric dosing)
Grain size	600 - 710 µm

After the milling test, the fraction of fines (d < 200µm) is obtained by sieve analysis and referred to total mass (eq. 3.1). Results are presented in **Fig. 3.3**.

$$\text{Attrition} = \frac{m_{material}(d < 200\mu m)}{m_{material,total}} \qquad \text{(eq. 3.1)}$$

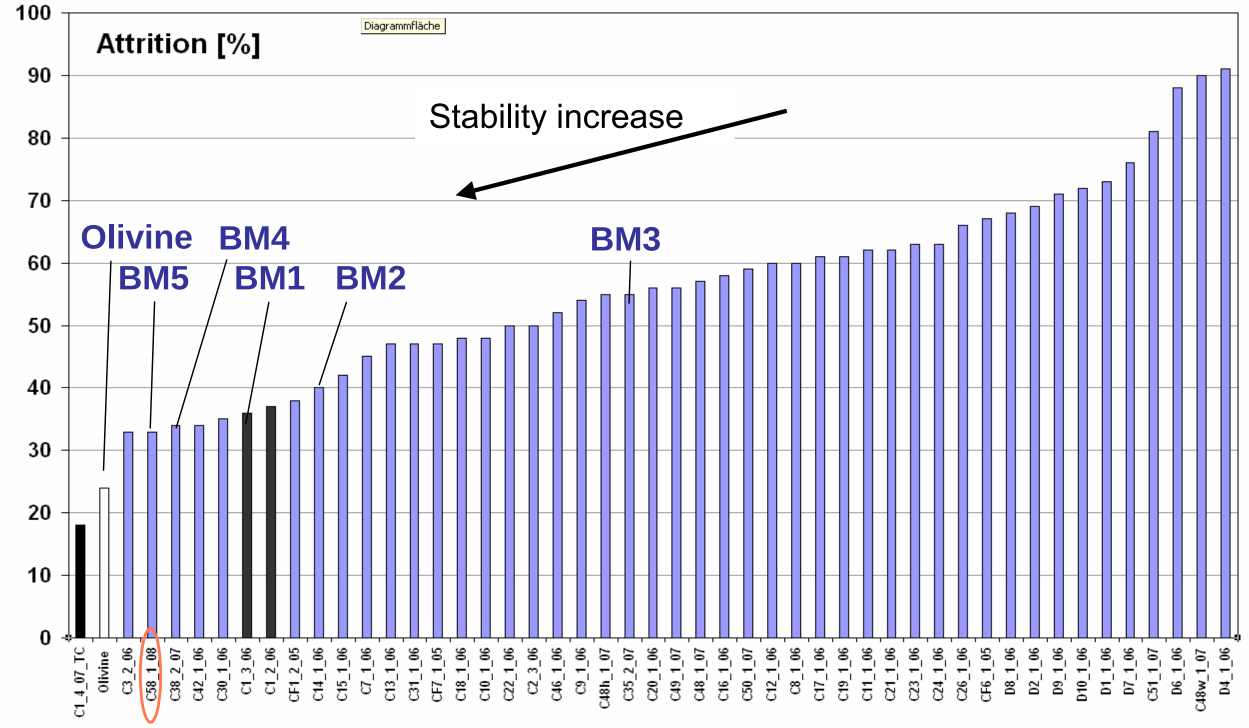


Fig. 3.3: Mechanical stability of natural Carbonates tested in ball mill (by ZSW), d_{raw} = 600 – 710µm.

B) Mechanical stability in micro fluidised bed reactor (ICE-HT)

The small-scale FB reactor consists of a 30 mm OD x 60 cm L tube (made of rigid polymer) with a perforated steel plate at bottom. A cloth filter on top is used to retain fine particles. A flow of N_2 is employed to fluidize the bed.

The material to be tested is sieved with the 0.71 and 1.4 mm sieves before introduction to the FB reactor and only particles in the range 0.71-1.4 mm are used. After fluidisation for specific time intervals, the material is taken out of the reactor and sieved with the 0.710 mm sieve. The mass of particles with size smaller than 0.71 mm is used to define the attrition as follows:

$$\text{Attrition} : \frac{m(d < 710\,\mu m)}{m_{\text{total,end}}} \qquad \text{(eq. 3.2)}$$

Results are summarised in **Fig. 3.4**.

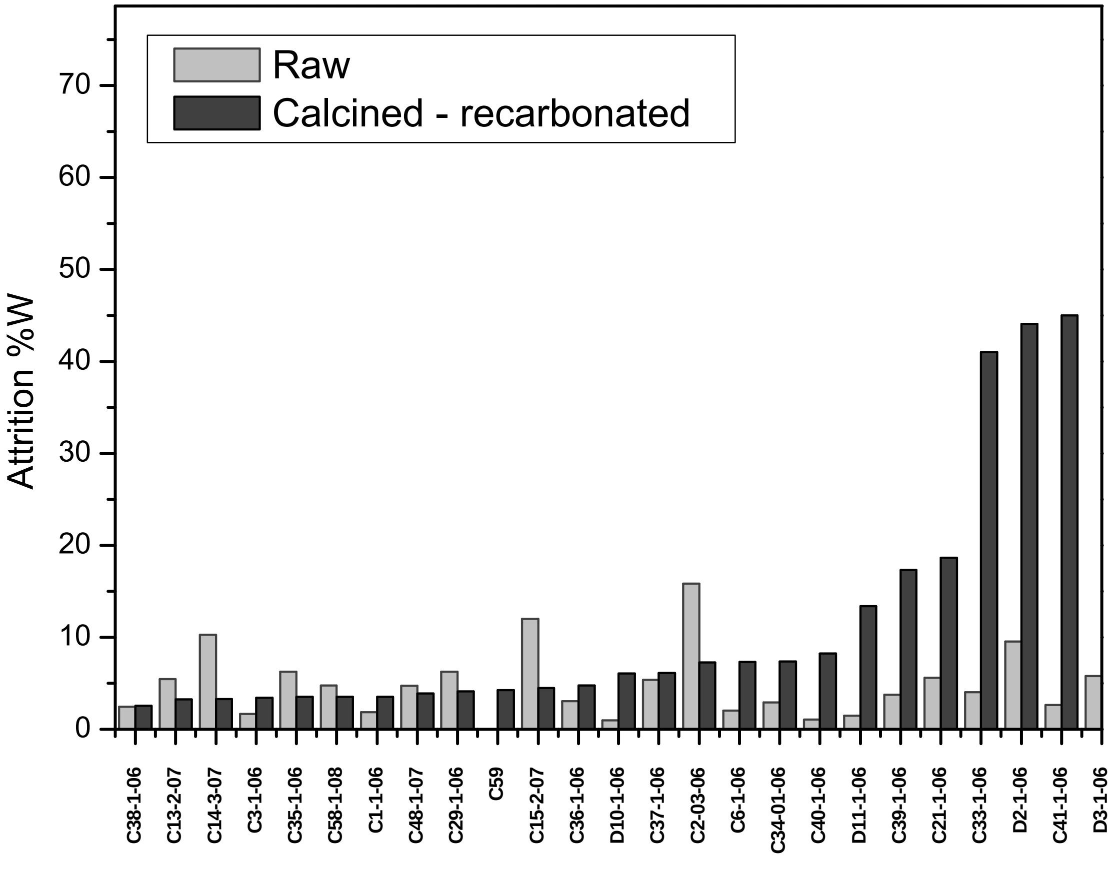


Fig. 3.4: Attrition performance of raw and calcined-carbonated materials in micro FB (ICE-HT).

A more detailed analysis of attrition performance can be also conducted by measurement of the particle size distribution of the material before and after the fluidisation test. Calculation of the mass-weighted, average particle diameter before and after the test provides an accurate measure of material tendency towards attrition.

C) Mechanical stability in terms of crush strength (IFE)

The equipment located at IFE is a digital gauge force of type Shimpo FGE/V-10X mounted on a vertical test stand, shown in **Fig. 3.5**.

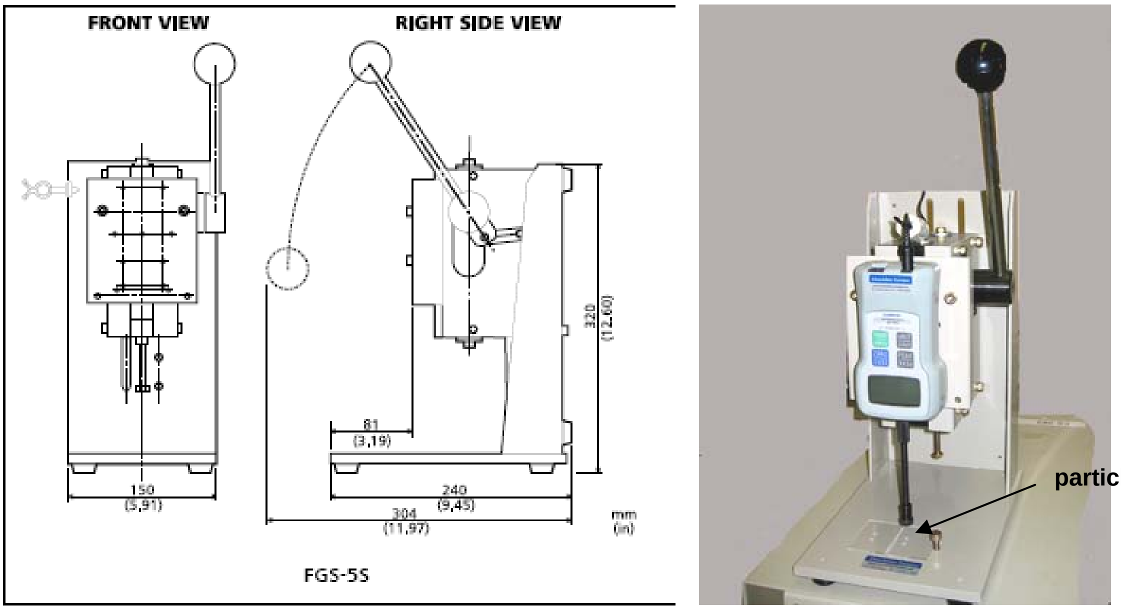


Fig.3.5. Shimpo digital gauge force, type FGE/V-10X (IFE).

The capacity, i.e. crushing strength, is measured as the compression force at the point of breakage, and can be recorded in lb, Kg and N. Here is used N with a maximum strength of 50.00 N, and a resolution of 0.01 N.

The crush strength, i.e. the force necessary to break down one single sorbent particle, is considered to be a measure of its ability to resist repeated impacts which will occur in a FB process. This strength is measured in N, and the values will vary with particle size for the same sorbent, the larger particles being the more resistant to disintegration. Although the attrition of particles that occurs in a FB environment obviously will be due to a combination of chemical and mechanical processes, the crush strength measured on raw material (carbonates) can be used as a screening method in the selection of the best bed material.

The results are summarised in **Fig. 3.6**, containing also some pre-treated sorbents.

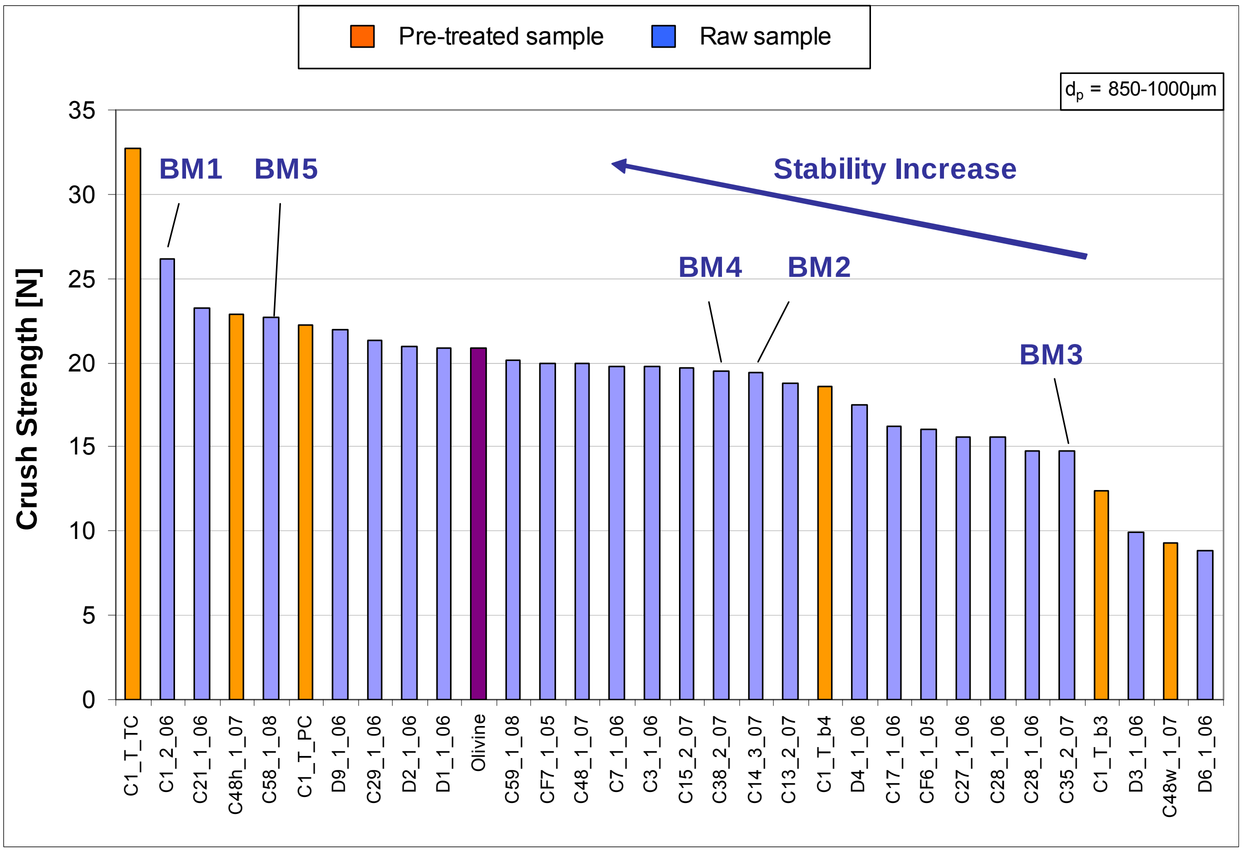


Fig.3.6: Crush strengths of natural calcites and dolomites in N, particle size 850-1000µm.

D) Mechanical stability during "flash calcination" in bubbling fluidised bed (ZSW)

Using a fluidised bed (FB) reactor for the investigation of the attrition behaviour of sorbents during sorption reactions is surely the most relevant method. In this final mechanical stability test, the material is not only mechanically stressed (by fluidisation and by sorption reaction), but also thermally (by temperature cycling) and chemically (by calcination / carbonation). The gas atmosphere and the temperatures of ab- and desorption can be adjusted to real AER process conditions. However, this kind of fluidised bed experiment should be limited to materials of high interest due to the high effort required for the operation of the test facility including the prior and final sieve analysis.

The lab-scale fluidised bed reactor, presented in **Fig. 3.7**, consists of a heat resistant steel tube (inner diameter = 70 mm; length = 560 mm). It is completely enclosed in an electric heated oven. Fluidising gas (10 vol.% CO_2 in N_2) is externally pre-heated. The exhaust gas is cleaned at the reactor top by three fine porous ceramic candle filters. The CO_2 content is measured online by a ND-IR analyser.

For the material assessment, presented in **Fig. 3.8**, a sorbent sample (200 g, particle size 200-710µm) was injected into a hot (880°C) fluidised bed of SiO_2 particles (650 g, 200-710µm) using the injection tube in the upper zone of the fluidised bed as shown in **Fig. 3.7**. A rapid start of the calcination reaction ("flash calcination") is observed by product gas analysis (CO_2 content, measured continuously by non-dispersive infrared analyser, rises from 10 vol.% up to ca. 25 vol.-%). During cooling-down, re-carbonation takes place (in order to avoid subsequent hydroxide formation). It was proven in preliminary tests, that the particle size distribution of SiO_2 remains constant during fluidisation (8h, 900°C). Therefore, the change of the particle size distribution could be referred to the sorbent material. The attrition value is defined in a similar way as for the ball mill test and it is calculated from the mass of the particle produced during fluidisation (with a diameter smaller than 200µm) referred to the initial mass of the sample.

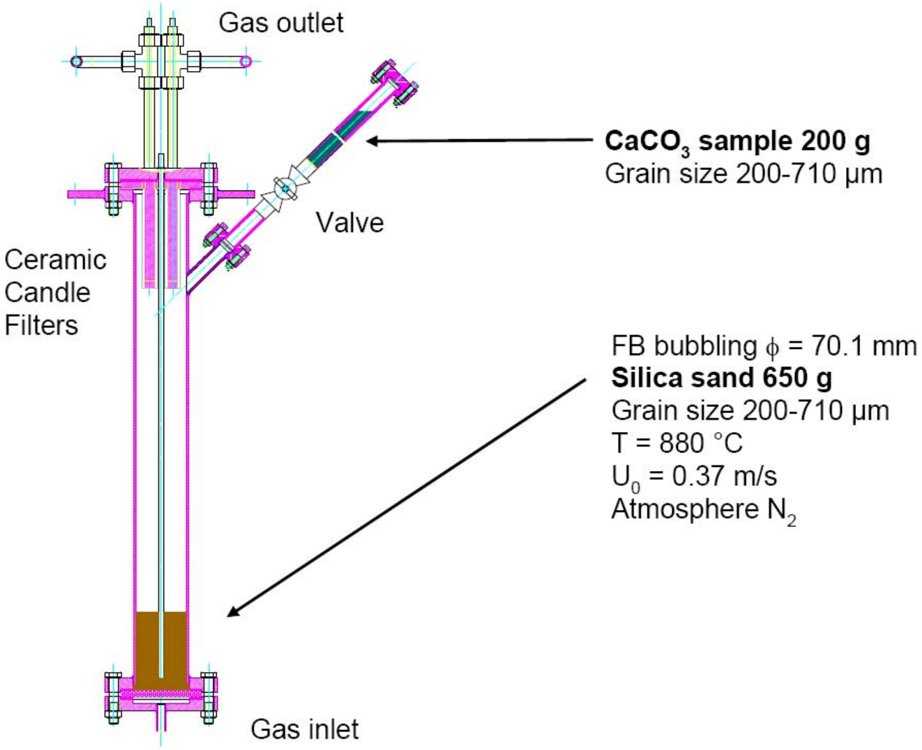


Fig. 3.7: Lab-scale FB reactor for mechanical stability tests at ZSW: Sorbent sample is injected into a hot fluidised bed of SiO_2 particles (used to stabilise the temperature). The attrition under these "flash calcination" conditions is obtained by pre and post sieve analysis.

Experimental results of the attrition (produced fine-grained particles smaller than 200 µm in wt.-%) for several carbonates, as well as the residual CO_2 capacity after 20 cycles of calcination and carbonation (determined by TGA) are summarized in **Fig. 3.8** for selected carbonates. In general, dolomites ($CaMg(CO_3)_2$; code D) appear to be mechanically less stable than limestones ($CaCO_3$; code C). However, there is no clear difference in the CO_2 capacity within the two carbonate groups, even though dolomites have a higher inert content (related to MgO, which is not active for CO_2 absorption). The standard bed material (olivine) is included in the diagram, showing a high mechanical stability but no reactivity towards CO_2 removal. The catalytic activity of the oxides toward phenol steam reforming is included in the diagram as well and is characterised by the colour of the symbols. This characterisation method was performed by UOC and it is presented in the following section E).

Based on this material assessment, the following 5 carbonates were selected and recommended as promising sorbent bed materials (BM1 – BM5) for AER gasification tests in the DFB facilities at partners TUV and USTUTT:

C1, C14, C35, C38, C58.

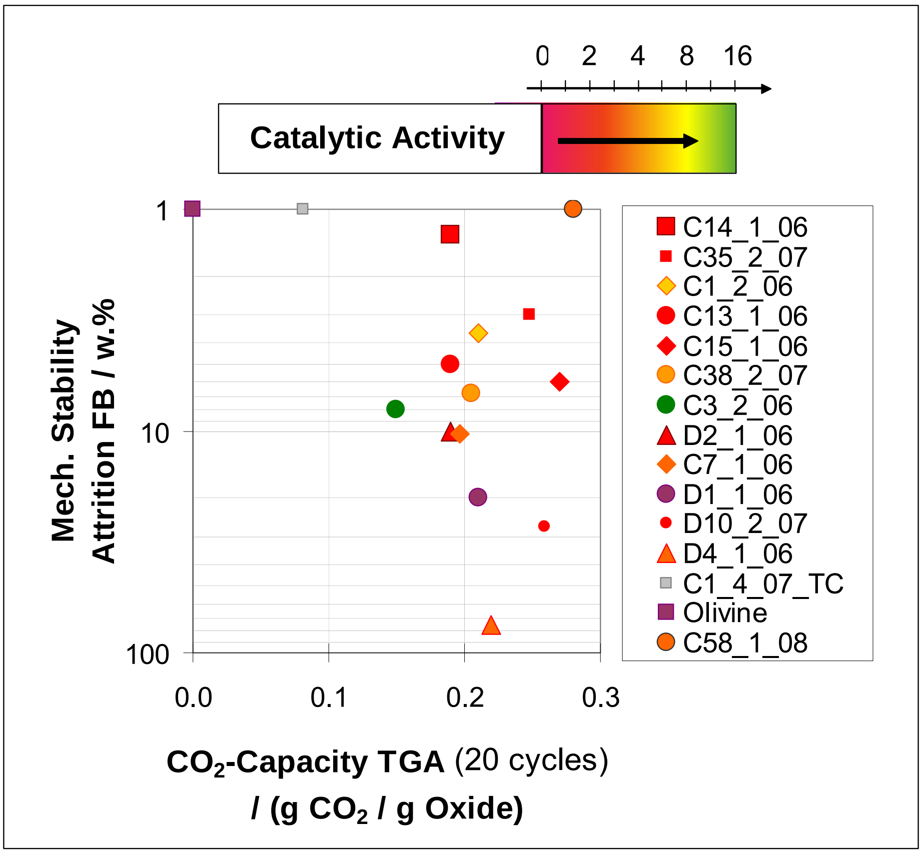


Fig. 3.8: Assessment plot for identification of best sorbent materials. Summary of important material properties: extent of attrition during "flash calcination", CO_2 capacity after 20 TGA cycles (d = 200-710 µm; T =. 650–840 C; CO_2 10%; H_2O 30%, N_2 90%), and catalytic activity towards phenol steam reforming (highlighted in colour; results from UOC).

Summary and conclusion of mechanical stability tests (ICE-HT, IFE, ZSW)

Carbonates are widely available worldwide. Natural carbonates (like limestone, dolomite) significantly differ in their mechanical stability. In general, dolomites seem to be less stable than limestones. In addition, the mechanical stability can be strongly affected at high temperatures, when the calcination and sintering take place (some carbonates lose stability, others become more stable). Up-to date, no correlation of the mechanical stability with material properties (e.g. chemical composition; age, BET surface) could be defined, which would facilitate the selection of a promising candidate. Therefore, a broad screening of diverse carbonates was carried out by applying simple test methods. The methods developed within this project showed a good agreement of results. Thus, promising sorbent bed materials were identified and enabled the recommendation of materials, which showed a low attrition rate during AER operation in the DFB facilities at partner TUV and USTUTT.

E) Catalytic activity of CO_2 sorbent towards tar steam reforming (UOC)

The main target concerning the catalytic work performed by UOC is to identify and propose the best CO_2-sorbent natural materials towards steam reforming of phenol and toluene for use in the AER process. In addition, to contribute via fundamental research work to the understanding of the catalytic behaviour of these materials and how this is related to their basic physico-chemical properties.

Methodology / approaches

Natural CO_2 sorbent materials such as calcites and dolomites were tested for their catalytic activity towards steam reforming of phenol and toluene using fixed experimental AER conditions. A correlation of physicochemical properties and catalytic activity of five promising calcite materials was attempted. In addition, the activity towards steam reforming of phenol over the best natural calcite, dolomite and olivine materials was compared.

Main achievements

A large number of natural CO_2 sorbent materials was tested for their catalytic activity towards steam reforming of phenol and toluene using fixed experimental conditions. The results are presented in the following diagram.

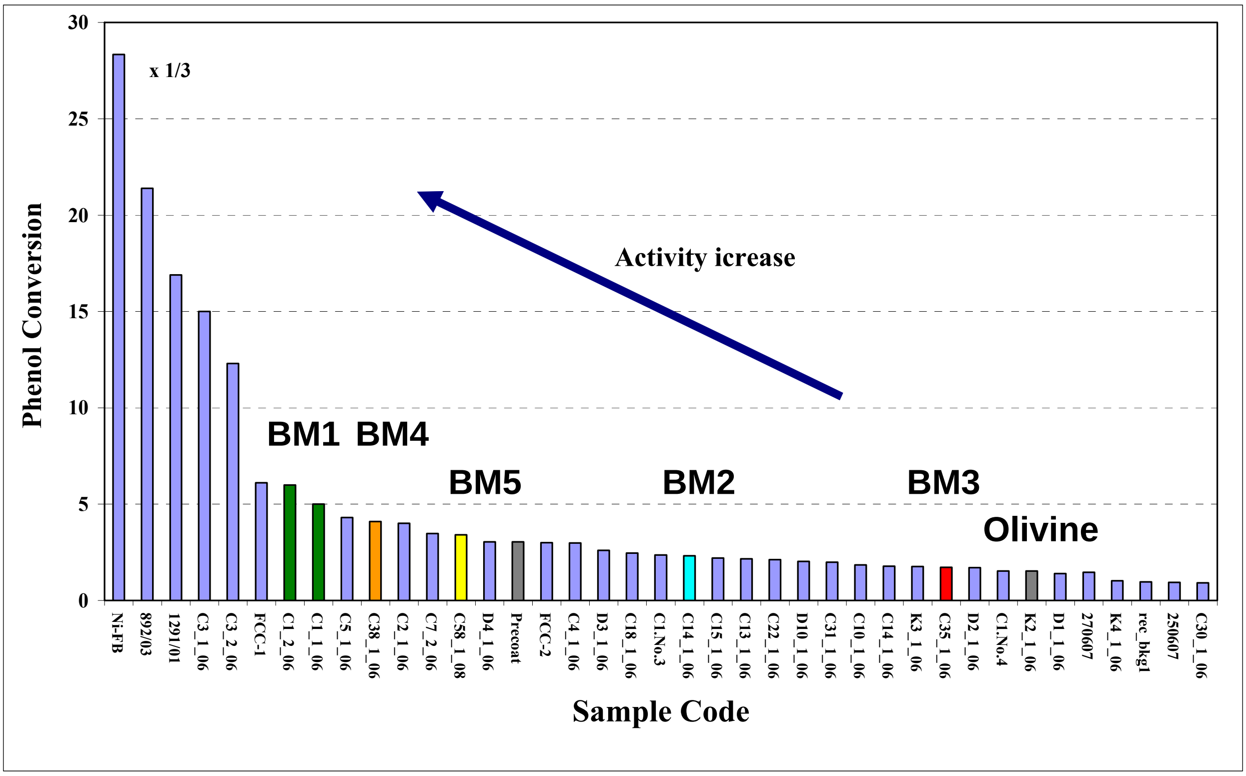


Fig. 3.9: Catalytic activity of tested carbonates (calcined at 850°C) in comparison to selected natural catalysts (Olivine coded K2_1_06, ash coded K3_1_06).

The calcite coded C3_1_06 was identified as the best natural CaO-containing material. The activity towards the steam reforming of phenol over the best natural calcite, dolomite and olivine materials was compared: C3_1_06 > D4_1_06 > K3_1_06. Relationships between physicochemical properties (e.g. primary particle size, BET area, mean pore diameter, surface elemental composition, surface morphology, distribution of surface basic sites) among the five calcites (C1-C5) and their catalytic behaviour were found.

Conclusion: test of catalytic activity

Natural calcites (cheap, non-toxic) can be considered as potential materials in industrial biomass and waste-biomass gasification plants for the purification from tars of the H_2-rich gas produced. It is the first time to show that the surface morphology (e.g. distribution of surface defects, crystallographic planes) of CaO derived after calcination of calcite at 850°C plays an important role on its phenol steam reforming activity. This surface morphology depends on its geological history of formation. Thus, besides the BET area that controls the number of active catalytic sites, the specific site reactivity different for each calcite also will affect the overall reaction rate.

F) CO_2 sorption properties by TGA (ZSW, ICE-HT)

It is well-known from literature and former experiments (AER-GAS), that the CO_2 capacity decreases during multi-cycle processes. Especially during the first cycles, the deactivation is high. Most carbonates tend to stabilise after about 10 to 20 cycles. Typical multi-cycle curves of carbonates, selected within this project, are presented in the next plot.

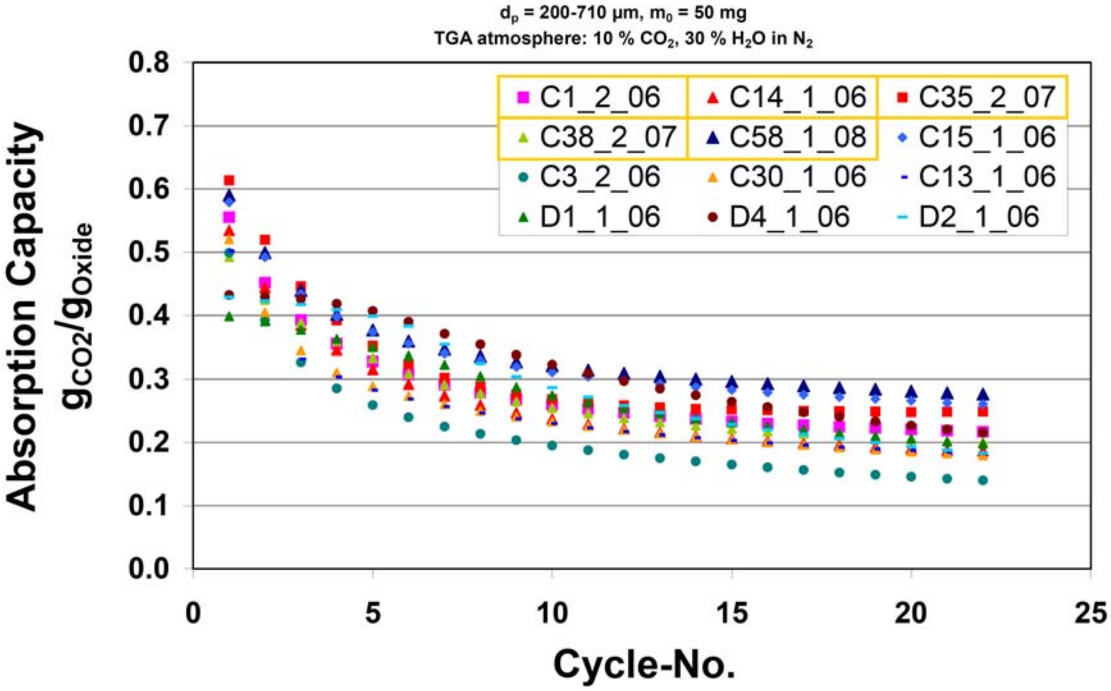


Fig. 3.10: CO_2 capacity of various carbonates in multi-cycle TGA tests with calcination (840°C) and "total" re-carbonation (650°C) in 10 vol.% CO_2, 30 vol.% H_2O, and 60 vol.% N_2.

The difference between Dolomites ($CaCO_3MgCO_3$, code D) and Calcites ($CaCO_3$, code C) disappears already after a few cycles, even though the theoretic CO_2 capacity of Dolomites is lower due to the high MgO content (being inert for CO_2 up-take).

The increase of the calcination temperature from 850 to 1100°C was found to decrease considerably the first-cycle absorption capacity of calcites but to have only minor effects in the case of specific dolomite samples.

The degradation of the material is mainly caused by changes of the sorbent structure (CaO – $CaCO_3$) during cycles of calcination and re-carbonation. Many micro pores "sinter together" to a smaller number of big pores. Thus, the surface area decreases and active CaO is "isolated" inside the particle. In other words, the more the sorbent is cycled and therefore sintered, the more is the CO_2 up-take limited by diffusion of CO_2 towards active CaO. In case of dolomites, the pore structure might be stabilised by the inert MgO grid, resulting in a increased cycle stability. Sintering is also enhanced at increased calcination temperatures / durations.

In the DFB gasifier, the residence time of the sorbent bed material in the gasifier is comparable short. Thus, only partial carbonation occurs, leading to a high cycle stability with nearly constant CO_2 capacity. Thus, sintering does not take place in the same extend. This was confirmed by the analysis of samples from DFB gasification: The sorbent bed material nearly behaved like the raw material.

Conclusion of sorbent characterisation

A broad screening of a large number of carbonates was carried out in order to recommend 5 CO_2 sorbent bed materials for AER-DFB gasification. Materials were characterised in terms of mechanical stability, catalytic activity, and CO_2 sorption behaviour under multi-cycle conditions.

Carbonates behave very differently. Also in the lime industry AND in the literature no reliable method (indicator, set of criteria) is available to decide on the functionality of raw material for different purposes. Thus, simple test methods are necessary to identify promising candidates.

A stable CO_2 sorbent bed material is not only required for AER biomass gasification, but also for high temperature CO_2 separation, e.g. from flue gases. In addition, carbonate based bed materials are also promising alternatives for Olivine in standard DFB gasification. With view to the increasing work performed on CaO based bed materials, a common method should be developed and defined as standard in order to compare results from different origins.

2) Improvement of mechanical stability of CO_2 sorbent bed materials

A sorbent bed material with a high mechanical stability (related to a low attrition rate) is essential for stable operation of a power plant. It avoids dust problems in downstream process units and increases the efficiency and economy of the process. On the one hand, carbonates with a high abrasion resistance (low attrition) for fluidised bed applications can be identified by this efficient and reliable screening method (as presented above); on the other hand, the mechanical stability of a promising carbonate can be further improved by pre-treatment. Therefore, besides the selection of natural materials with high mechanical stability, additional focus was on methods to further improve the mechanical stability.

A) Thermal pre-treatment (ZSW)

In order to minimise the risk for the commercial power plant at Güssing, Austria, during the AER test campaign, a CO_2 sorbent bed material with a low attrition rate should be used. Therefore, the C1 limestone was selected to produce about 12 t of re-carbonate in an industrial pre-treatment process.

Methodology / approaches

The here performed thermal pre-treatment consists of a calcination step at increased temperature (>1000 °C) and a subsequent re-carbonation step. The material was sieved before and after the thermal treatment. The whole procedure is illustrated in the following figure.

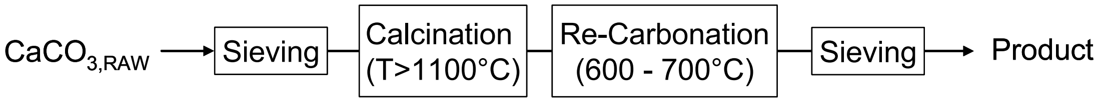


Fig. 3.11: Thermal pre-treatment method applied for production of bed material for AER tests in the Güssing gasifier.

Re-carbonation was carried out to facilitate the handling and storage of the sorbent, since CaO would form $Ca(OH)_2$ resulting in a poor mechanical stability. Calcination and re-carbonation were done in an industrial rotary kiln, each heated by a natural gas burner. In case of the re-carbonation kiln, CO_2 was added to the reactor in order to increase the CO_2 content, hence to accelerate the carbonation reaction.

Main achievements

The obtained CO_2 sorbent material showed an increased mechanical stability, because the material got sintered in the calcination step, hence the initial high attrition already occurred during the pre-treatment. Furthermore, fine particles were removed by the flue gas stream during the pre-treatment process. As displayed in **Fig. 3.3** and **Fig. 3.8**, the pre-treated limestone (code: C1_4_07_TC) has a higher mechanical stability than the original raw material (code: C1_2_06) in the "flash calcination" fluidised bed experiment. However, the reactivity is reduced due to the sintering process, resulting in a lower CO_2 capacity compared to the raw material. The stronger the material is sintered, the higher becomes its stability / hardness, but the lower is its reactivity (due to loss of surface area). Thus, a compromise between the mechanical stability and the reactivity of the sorbent bed material must be identified for the pre-treatment process. This method was elaborated for the C1 material. It must be carefully checked, if it can be applied to another limestone.

Conclusion

A thermal pre-treatment method is a suitable way to increase the mechanical stability of a carbonate. Besides the re-carbonation process, it is a well-known commercial process, e.g. in the lime and cement industry. Therefore, it could be transferred into industrial scale in order to produce the quantities for the test campaign at BKG. Hence, promising CaO based bed materials are available for diverse fluidised bed applications (not only for AER biomass gasification processes). Besides low costs, the catalytic activity of the limestone towards steam reforming and tar removal is a material specific advantage.

However, the method can not be applied to all materials, because some sources lose their mechanical stability at increased temperatures. Thus, the effect of the calcination / sintering conditions on the mechanical stability is strongly dependent on the temperature and duration as well as on the individual material properties. This effect was observed within project work but could not be analysed in more detail. It is known from lime industry that limestone properties significantly affect the lime quality and the burning conditions must be adjusted to the limestone properties individually. In other words, even in the well established lime industry, the different behaviour of limestones in the sintering process can not be predicted and must be examined for each material.

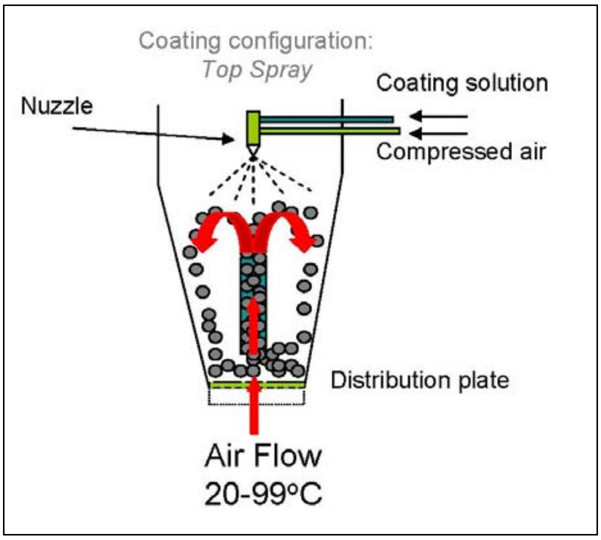
B) Coating of Carbonate particles (IFE, ICE-HT)

The main objective of this work was to develop methods to improve the mechanical stability of the CO_2 sorbent materials by coating the particles with an appropriate material, thus making the surface harder and less prone to attrition but without significant reduction in their absorbance capacity.

Methodology / approaches

B1) Coating in fluid bed agglomerator (IFE)

The approach made by IFE was to develop a novel coating method using a fluid bed agglomerator (**Fig.3.12**). The experiments focused on the BM2 / C14 sorbent. Silica-based, alumina, calcium and alumina silicate-based coating materials were tested in this project.



Optimal process parameters:

Particle size: 0.5-0.85mm

Air flow: 1100 LPM,

Nozzle air: 6.0 PSI

Gas temperature: 90°C

Pump speed: 40 RPM

Bed charge: 30g

Fig.3.12: Principle of coating procedure using a FB reactor, including the optimal process parameters found by extensive testing

The resultant coatings were characterized by examination in a scanning electron microscope (SEM) and by XRD. The mechanical properties were tested by measuring the crushing strength as described earlier. The influence of calcination temperatures on C14 particles varying from 900 to 1150°C was used as a reference base for evaluation of improvement.

Main achievements

Effect of calcination temperature on mechanical properties:

The crush strength of the calcite particle decreases after decomposition of the carbonates species after calcination at 900^{o}C but increases with increasing further the calcination temperature and time, due to sintering of the particle.

Coating of C14 particles by colloidal silica suspension:

A homogenous coating (5-20 micrometers) appears to be well attached to the surface of the calcite particle and presents a good chemical homogeneity. The coating is not continuous along the surface and presents only few cracks at different locations around the particles. This cracking is presumably beneficial for the process since it will allow CO_2 to diffuse within the particle to react with CaO.

Coating experiments with calcium nitrate and Al-based solutions:

No coating could be observed on the surface of the particles, due to low interaction between the surface of the calcite particle and the particles in the solution. The low viscosity and the chemical nature of the solutions is a critical parameter for FB coating and exclude most of Ca and Al-based solutions studied in this work.

Coating experiment with a natural mineral: kaoline (kaolinite):

A thin coating of 20µm was observed on the SEM.

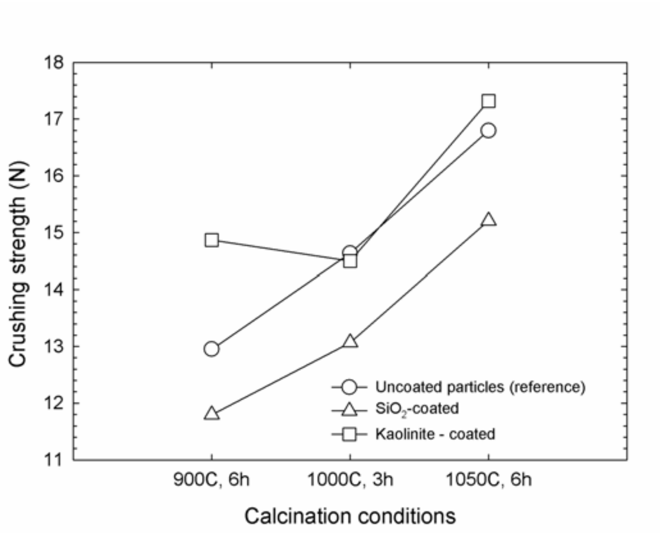


Fig.3.13: Crushing strength for coated and uncoated (references) calcite C14 particles (0.5-0.85mm) as a function of the calcination temperature

Tests of optimization conditions (**Fig.3.13**) show that after calcination at 900°C for 6h, SiO_2-coated particles show a lower crushing strength than that of the reference particles, probably due to the reaction of CaO with the water solvent of the silica sol. Increasing the calcination temperature increases the mechanical strength of the SiO_2-coated particles, too.

Kaolin-coated particles of C14 show a crushing strength higher than the uncoated particles. When the calcination temperature for the kaolin-coated particles is increased up to 1050°C, the crushing strength goes through a minimum for a calcination temperature of 1000°C followed by a sharp increase when calcined at 1050°C. Those unexpected variations of the crushing strength of the kaolin-coated C14 with temperature might be related to modifications in the structure of the kaolin.

TGA tests (ZSW) showed that the coated samples has a very similar behavior during multi cycling as the standard C14 particles.

B2) Coating in colloidal, aqueous silica or alumina dispersions (ICE-HT)

Use of colloidal, aqueous silica or alumina dispersions to deposit respective layers on the surface of sorbent particles. Variation of pre- and after-treatment conditions for optimization.

Main achievements

Positive effect of coating was identified for specific combinations of sorbent type and coating agent. Examples are: (i) coating of C6 calcite with silica, (ii) coating of C1 calcite with alumina. However, a positive effect of coating is not always observed and many cases were found whereas coating had rather a negative effect possibly due to inadequate adherence of the coating layer. The effect of coating of C6 calcite particles with silica on attrition performance is shown in **Fig. 3.14**. Three differently pre-treated samples of C6 material were examined. The loading of silica was 1 wt.%. In all three cases, the beneficial effect of coating is clearly evident.

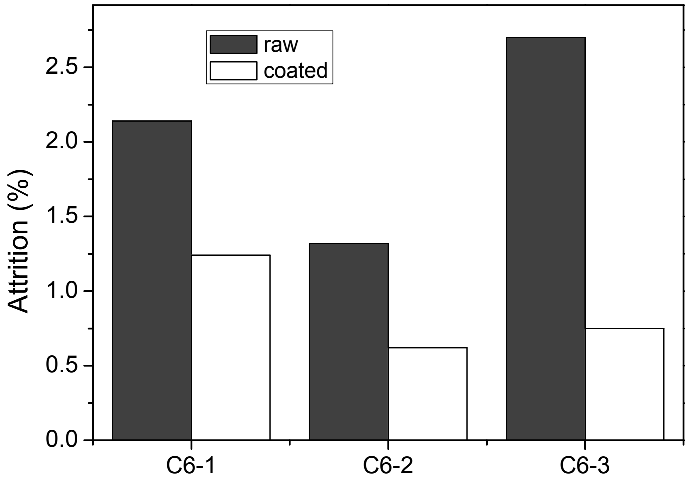


Fig. 3.14. Effect of coating of C6 particles on attrition.

Conclusion

Coating of uncalcined particles was shown to be highly preferable due to the formation of $Ca(OH)_2$ with aqueous solutions and deterioration of the mechanical properties due to in-situ attrition during FB-coating

FB coating is not suitable for coating of sorbent with Al- and Ca-based solutions due to:

- low viscosity
- acidity of the solutions dissolving the surface of the sorbent
- poor attachment of the coating on the after drying

Particles were successfully coated with SiO_2-based solution and kaolin-based solutions.

The absorption of the kaolin coated sample remains acceptable for a AER type of process while the improved attrition properties of the particles is a very promising result and a valuable work that will be pursued by IFE in the next years in various high-temperature CO_2-capture technologies. Kaoline is a common available mineral (Al-sheet silicate).

The FB method can easily be scaled up for further industrial application.

However, the optimal coating procedure has to be determined on a case-by-case basis for the specific natural sorbent. The advantages of coating have to be weighted against the increased cost of the modified sorbent.

3.2 WP 2: Analysis of tar formation/decomposition process

(USTUTT, ICE-HT, PSI, TUV, UOC, ZSW)

Introduction / Motivation and goals

Even though the gasification temperature is moderate (600 – 700°C) in the AER process, the tar content of the raw gas is very low (< 1 g/m³), even lower than under standard conditions at 850 – 900°C. Tar analysis showed that the majority of tars are secondary tars (phenol, toluene). The goal of this work package is to further reduce the tar content of the AER product gas by identifying bed materials with catalytic activity (besides CO_2 sorbents, also catalysts are regarded) and suitable process conditions, which improve the decomposition of formed tars respectively which reduce tar formation.

1) Screening, characterisation, and delivery of catalytic bed material

(UOC, PSI, TUV, USTUTT)

Goal

The main target concerning the catalytic work performed by UOC, PSI, and TUV was to identify and propose suitable commercial catalysts containing no nickel (Ni) with good attrition properties that could be used as catalytic bed materials (CO_2 sorbent + catalyst) in the AER process in order to further reduce the tar content and increase the H_2 product concentration (vol%).

The stresses of a catalyst in a DFB reactor are high with respect to mechanical abrasion, rapid temperature loops as well as changing RedOx-conditions. In addition, catalyst poisoning must be considered by S, tars, and halogens. Therefore, the catalyst must show a high mechanical stability, should be non-toxic (with view to recycling the ash into nature) and be available at low costs.

Methodology / approaches

UOC has investigated natural catalysts (besides CO_2 sorbents (see WP 1), Olivine, ash and LD sludge) as well as commercial solids (MEL Chemicals Ltd, UK) *not containing nickel metal* (e.g., $Ni/\gamma\text{-}Al_2O_3$) in terms of catalytic activity properties for phenol steam reforming. A micro fixed bed reactor was employed.

The study of powder and pellet form of the best commercial solids identified was achieved by UOC, and moreover, a possible reaction mechanism of the secondary tar cracking over a CO_2-sorbent catalyst was proposed.

At **TUV**, the catalytic activity of selected bed materials was determined in a lab-scale fixed bed reactor. These laboratory tests are very useful to determine the efficient catalytic activity and stability of various catalysts and bed material additives in the particular case under conditions of biomass steam gasification. Synthetic gas mixtures are used with naphthalene and toluene respectively as tar model compounds for this purpose. In the following a screening of several bed materials and additives is presented. On this basis catalytic active materials for pilot scale experiments can be chosen.

The experiments were carried out in a fixed bed quartz reactor with 4 mm inner diameter. The reactor is charged with about 400 mg of catalyst and hold in the temperature zone by quartz wool. The particle size was selected between 250-500 µm. The catalyst bed temperature is monitored by a thermocouple placed outside of the reactor near to the catalyst bed. The furnace temperature is controlled by a Jumo temperature controller. The gas volume flows are adjusted by mass flow controllers. For the toluene reforming experiments a mixture of helium (20 ml/min) and hydrogen (10 ml/min) is used which gives residence times of about 0.5 seconds. Water and toluene are inserted by motorised syringes (see **Fig. 3.15**)

After the reactor a cryo trap is installed to cool down the gas and condense unconsumed toluene as well as water and condensable by-products of the steam-reforming reactions. The condensate is separated from water and analysed by an off-line gas chromatograph. The gases are analysed by an on-line gas chromatograph to get the amounts of CH_4, CO and CO_2.

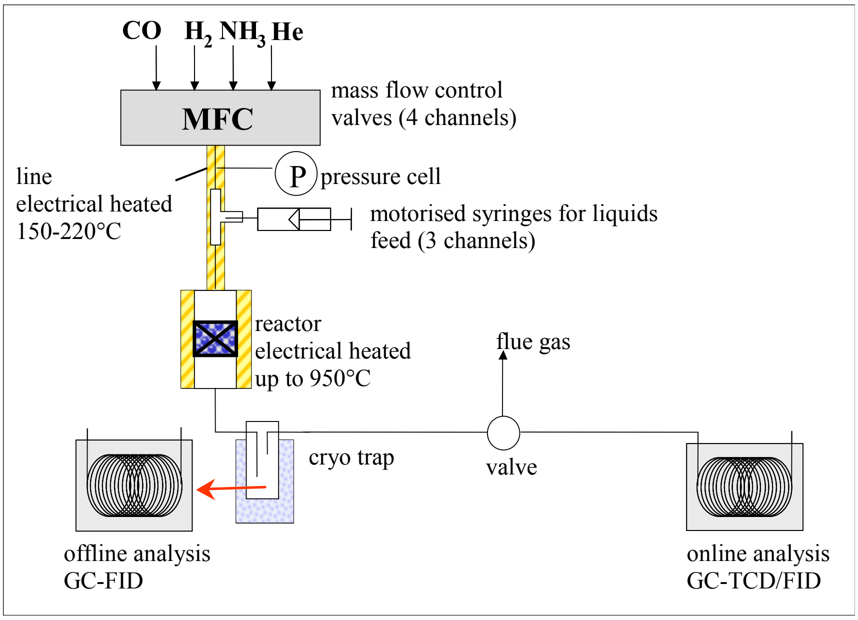


Fig. 3.15: Set-up of the laboratory scale experiments.

Moreover, the fact that the 100 kW DFB process development unit at TUV was available for the whole duration of the project (instead of only the first half of the project as originally scheduled), it was considered to be advantageous to test new bed materials directly in pilot scale. This test facility simulates the process conditions of a commercial power plant (like the Güssing gasifier) best, because all material stresses (thermal, mechanical, chemical) occur simultaneously.

At **PSI**, the mechanical properties were investigated in a lab-scale fluidised bed facility under temperature- and Redox-Cycle conditions. A suited experimental set-up was built up at PSI for this purpose. These tests comprised several cycles between reducing atmosphere at 680ºC and oxidising atmosphere at 900ºC. To understand the interdependent influence between sorbent and catalyst material, the tests were carried out with the two pure materials and a mixture of both.

Finally, the best metal oxide catalyst was tested under AER gasification conditions in the DFB reactor at **USTUTT**, described below in more detail.

Main achievements

Results on screening of catalysts as additive bed material (UOC)

Results of the screening of low-cost commercial catalysts that contained no nickel (Ni) are presented in the following diagram. For comparison, one Ni-containing catalyst is included in the diagram, which shows the highest catalytic activity under the test conditions examined.

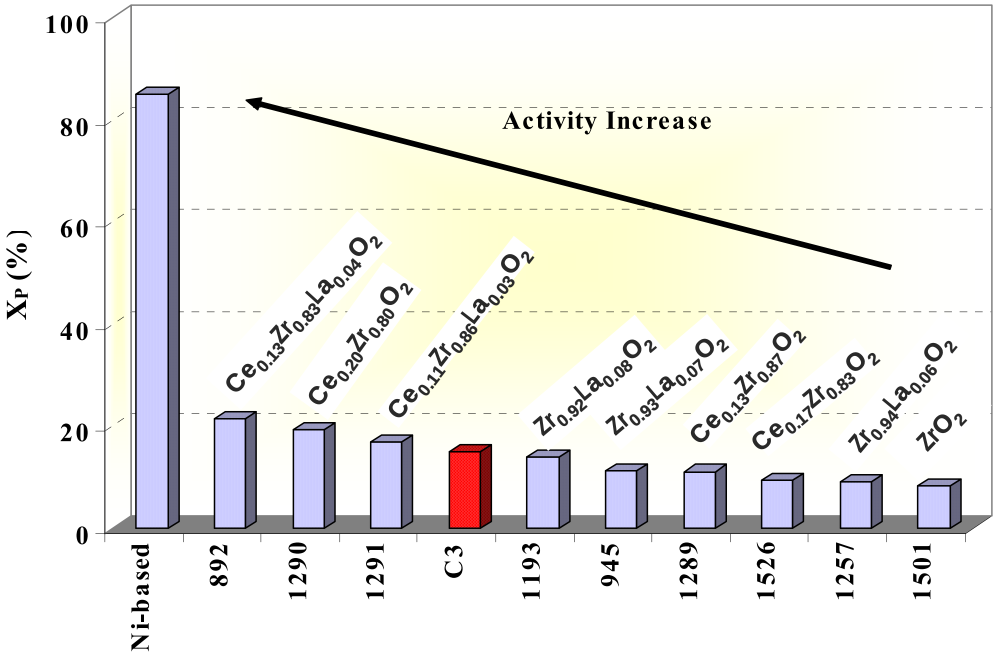


Fig. 3.16: Catalytic activity (C conversion X of Phenol steam reforming) of tested catalysts (UOC) using the fixed experimental conditions.

In particular, *commercial mixed metal oxides* (MEL Chemicals, UK) containing CeO_2, La_2O_3, MgO, and ZrO_2 exhibited very good phenol reforming catalytic activity under the fixed experimental conditions within this project. Additionally, the steam reforming reaction of phenol was studied over two commercial FCC catalysts and one Ni-based catalyst. The Ni-based catalyst exhibited significantly higher catalytic activity compared to the calcite C3_1_06 (best natural material). In addition, no significant drop of activity was observed after studying the steam reforming of phenol over the best commercial mixed metal oxide in powder and pellet form.

Mechanistic studies using the Steady State Isotopic Transient Kinetic Analysis (SSITKA) technique for tracing the "H-path" of phenol steam reforming over the catalytically more active natural calcite, dolomite and olivine materials were performed. A good correlation between H_2-reaction selectivity and the concentration of active "H-containing" reaction intermediates with reaction temperature was found.

Various in situ DRIFTS and Mass spectrometry experiments revealed the main reason of the strong inhibiting effect of H_2 and CO_2 present in the feed stream of phenol steam reforming reaction. Both molecular species strongly compete for the same surface active sites with water. The latter provides necessary intermediates (OH/H) for the conversion of phenol into H_2, CO and CO_2.

Results on catalyst tests in lab scale FB facility (PSI)

The results of the six experiments showed that the catalysts are resistant against purely mechanical attrition, but the nickel based catalyst is destructed by thermal and/or chemical stress during the AER test cycles. Although the commercial nickel based catalyst has shown in tests at the University of Cyprus (UOC) its ability for tar reforming, an application in a real reactor (where the mechanical stress is bigger than in the test set-up) cannot be recommended.

The mixed oxide catalyst was fairly stable with respect to attrition, but it is a more expensive catalyst and did not show activity for WGS or ethylene reforming under the AER conditions, while the nickel based catalyst was very active for both reactions.

Results on catalyst tests in lab scale fixed bed facility (TUV)

To find a basis for the catalytic activity of different bed materials the following candidates have been tested:

- Olivine fresh/used from Güssing
- Silica sand
- Calcite fresh/calcined and recarbonated
- Ilmenite
- Blast furnace slag

Olivine (fresh/used) and Calcite showed reasonable conversion of more than 50%, all other materials were more or less inactive.

Generally it can be stated that two groups of materials showed good/reasonable catalytic activity:

- nickel and iron containing materials (Olivine and to a low extend Ilmenite)
- and calcium containing materials (Calcite).

Summarizing, the laboratory scale fixed bed reactor for steam reforming of tar model compounds as well as gaseous hydrocarbons is well suited for preliminary tests regarding catalytic tar removal. However, materials might behave differently if used in a dual fluidised bed system due to the alternating oxidation and reduction.

Results on gasification with a catalyst in AER batch mode (USTUTT)

The mixed metal oxide catalyst (provided by MEL Chemicals, UK), which was recommended by UOC and PSI, was used in AER gasification experiments in batch mode in order to further reduce the tar content of the AER product gas by direct catalytic reactions inside the gasifier with effects on the gas phase reactions (e.g., catalysis of the Water-Gas-Shift-Reaction).

Each experiment consists of 3 cycles (experimental phases), using different bed materials (pure sorbent material and mixtures with 2 different catalyst concentrations). Between every experimental phase, the experiment was interrupted to remove the char and regenerate the bed material by switching the fluidization gas from water vapor to air and changing the temperature of the gasifier to 850°C. After the char was burned and the bed material was fully regenerated, the next experimental phase was prepared and carried out. During each batch mode gasification experiment (experimental phase), one tar sample was taken.

In **Fig. 3.17**, the first three columns represent the product gas composition in vol-% of the experiments without any catalyst added; the other two groups of columns represent experiments with 50g and 200g of catalyst added, respectively. The total product gas yield does not change much, though at closer inspection, the hydrogen concentration at the first experimental phase was less, while more CO and CO_2 were produced. This can mean that the catalyst also affected the gas yield.

All three experiments show a little decrease in AER gas quality towards the third experimental phase. This shows the decreasing effectiveness of the bed material in general and does not result from the catalyst itself. The use of the catalyst slightly improves the product gas composition since the water gas shift reaction is enhanced.

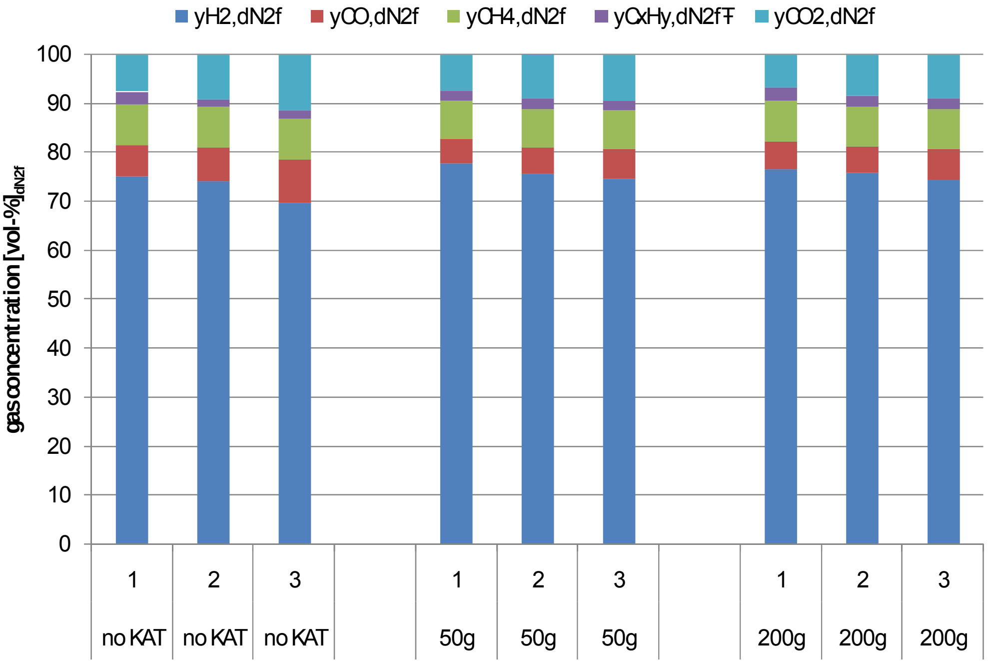


Fig. 3.17: Product gas composition during three step AER gasification experiment with different bed material mixtures (reference case: no catalyst, pure sorbent C60 (3 kg); catalyst tests: addition of 50g / 200g catalyst). Each bed material (mixture) was used for three gasification runs (3 cycles of the sorbent material).

As presented in the next diagram, there is a positive effect of the mixed metal catalyst on the formation of gravimetric tars. In the diagram, the gravimetric- and GC-MS tar concentrations are represented as stacked columns, with the gravimetric tars concentration as the top column. In the reference experiment, in which the bed material consisted of pure sorbent without an additional catalyst, the formation of gravimetric tars was significantly higher, in particular by factor 2. Thus, the catalyst does have a clear beneficial effect on the formation / reduction of tars.

The increase of the overall tar yield during each gasification experiment is most probably related to the loss of catalytic activity of the CO_2 sorbent bed material due to ongoing CO_2 loading. Also the catalyst could have lost its catalytic activity due to poisoning.

A closer analysis of the tars with respect to GC-MS tars confirmed the positive influence of the catalyst on the tar removal. However, the effect is much smaller in case of gravimetric tars. It is surprising that an increased content of catalyst in the bed material does not further enhance tar removal.

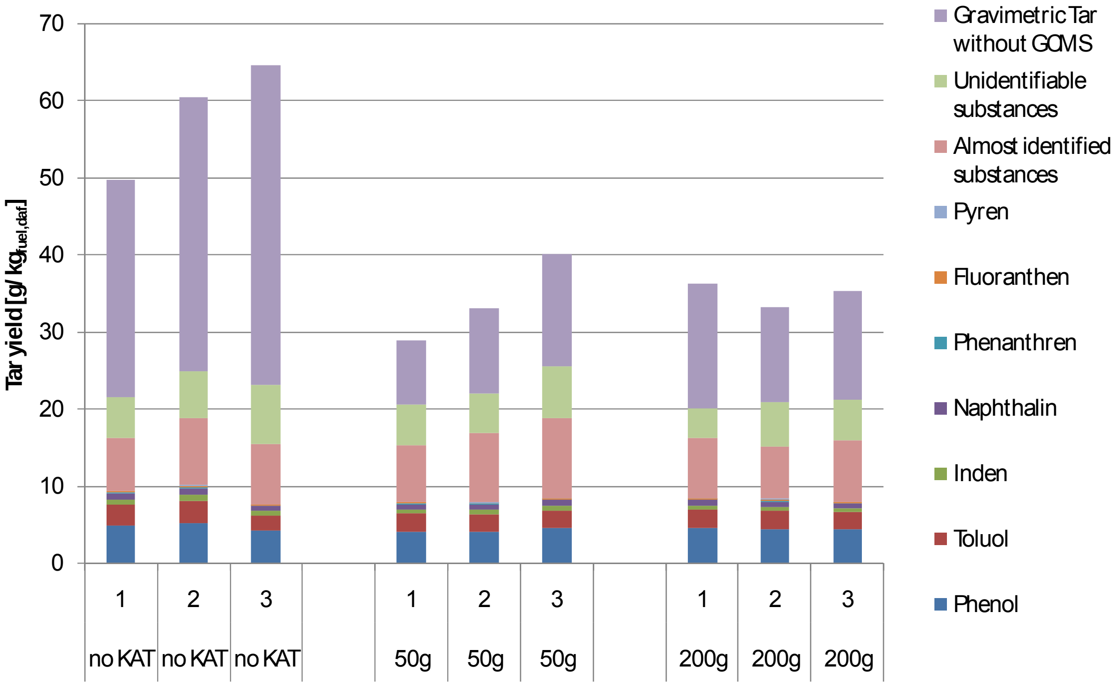


Fig. 3.18: Tar yield and composition during three step AER gasification experiment with different bed material mixtures (reference case: no catalyst, pure sorbent C60 (3 kg); catalyst tests: addition of 50g / 200g catalyst). Each bed material (mixture) was used for three gasification runs (3 cycles of the sorbent material).

Conclusion

Several of the commercial metal oxides tested at UOC have better catalytic activity and H_2-yield per gram basis, and that all promoted to a large extent the Water-Gas Shift reaction compared to the calcite material C3_1_06. However, the low-cost of natural materials compared to these commercial metal oxides is still advantageous for an industrial scale application.

It should be emphasised that several calcite materials appear to be catalytically active, especially as oxide.

In the batch mode AER gasification tests at USTUTT, the used mixed metal oxide catalyst showed a slightly positively influence on the water gas shift reaction and, therefore, on the hydrogen yield. With view to the gravimetric tar results, the catalyst significantly reduces the content of gravimetric tar, which is divided in halves compared to the reference case without the catalyst. The GCMS tar concentration is influenced by the catalyst in a lower extent.

Concluding, the use of an additional catalyst does not significantly improve the product gas quality under the conditions examined. Thus, the additional effort and expenses for such a catalyst can not be justified, especially, when considering the high product gas quality, obtained in the AER process. All AER experiments (employing solely a CaO based CO_2 sorbent bed material) in pilot scale (100 kW dual fluidized bed steam gasifier at TUV) as well as in demonstration scale, showed that no additional catalyst is needed to reduce the tar levels. Despite the low gasification temperature, the tar levels measured during AER operation were always significantly lower than for standard conditions (gasification temperature: 850 °C, bed material: olivine).

Hence, it is recommended to select a CO_2 sorbent bed material with a good catalytic activity in order to further improve the product gas quality. Such a "catalyst" provides the important advantage not to deactivate in the AER process due to RedOx cycling and / or fast temperature looping – compared to commercial industrial catalysts. In addition, it is a low cost material and, in general, non-toxic.

2) Tar removal / decomposition using model tar compounds

Goal

The over-all goal is to identify optimal reaction conditions to minimise the tar content of the AER product gas. Therefore, lab-scale tests were performed using selected primary and secondary model tar components. The expected effect of the AER process on the tar conversion (carbon conversion) is presented in the Figure beneath.

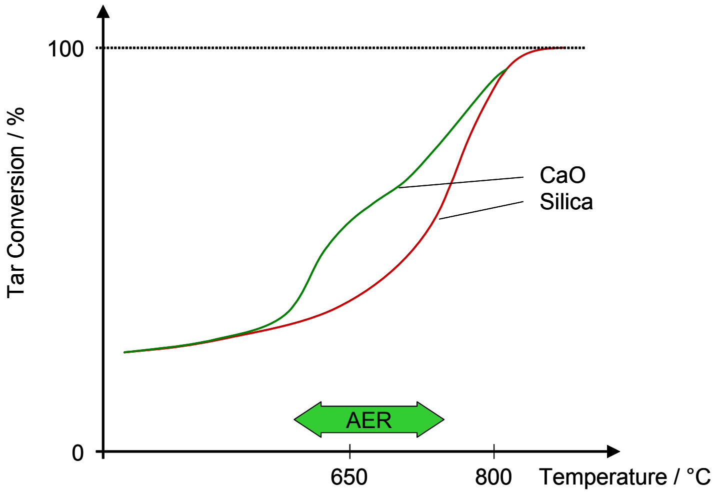


Fig. 3.19: Improvement of the tar conversion by AER at temperatures < 800°C, using CaO as bed material.

Methodology & results

A) Micro reactor (ICE-HT)

A micro fixed bed quartz reactor (d = 4 mm, l = 200 mm) was employed to assess the catalytic function of sorbents in carbonate, oxide, and partially carbonated forms for primary tar (model components: Acetol, Glycolaldehyde, Guaiacol) reforming. The reaction conditions examined were: T=550-650°C, Feed gas: 0.6% primary tar, 40% H_2O in helium, catalyst weight: 0.3 g.

Results

A quartz reactor of small residence time was employed to minimize the extent of homogeneous reactions and obtain meaningful results. Calcite C1 in its calcined form is the most active catalyst for reforming of all examined compounds. Calcite C1 in carbonated form is less active, but in all cases, C1 is almost an order of magnitude more active than Olivine, leading to highest hydrogen production and shift of products to C1 compounds. The conversion of acetol – a representative primary tar compound – obtained over olivine and C1 calcite C1 is shown in **Fig. 3.20** as a function of temperature. The higher activity of both raw and calcined C1 compared to olivine is clearly seen.

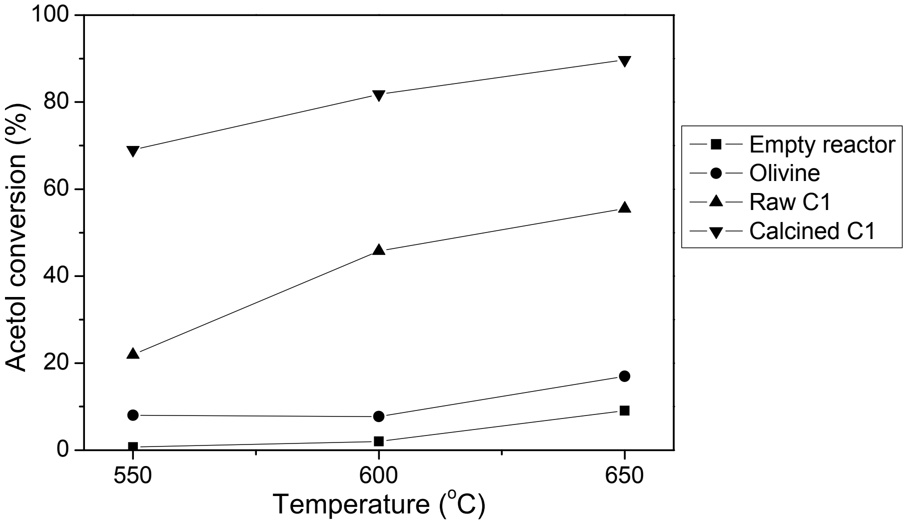


Fig. 3.20. Reforming of acetol over olivine and calcite C1.

B) Fluidised bed reactor (ZSW)

Batch mode fluidised bed experiments were carried out at ZSW with CO_2 sorbent (Calcite C1) and non sorbent (SiO_2) bed materials using selected primary (Acetol) and secondary (Phenol) model tar components. The reactor is an electrically heated stainless tube (inner diameter = 43.1 mm; height = 870 mm; optimal amount of bed mass approx. 400g). The model tar is premixed with water and inserted into the reactor as vapour. Tar conversion was investigated for different temperatures.

Results

The following diagram shows the influence of the temperature on the gas yield and H_2 yield in case of a CaO-based bed material (C1 calcined) and of a SiO_2 bed material. The Acetol conversion clearly increases with increasing temperature. This effect is significantly improved by using CaO as bed material. The latter is related to both, higher catalytic activity of the bed material and simultaneous CO_2 separation.

Phenol conversion was observed at temperatures above 700°C using C1 in its oxide form. Thus, an AER effect could not be realised due to low CO_2 partial pressures in the fluidised bed, inhibiting carbonation of CaO. In all cases, the decomposition of tars is clearly reduced in case of $CaCO_3$ (raw material) as bed material.

Due to the complex reactor system, the in situ COs separation, and decomposition mechanisms, it was not possible to identify all by-products and minor components (which are available in the gaseous, liquid, and solid phase). Thus, the calculation of the carbon conversion was not properly possible.

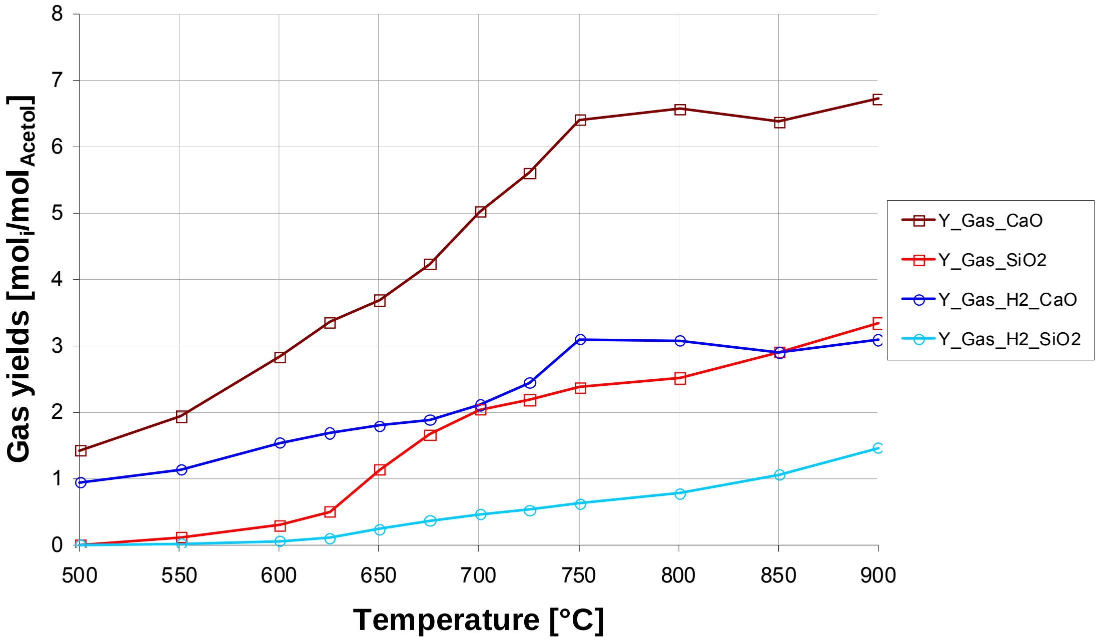


Fig. 3.21 Gas yield and H_2 yield of Acetol decomposition for different bed materials (Calcite C1, SiO2) in dependence of the reaction temperature in a bubbling fluidised bed facility..

Main achievements (ICE-HT, ZSW)

Primary tar compounds are thermally not stable and therefore difficult to inject into a fluidised bed reactor. In the presence of a catalyst (i.e. CaO), the decomposition as well as the steam reforming / CO shift reaction are increased. Furthermore, the equilibrium is shifted towards H_2 by CO_2 separation. Thus, the follow-up reactions towards secondary and tertiary tars are reduced, which generally take place mainly at increased temperatures (> 700°C).

At temperatures below 700°C (typical range for AER gasification), secondary tars (i.e. Phenol) appear to remain stable. Once Phenol is formed, it remains in the product gas. Therefore, the raw product gas of an AER gasifier contains comparable high amounts of secondary tars like Phenol, Toluene. The high catalytic function of calcite for reforming of primary tars at temperatures around 650°C leads to low tar content of AER product gas.

Conclusion

To reduce the tar content, it is important to use a CO_2 sorbent bed material (in oxide form), which shows catalytic activity towards tar removal (e.g., according to screening test at UOC). The effect of the temperature must be distinguished as follows: The higher the temperature, the faster is the decomposition of the tar compounds. However, the temperature should not be that high, as the formation of secondary and especially of tertiary tars is favoured at higher temperatures (> 700°C) and because these tar compounds are much more stable and therefore, they remain in the product gas. This conclusion is confirmed by the tar analysis, carried out at e.g. by USTUTT (see next section).

Concluding, decomposition of gaseous products (like primary tars) is improved at comparable low temperatures (<700°C) and increased residence times and the presence of a catalytically active CaO based bed material. Contact of the raw gas with hot CaO significantly supports the tar decomposition.

3) Tar formation / decomposition during biomass gasification (USTUTT)

Goal

AER biomass gasification experiments were carried out to investigate the effect of the gasification temperature, CO_2 sorbent bed material source, and the CaO looping rate on the tar formation. The over-all goal was to identify optimal reaction conditions to minimise the tar content of the raw product gas.

Methodology / approaches

The experiments were carried out with wood pellets and different limestones in a 20 kW dual circulating fluidised bed system at USTUTT.

A DFB gasifier facility has been built with a 12.4 m high, 7 cm diameter riser as the regenerator and a 3,5 m high, 11.4 cm diameter BFB as the gasifier, as shown in the **Fig. 3.22**. The core of the AER-Process is the *in situ* CO_2 capture with lime based bed material. The design of the facility is based on fundamental research for post combustion CO_2 capture with CaO as sorbent bed material. Therefore, the reactor design is well transferable to the AER process. Only the feeding system of biomass and steam as fluidization agent as well as the measurement technique had to be adapted. To assure the suitability of the facility previous scaled cold model testing has been performed. The BFB is used as the gasifier (1) and the riser as a regenerator (2). The lime-based bed material is transported between the gasifier to the calciner via an internal loop and loop seal, thereby allowing continuous operation of the AER-reforming process. The novelty of this rig in comparison to other DFB systems is the control of the solid looping rate between the beds by a cone valve (4). Steam and carrier - N_2 enters the BFB carbonator, while regenerated CaO flows from the double exit loop seal (3) through the cone valve (4) and enters the BFB carbonator where CO_2 is absorbed by CaO. The CaO looping rate is controlled by varying the cone valve opening and the BFB absolute pressure through a pressure control valve (5) in the range of 0-100 mbar. An equal molar flow of partially carbonated CaO to the incoming exits the gasifier through the overflow (6), enters the lower standpipe (7) and subsequently the lower loop seal (8) through

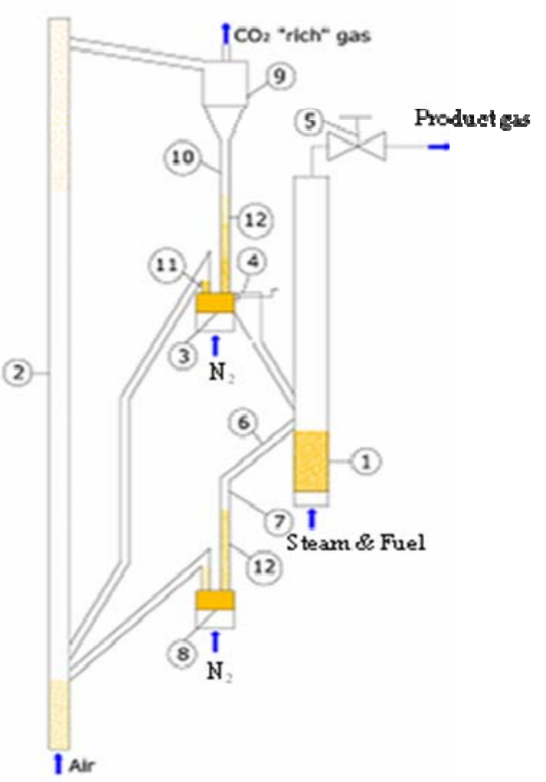


Fig. 3.22: Scheme of IVD DFB gasifier facility: (1) BFB gasifier, (2) riser regenerator, (3) double exit loop seal, (4) cone valve, (5) pressure control valve, (6) BFB overflow, (7) lower standpipe, (8) lower loop seal, (9) cyclone, (10) upper standpipe, (11) loop seal weir, (12) quartz standpipe segments

which the sorbent flow proceeds to the regenerator. The regenerator off gas proceeds to the stack while the riser entrainment is separated with a cyclone (9), proceeds to the upper standpipe (10) and reaches the double exit loop seal. The CaO looping rate proceeds to the BFB gasifier and the rest of the flow returns to the riser through the loop seal weir (11). The product gas leaves the gasifier is separated from particles via cyclone and candle filter. A by pass of the product gas is analyzed for non condensable and condensable gas components as well as tars and afterwards burnt in a after burner together with the mainstream.

The influence of different process parameters, e.g. gasifier temperature and circulating rate, on the tar concentration and tar composition during the absorption enhanced reforming of wood pellets was investigated.

Following research goals were set:

- “Reference tars” Bio-Crude-Oil (BCO) will be used to investigate the tar conversion and formation under AER conditions.
- Fundamental tar research in a DFB at standard AER conditions
- Investigation of tar cracking potential of different sorbent. Bed material: C1, C58, C60
- Influence of gasification temperature on tar formation Gasifier temperature: 600, 650, 700, 750, 800, 850°C
- Influence of circulation ratio on the tar formation
- Testing of a tar cracking catalyst under fluidized bed conditions

Main achievements

AER Gasification at 650°C with C1 Bed material

Under AER conditions at 650°C long term experiments over 7h (for C58) were conducted for the bed material C1, C58, and C60. The following diagram shows the measured product gas composition (dry basis) over the experimental time. It’s clearly shown that constant gas concentrations were reached over an experimental time of 4h. The hydrogen concentration is very constant and above 75 vol-% whereas the CO_2 and CO concentration is clearly lower than 10 vol-%. Therefore, the bed activity was very high during the whole experimental. Furthermore, the gravimetric tar concentration is shown as a red line. The gravimetric tar concentration is averaged to 4,5 $g/kg_{Fuel,Daf.}$

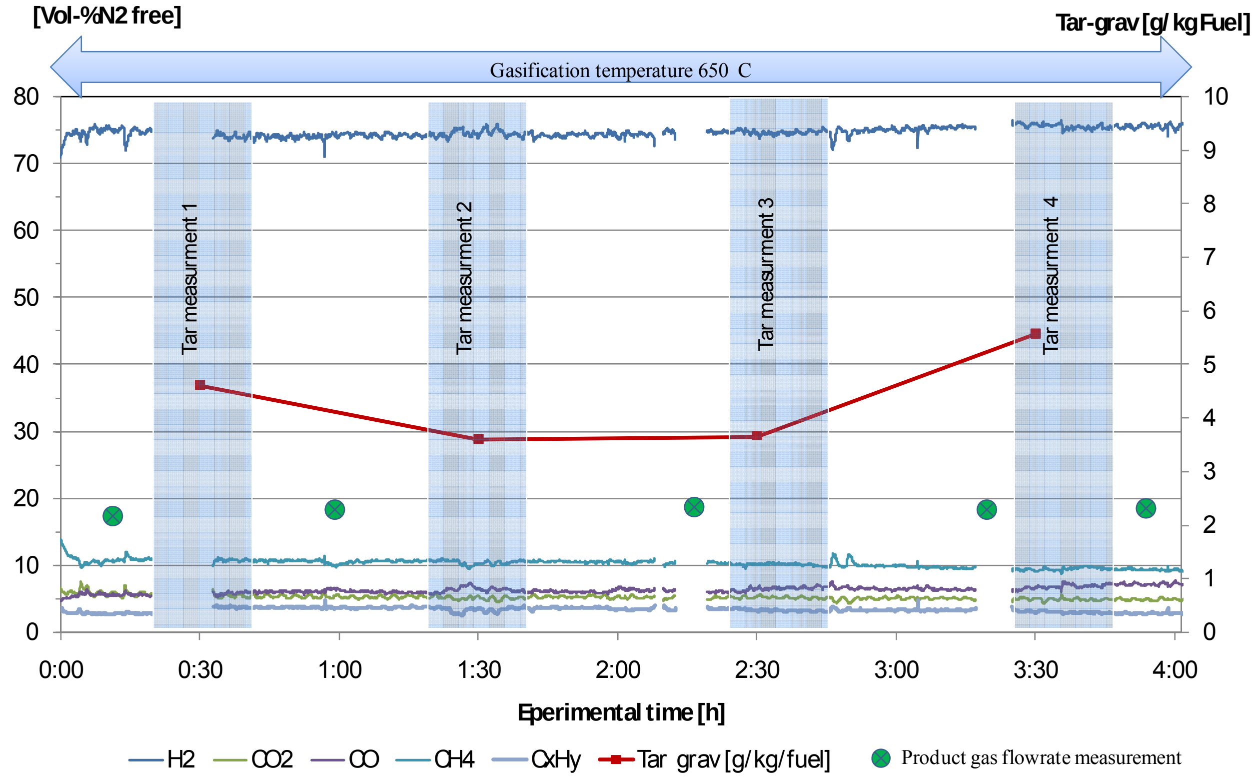


Fig. 3.23: Results for the gas composition and gravimetric tar concentration for the long term experiments with C1 as bed material

The next table summarizes the results for the gas composition and grav. tar concentration for bed material C1, C58, and C60.

Tab. 3.2: Product gas quality for wood gasification using limestones C1, C58, and C60 as bed material

Bed material			**C1**	**C58**	**C60**
Experimental time			4 h	7 h	4 h
Non-condensable gases	H2	[vol-%]	74,9	73,1	75,4
	CO2	[vol-%]	5,2	5,5	5,3
	CO	[vol-%]	6,3	6,8	5,8
	CH4	[vol-%]	10,2	11,1	10,8
	CxHy	[vol-%]	3,4	3,5	2,7
	Tar Grav	[g/kgFuel]	4,4	19,9	13,0

The CO_2 absorption and the hydrogen concentration is very high for all tested limestones over the investigated period. The product gas composition is not influenced by the limestone source used. However, there are significant differences in the gravimetric tar concentration. The Greek limestone C1 results in low tar concentrations, while the tar content was highest in case of limestone C58.

The influence of the gasification temperature

The following diagram presents the product gas composition with respect to the gasification temperature. Experiments with temperature variation were conducted for all three limestones. It is clearly shown that the gas composition is not influenced by the limestone. All measurement points in this chart correspond to averages from at least 1 hour steady state conditions. For 650°C the average values corresponds to at least 4 hours. The transient of the product gas composition is according to equilibrium considerations: With increasing temperature the hydrogen concentration decreases and the CO_2 and CO content increase because less CO_2 is separated from the raw gas.

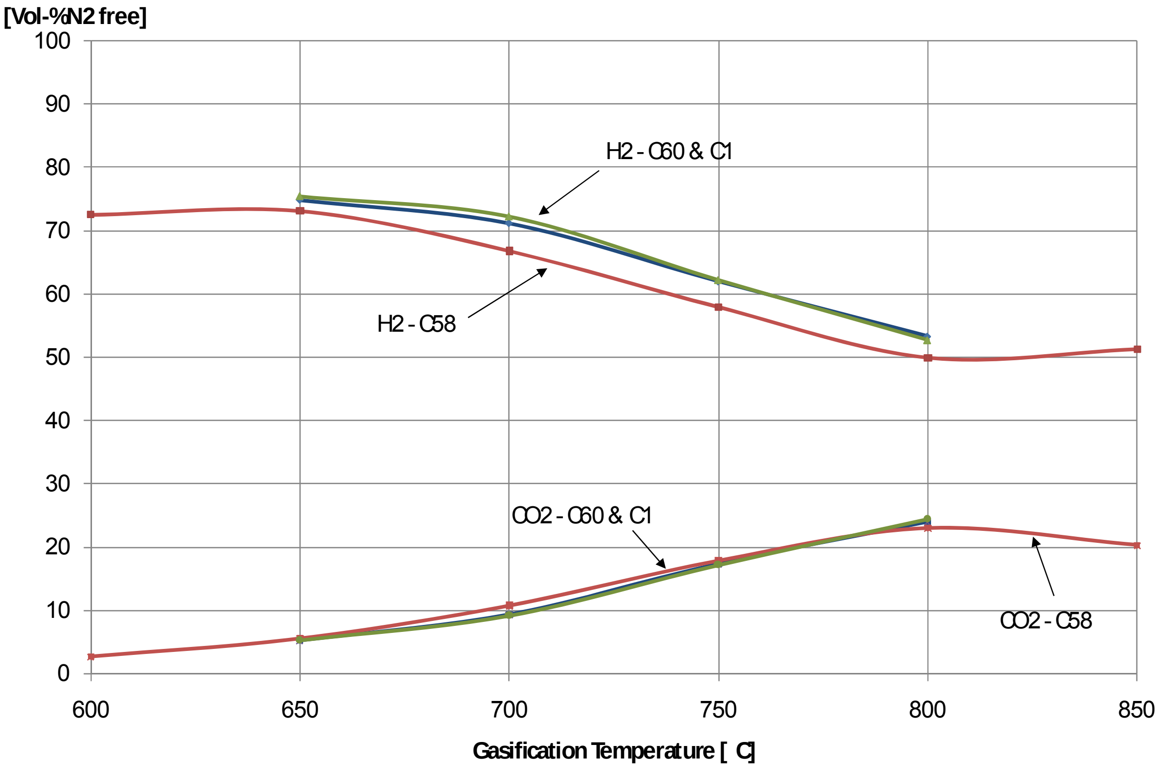


Fig. 3.24: Gas composition with respect to the gasification temperature for 3 different bed materials

In the following diagram the gravimetric tar concentration with respect to the gasification temperature is shown for all three limestones.

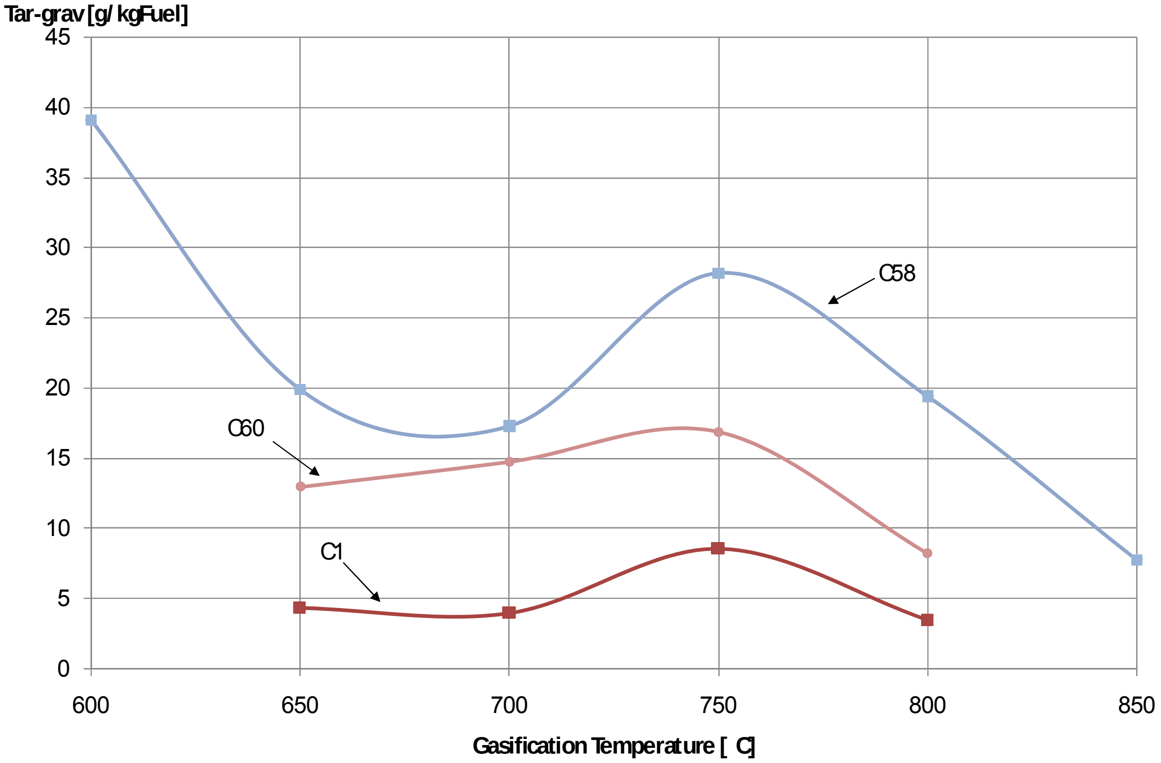


Fig. 3.25: Grav tar concentration with respect to the gasification temperature for 3 different bed materials.

The gravimetric tar concentration reaches a local minimum at 650-700°C over the tested temperature range of 600-850 °C. This tendency was observed for all investigated limestones.

In the temperature range of 650-700°C, the same tar concentrations were obtained as those measured at 800°C. Since CO absorption only occurs in a significant degree at temperatures below 700°C, it seems that the CO_2 absorption has a positive influence on the decomposition of tar species. Furthermore, it’s clearly shown that limestone C1 has the best tar catalytic cracking property for all tested bed materials over the investigated temperature range.

The GC-MS tars are shown in the following figure. It is clearly visible that with increasing temperature the fraction of phenol is decreasing whereas the fraction of tertiary tars (in particular, naphthalene and indene) is increasing. The concentration of toluene is more or less independent on the gasification temperature.

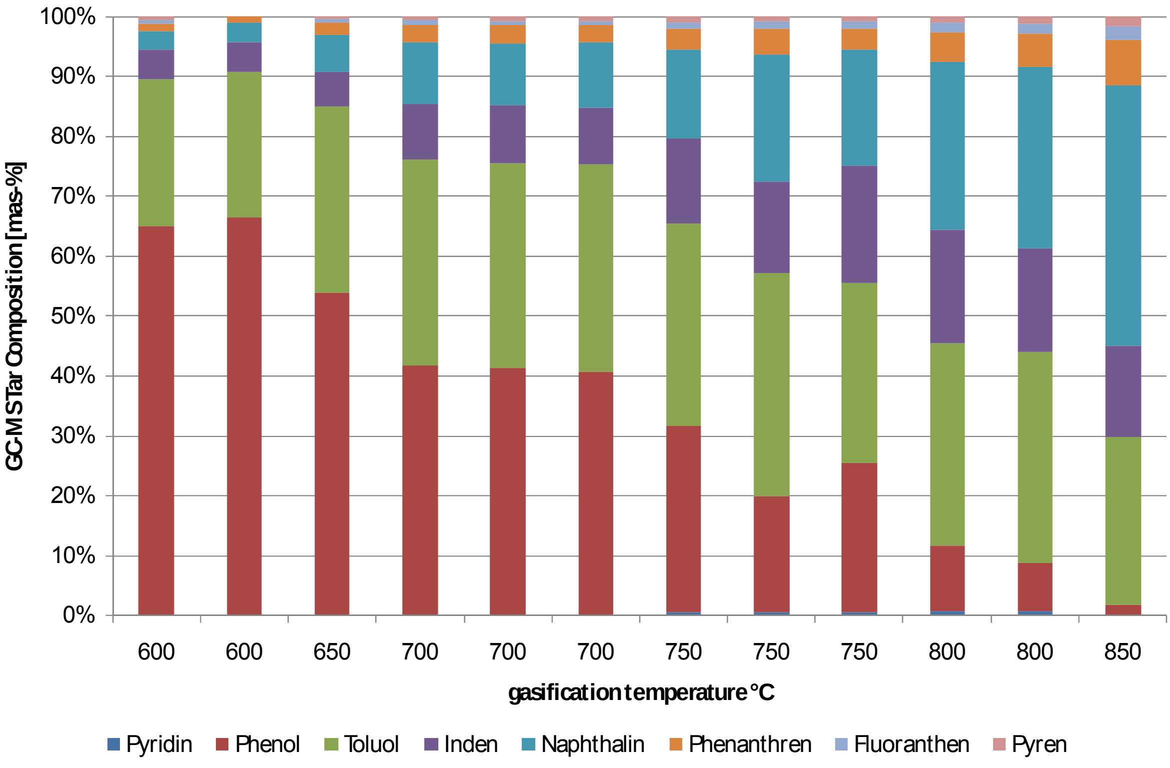


Fig. 3.26: Tar composition of the GC-MS tars over the gasification temperature for sorbent bed material C58.

Conclusion

Different CO_2 sorbent bed materials were used in DFB gasification experiments at USTUTT. While the composition of the product gas remains approximately the same, the tar formation is highly influenced by the bed material used. Concluding, there are clear differences in the catalytic activity of CO_2 sorbents, which were found in both, micro-fixed bed experiments (UOC) as well as DFB gasification runs (USTUTT).

The temperature variation has shown, that the composition of the main gas components (H_2, CO, CO_2) is as expected from thermodynamic equilibrium considerations. The maximum H_2 content (75vol.%) is obtained at 650°C. Regarding tar formation, there is a clear minimum at AER temperatures of 650 – 700°C, which reaches the tar concentrations of standard gasification at 800°C. With increasing gasification temperature, the composition of tars changes. While at 650 – 700°C, mainly Phenol and Toluene were found, the amount of tertiary tar compounds increase at higher gasification temperatures. Concluding, the highest product gas quality is obtained at temperatures of 650 – 700°C.

3.3 WP 3: Multi feedstock and gas quality assessment

(TUV, USTUTT)

Introduction / Motivation and goals

Biomass steam gasification allows the conversion of solid biomass to a medium calorific gas (12 – 14 MJ/Nm³) consisting mainly of H_2, CO, CO_2, CH_4 and H_2O (see **Tab. 3.3**). The gas may either be used for electricity production (turbines, engines, fuel cells), or it may be used as renewable source for chemical synthesis (liquid hydrocarbon fuels, pure hydrogen synthetic natural gas, etc.). The dual fluidized bed steam gasification technology, developed at Vienna University of Technology, provides the heat for the gasification reactor by circulating bed material. For conventional gasification with this dual fluidized bed steam gasification system, Olivine, a natural mineral, is used as bed material. This material has proven to be a suitable bed material showing enough resistance to attrition and moderate tar cracking activity during gasification. 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 (4 – 8 g/Nm³db of so called tars, heavier than toluene), low N_2 (<1 vol%db), and high H_2 contents of 35 – 40 vol%db.

The further development of this technology, the AER gasification, requires relatively low gasification temperatures. In order to achieve these conditions a reduction of the bed material circulation rate is necessary. The low circulation rate is obtained by increased particle size of the bed material and reduced primary fluidization in the combustion zone. The primary fluidization can be varied by adopting air staging.

The difference of the measured producer gas between the conventional dual fluidized bed steam gasification and the AER process is shown in **Tab. 3.3**. It should be mentioned that the hydrogen fractions strongly depend on the circulation rate and the CO_2-capturing rate of the bed material, the gasification temperature and the steam/fuel ratio. The influence of the selective CO_2 removal and the shift-equilibrium on the H_2, CO, CO_2 concentrations in the gasification zone is significant. The hydrocarbon concentrations remain largely in the same range despite changes in the reaction conditions.

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

[a] 8MW_{th} demonstration plant in Güssing, Austria according to Pröll et. al., 2005

[b] 100kW_{th} process development unit at the Vienna University of Technology, Austria

Table 3.3: Typical producer gas range for standard as well as AER gasification

Fuel prices are significantly rising over the years. Thus, it will be of big importance in the future to use low cost fuels such as forestry or agricultural residues with high water contents resp. high alkali contents. Therefore, this WP3 aims on the one hand to improve the know how about AER gasification in general and on the other hand gather information about the usage of alternative fuels to wood chips from forestry.

1) AER gasification (TUV)

Methodology / approaches

Experimental

Fig. 3.27 shows the principle of the dual fluidized bed steam gasification process whereas **Fig. 3.28** shows the simplified flow sheet of the pilot plant. 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 is used for heating up the bed material and is designed as highly expanded fluidized bed (riser). Air is used as fluidization agent in the riser. 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. 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 in the DFB reactor.

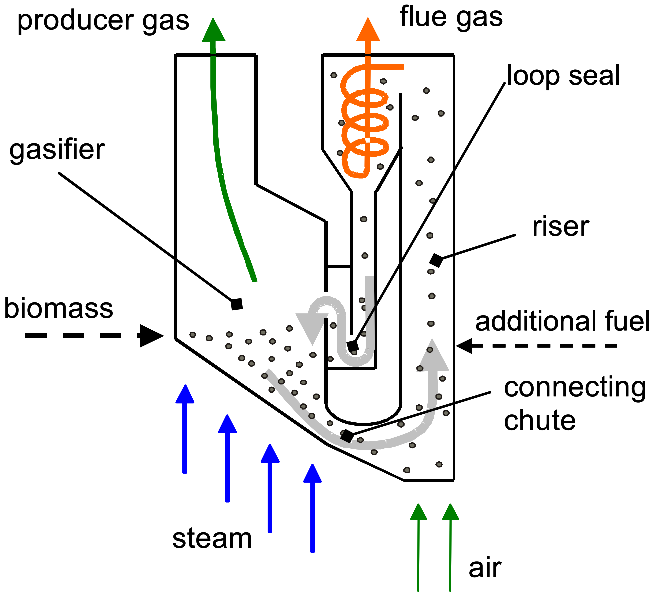


Figure 3.27: Principle of the dual fluidized bed steam gasification process

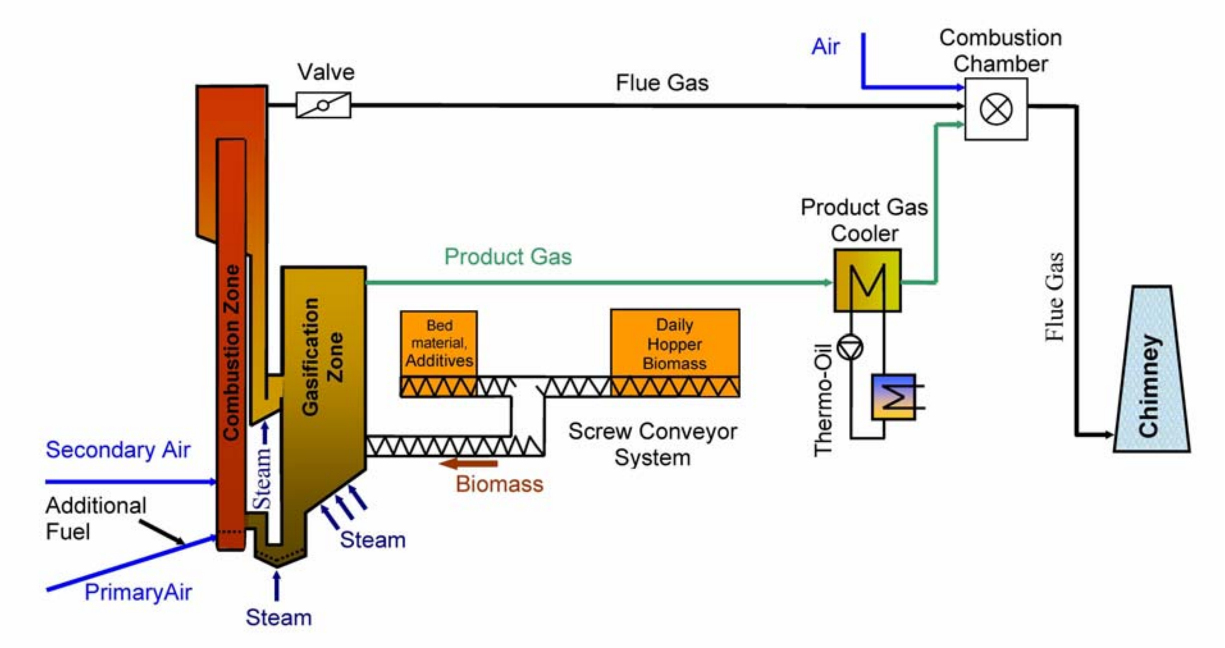


Figure 3.28: Simplified flow sheet of the 100 kW_{th} process development unit at the Vienna University of Technology (TUV)

Analytics

Gas measurements

Determination of CO, CO_2 and CH_4 (0-100 %) is performed with infrared absorption. Oxygen (0-25 %) is measured with a paramagnetic cell and hydrogen (0-100 %) with a thermal conductivity sensor. Furthermore, NO_x (also with speciation of NO and NO_2) can be measured by infrared absorption (0-2500 ppm).

Tar measurements

Gas is sampled isokinetically from the product gas stream via a probe. Particulate matter is separated using a cyclone and a thimble stuffed with quartz wool. To avoid condensation and thereby loss of analyte in the sampling line the sampling line including the solids removal apparatus is heated. Gas is pumped through gas washing bottles where it is scrubbed by a solvent. The solvent is kept at a temperature of -10° C. The gas pump also contains a volume meter and a thermometer to allow later for normalization of the values. The main difference from CEN/TS 15439 is the use of toluene as a solvent, this allows the easy measurement of the water content in the producer gas.

After the sampling is completed, the solids from the cyclone and the thimble are dried and weighed and are extracted with isopropanol under reflux. The residue is dried and weighed again thus yielding the values for total particulate matter. The residue gets burned in a muffle furnace, the mass of the ashes is weighed as the amount of dust, the mass difference equals the amount of entrained coke.

The liquid phases are poured together, water is being separated and metered volumetrically yielding the water content in the gas. A sample of the toluene phase and the isopropanol phase (from the extraction) is taken for GC/MS analysis. The solvent is removed from both phases by evaporation in a rotary evaporator und storage in a drying oven. The residue is weighed and yields the amount of gravimetric tar.

For the measurement of the GC/MS-detectable tar an internal standard (tetrahydronaphthalene) is added to the samples. The samples get analyzed by a PerkinElmer Autosystem XL GC with PerkinElmer Turbomass mass spectrometer. All GC/MS measurements are performed in triplicate.

Ion Chromatography

The following ions can be determined from aqueous samples using ion chromatography:

Anions: Fluoride, Chloride, Nitrite, Nitrate, Sulphate

Cations: Sodium, Ammonium, Potassium, Magnesium, Calcium

Ammonia

Gas is sampled analog to tar maesurements using washing bottles. The solvent used in this procedure is diluted sulfuric acid at a temperature about 2° C.

The amount of ammonium in this solution is analysed via ion chromatography. Hence the Ammonia concentration in the gas phase can be calculated.

Hydrogen sulphide

Gas is sampled again using washing bottles. The absorption liquid is aqueous potassium hydroxid solution at a temperature of about 2° C.

Subsequent analysis steps are based on the standard ISO 6326-3 “Natural gas -- Determination of sulfur compounds Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry”.

a) Wood gasification (different bed materials)

Several different bed materials (more than proposed in the Description of Work) were tested under different conditions during the project. To compare the different bed material behaviours in terms of their suitability for the gasification process, it is necessary to determine the boundary conditions. For the test runs, a gasification temperature of 660 °C and a low solid circulation rate of approximately Gs = 10...20 kg/m^2s for the bed material were adjusted). Wood chips were used with a water content of approximately 9.5 wt.%.The feed rate of biomass was held constant at 15 kg/h(wf) (LHV...18.5 MJ/kg). The temperature in the combustion zone depending on the heat demand in the gasification zone ranged between 800 and 860 °C.

Fig. 3.29 shows the average composition of the product gas (main components) dependent on the bed material used during the gasification process. Although the conditions of the two reactors are fixed and the bed materials consist mainly of CaO before the stable AER phase begins, clear differences in the bed materials used are observed. It is obvious that the chemical reactions occurring during gasification vary from one bed material to another. H_2 concentration (59...71 vol.-%db) and CO_2 concentration (5...20 vol.-%db) in the product gas greatly differ, whereas CO and CH_4 contents are lower (CO: 5...10 vol.-%db, CH_4: 8...13 vol.-%db). The confidence belts for all gas components are shown as error bars. Besides these four main components, representing about 95 % of the whole dry product gas stream, other gas components are present during gasification. Arranged according to their values, there are nitrogen (~2 vol.-%db), ethene (C_2H_4 ~1.8 vol.-%db), ethane C_2H_6 ~ 0.6 vol.-%db) and hydrocarbons (C3 fraction and larger < 0.6 vol.-%db). As to the measured nitrogen values, it should be mentioned that roughly half of the nitrogen amount is introduced into the reactor system via the feeding system where nitrogen is used as sealing gas.

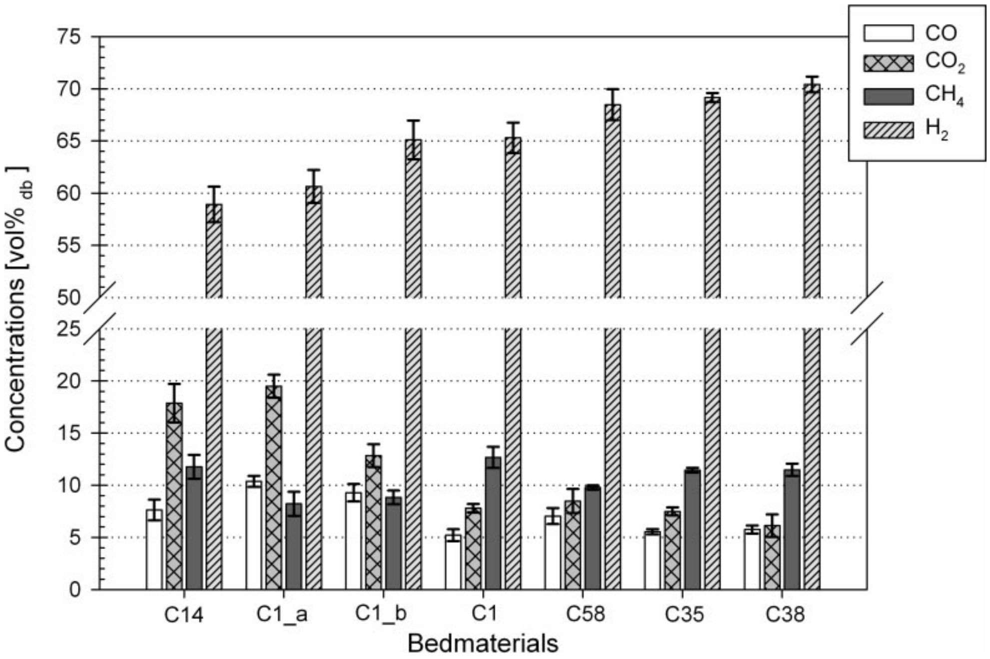


Figure 3.29: Product gas composition during gasification operation – wood chips as feed

The bed materials with their corresponding product gas compositions are sorted according to their hydrogen value. In **Fig. 3.30** and **Fig. 3.31**, the sequence of the bed materials was kept unchanged to allow direct comparison of their characteristics.

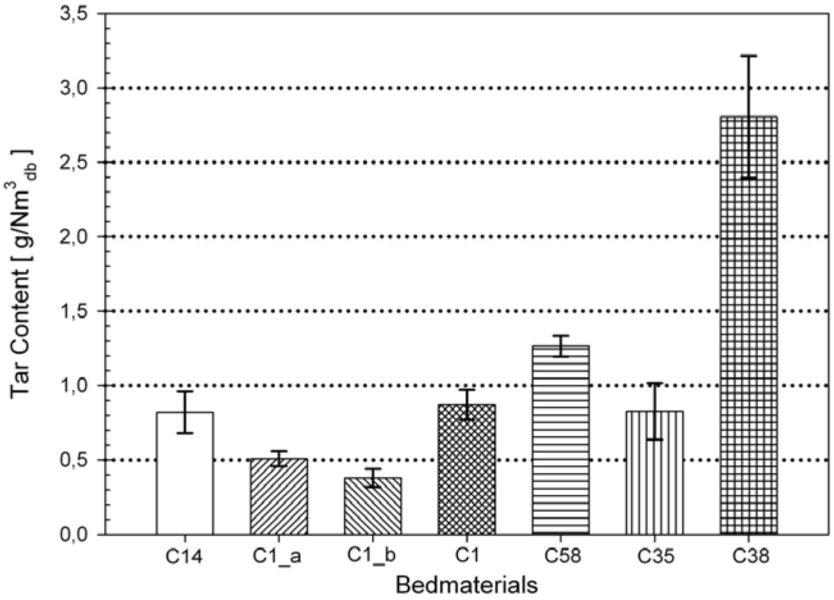


Figure 3.30: Tar content during gasification operation – wood chips as feed

Considering the gravimetric tar content in the raw product gas stream, most of the values were around or below 1 g/Nm³db. Only the gravimetric tar content measured when using C38 showed values definitely above the average tar content found during all test runs under AER conditions. The reason may be the different molecular composition of this bed material, but this is still under investigation. Considering the dust content in the raw product gas stream, the values differ between 10 and 40 g/Nm³db.

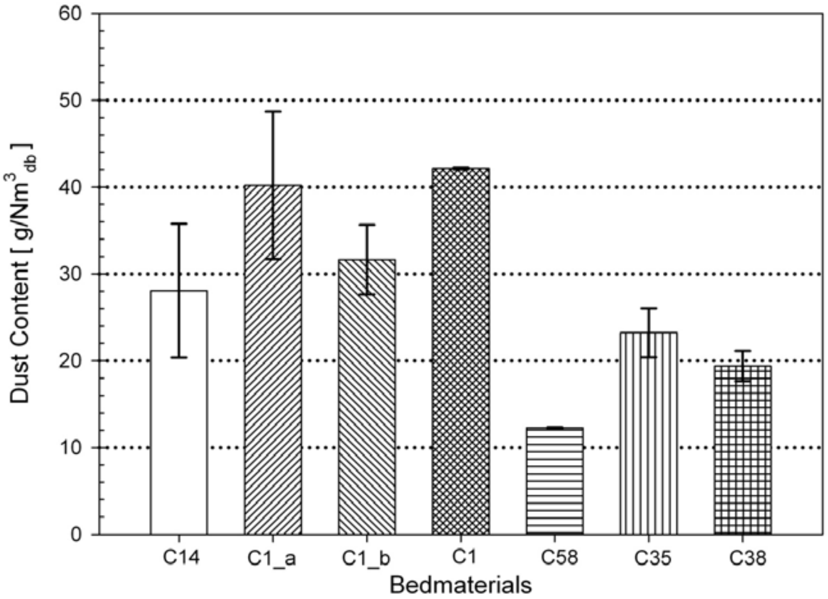


Figure 3.31: Dust content during gasification operation – wood chips as feed

To give a suggestion as to the bed material which should be used for a commercial biomass CHP plant operated as dual fluidized bed gasifier under AER conditions, it is necessary to compare the overall performance of each bed material tested. One possibility is to compare the influence of the tested bed materials on four different characteristics required for power plant operation:

– hydrogen concentration of the product gas,

– tar content in the raw product gas stream,

– dust content in the raw product gas stream,

– lower heating value of the product gas.

Of course, there are many other characteristics essential for power plant operation: bed material attrition, bed material loss, bed material costs, efficiency, etc., but here measurements focused on the characteristics mentioned above.**Fig. 3.32** shows seven different bed materials and their characteristics. The values are scaled in different ways:

– for hydrogen: 1 equals 100 %, whereas 0 equals 0 %,

– for tar: 1 equals 0 g/Nm³db, whereas 0 equals 3 g/Nm³db,

– for dust: 1 equals 0 g/Nm³db, whereas 0 equals 50 g/Nm³db,

– for lower heating value: 1 equals 15 MJ/Nm³, whereas 0 equals 0 MJ/Nm³.

According to this comparison, the best choice is bed material C35. Although it is not the best material in each category, it performs best overall if the above characteristics are the criteria for bed material selection. With C35 an average hydrogen content of 69 vol.-%db can be obtained, whereas the low gravimetric tar (0.8 g/Nm³db) and low dust (23 g/Nm³db) contents (indicating good attrition resistance) are very good. Due to the product gas composition shown in **Fig. 3.29**, a lower heating value of 14.5 MJ/Nm³ can be reached. This comparison is limited to values measured during the test runs performed and does not include other aspects (economic interests, etc.).

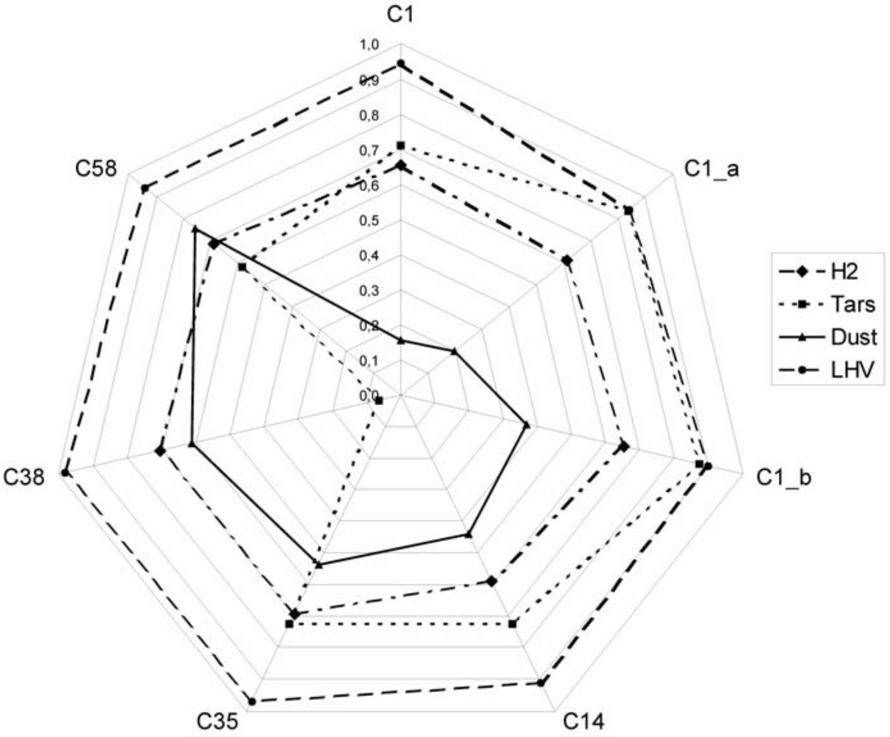


Figure 3.32: Bed materials – comparison of hydrogen, gravimetric tars, dust and lower heating value

b) Straw gasification

AER gasification tests with straw pellets as alkali-rich fuel (characterised by a low ash melting point) were done in summer 2007. The tests show that an AER-process with straw as biomass is possible. In these experiments a stable process could be achieved and a useable product gas had been produced (see **Fig. 3.33**). The hydrogen content had been lower compared with wood pellets. But the hydrocarbon content and consequentially the tar content had been higher. The dust content had been higher compared with wood because of the higher ash content (about 6 mass%$_{db}$) of straw pellets. Further tests are necessary to verify the results from these experiments.

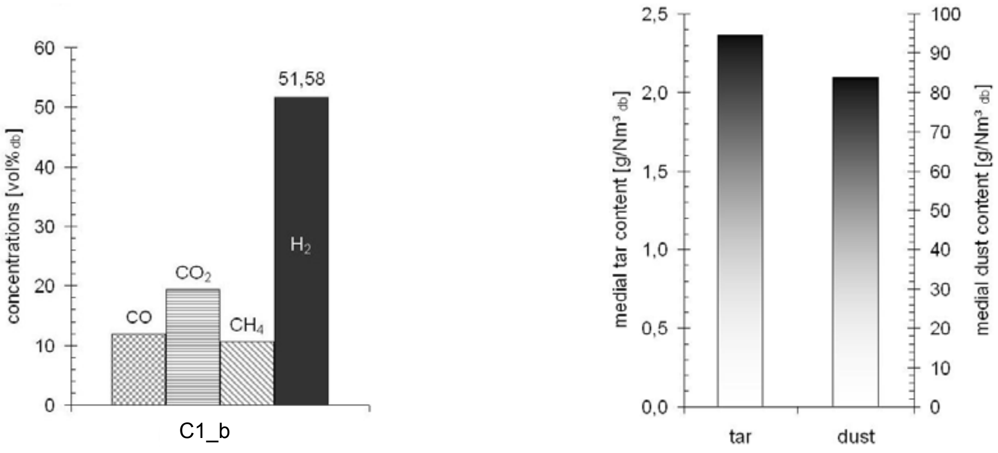


Fig. 3.33: Medial conditions during the stable phase - C1_b as CO_2 bed material - straw pellets as feed

The ash melting point of the straw pellets was measured as 720°C (beginning of sintering). Mixtures with different bed materials and additives showed that by using a Ca-containing bed material (additive), the ash melting temperature can be increased significantly. However, the first tests showed ash melting at the air inlet in the combustion zone of the gasifier. Therefore, additional tests are necessary to have more experience with the handling of the reactor when straw is used as biomass to achieve maybe higher hydrogen contents.

b) Influence of the fuel water content on the gasification process under AER conditions

Besides the influence of different bed material sources on the gasification performance, TUV focused on the effect of the water content of the fuel. For all experiments in this test period there are fixed main test parameters, in particular the gasification conditions. The gasification temperature (G3) is 660°C, the temperature in the combustion zone (C3) is between 800 and 850°C to ensure that desorption of CO_2 can take place. The mass flow of biomass is 15 kg/h dry substance. The amount of bed material filled in is 100kg $CaCO_3$ to provide the necessary height of the fluidised bed. As bed material C1-a was used. Due to the fact that woody biomass is not homogeneous only an average characterisation of the used wood chips can be given. Characteristics of these wood chips are listed in **Tab. 3.4**.

Table 3.4: Characteristics of the used wood chips

		Dry substance
Water content	[m%]	---
Ash content	[m%]	1,00
Carbon	[m%]	48,82
Hydrogen	[m%]	5,87
Nitrogen	[m%]	0,15
Upper heating value	[MJ/kg]	19.468
Lower heating value	[MJ/kg]	18.178

Gas composition

In **Fig. 3.34** the average composition of the product gas (main components) in dependency on the water content during the gasification process is pictured. Although we have expected a different product gas composition due to different water contents of the wood chips a significant trend is not observable.

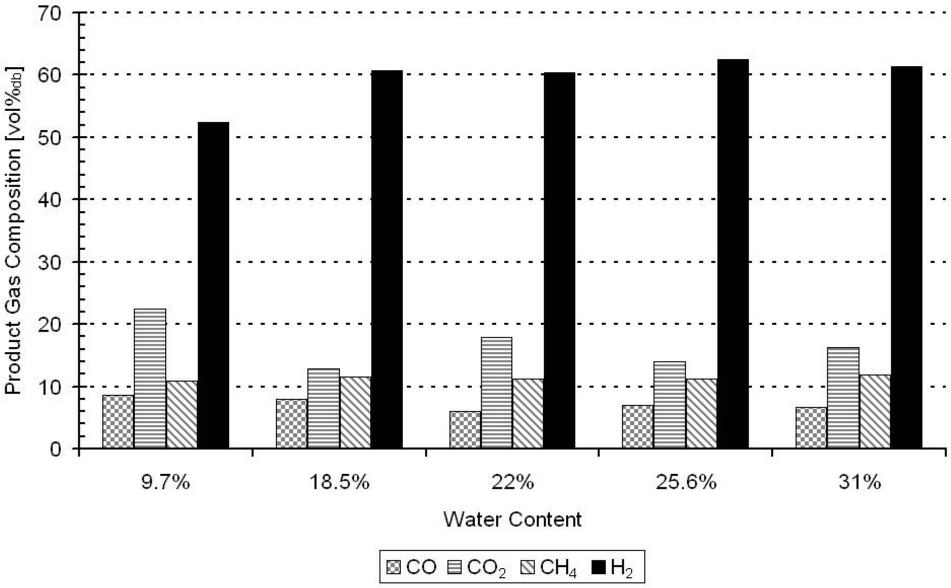


Figure 3.34: Product gas composition during gasification under AER conditions with various fuel water content, bed material C1_a

Obviously the difference of the water amount in the gasification zone does not effect the chemical gasification reactions. The water amount is mainly determined by the introduced steam for fluidization and the additional steam brought in via the biomass feed. The slight fluctuations in the product composition may also come due to the fact that woody biomass is not homogeneous. Only by the test run with 9.7% water content a reduced H_2 and a raised CO_2 amount is visible. Except the before mentioned test run the differences between the measured main components CO, CO_2, CH_4 and H_2 are in small ranges. The hydrogen content ranges between 60 and 63 vol%db. Also the CO - (6 - 8 vol%db) and the methane - amount (11 – 12 vol%db) are very good predictable if wood chips are used in combination with the AER - process. Only for CO2 the difference between highest and lowest level (13 - 18vol%db) is slightly higher compared with the other main components.

Tar composition

Tars in the product gas stream are very problematic for down stream devices due to fouling and deposits which can cause blockages and other problems (e.g. reduced heat transfer in heat exchangers). To avoid these problems it is always nesessary to separate tars from the product gas stream for instance with a scrubber. Therefore it is always a benefit if you are able to reduce the appearance of tars in the raw product gas stream to support this separation step. Normally during "conventional gasification" with Olivine as bed material, tar contents of 4 – 8 g/Nm^3 are common in our process development unit. By using the AER - concept tar amounts lower than 1 g/Nm^{3}db are achievable. As a very interesting result a different tar amount with different biomass water content occurred (see **Fig. 3.35**). It is clearly to see that a lower biomass water content causes a higher tar amount in the raw product gas stream. To investigate the behaviour of tar reduction dependency on the water content of the biomass further experiments are necessary in future work.

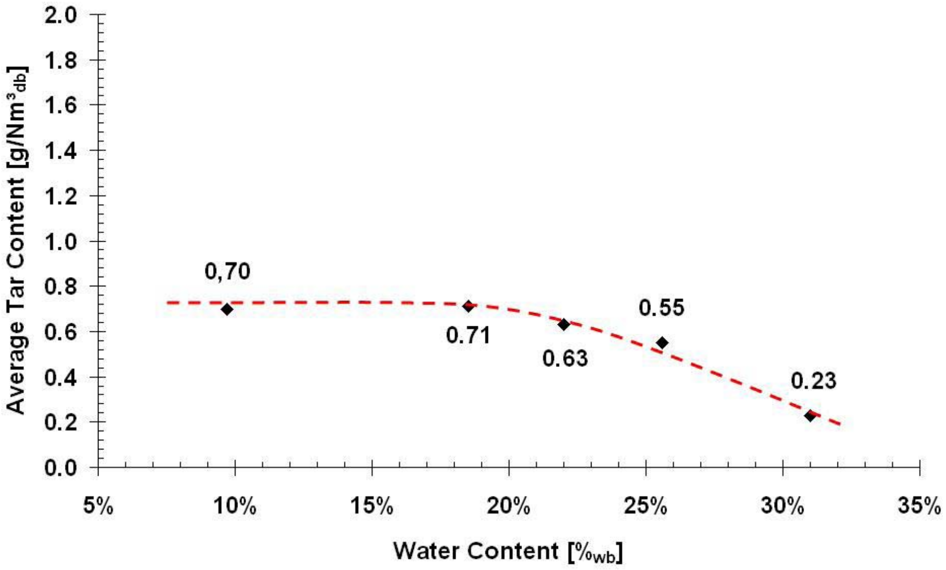


Figure 3.35: Average product gas tar content vs. water content of the wood chips

Dust composition

Dust is a permanent companion of any energy converting system of solid fuels. During this project work we observe dust contents in the raw product gas in a range between 20 and 50 g/Nm³ (see **Fig. 3.36**). These values are higher compared with "conventional gasification". This is due to the fact that the mechanical stability of $CaO/CaCO_3$ is lower compared with Olivine. But in fact the hardness is good enough to ensure long term runs only with a moderate bed material loss. We found no dependency between biomass water content and the dust content in the raw product gas.

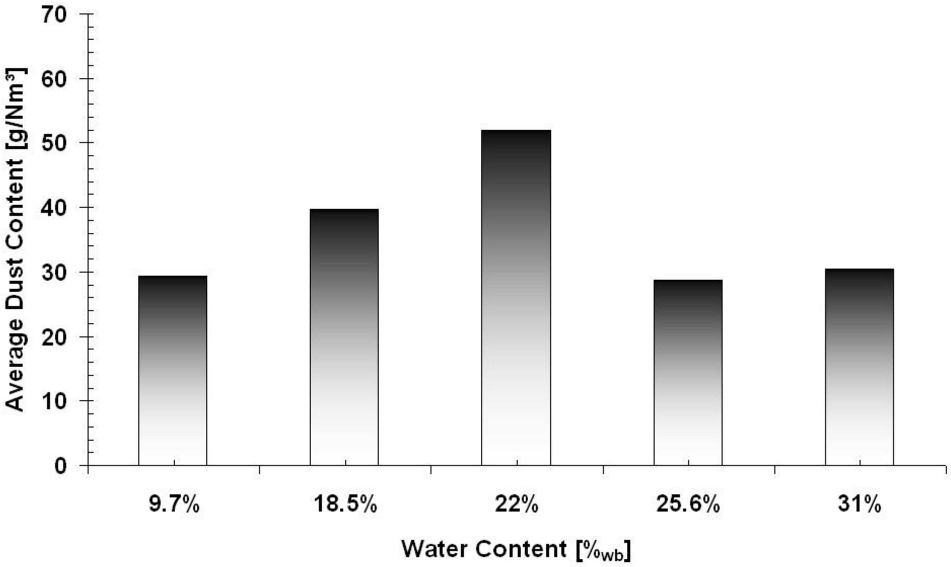


Figure3.36: Average product gas dust content vs. water content of the wood chips

Conclusion (TUV)

The AER concept is a very promising system for converting primary fuel energy into a hydrogen-rich gas that can be used for many downstream devices (e.g., combined heat and power production, Fischer-Tropsch synthesis, fuel cells). The main advantage of this system is its flexibility, meaning that a power plant based on the AER process is instantly adaptable to the demand in the energy market.

The AER process delivers a producer gas with hydrogen contents up to 75 vol% depending mainly on the gasification temperature and the solid circulation rate. Despite the low gasification temperature (650-700°C), all experiments showed that the tar levels are significantly lower than for standard gasification with Olivine as bed material at gasification temperatures of 850 °C. No problems occurred during the test series with different fuel water contents as well as during the test with high alkali containing fuels. Thus, it can be stated that the Absorption Enhanced Reforming gasification process is ready for commercial operation. The relation to the state-of-the-art is explained in detail in the description of results of WP´s 4 and 5.

The main impact on the research and industry sector is supposed to be the so called second generation fuels (Fischer-Tropsch diesel, Bio SNG etc.) due to the fact that with the developed technology a hydrogen/carbon monoxide ratio can be adjusted as needed for the synthesis step.

2) AER gasification of alkali-rich biomass sources (USTUTT)

Methodology / approaches

A) Equilibrium modelling

FactSage™ simulations are presented that were used to obtain phase equilibrium information about the alkali behaviour in the DFB gasification system.

In the first step, the gasification process was simulated for different realistic operating conditions between 600°C – 700°C with different bed materials. Therefore, in addition to CaO, sand was used as an inert bed material for the gasification process. The simulation results of the gasification process show the equilibrium composition of the gas phase and the solid phase. The calculated solid phase composition at 650°C, which is the ordinary AER gasification temperature, was used as the input for the combustion process. The next figure shows schematically the simulation steps.

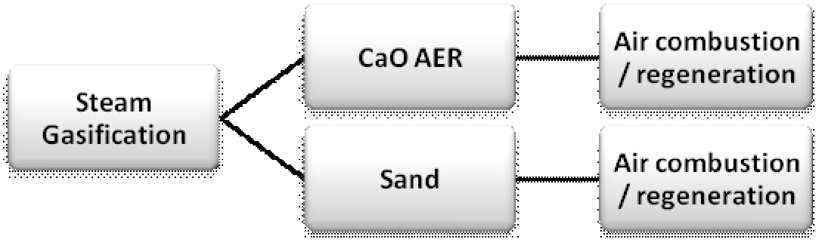


Figure 3.37: Schematic of the simulation

To simulate the char in the combustion zone, which is produced during the gasification step, an additional amount of carbon was included in the input species. Therefore 20%$_{mol}$ of the fuel carbon input for the gasification was estimated as unburned carbon which will be transported from the gasifier to the regenerator. The steam gasification was calculated with a molar stochiometric steam-to-carbon ratio, s/c =1 in a temperature range between 600°C-750°C. As fuel input, literature data of wheat straw with a relatively high alkali content in the ash phase, was used. The combustion where the regeneration of the carbonated CaO takes place, was simulated in a temperature range between 800°C – 900°C with under stochiometric conditions (λ =1.0). The following table shows the proximate analysis of the fuel und bed material.

Table 3.5: Fuel and bed data for thermodynamic simulation

Fuel **Wheat Straw**	**Fixed Carbon**	**Volatile Matter**	**H_2O**	**Ash**	**Alkalis in ash (K_2O Na_2O)**
[mass%]	16.5	70.0	7.1	6.5	27.3

Bed material	**CaO**	**MgO**	**$CaCO_3$**	**SiO_2**
Calcit [mass%]	94	1	2	3
Sand [mass%]	-	-	-	100

Main achievements

The thermodynamic investigation of the alkali behaviour during steam gasification shows:

- The alkali concentration in the gas phase increases with increasing gasification temperature for both CaO and sand
- There is no influence of the bed material on the alkali distribution at 650°C
- At 650°C , 98 mol-% of the alkalis remain in the solid phase. Thus, they are transported into the regenerator

The thermodynamic calculations for the combustion /regeneration shows:

- The alkali concentration in the gas phase increases with increasing combustion temperature for both CaO and sand
- With sand as bed material, significantly more alkalis remain in the solid phase compared to when CaO is the bed material. Therefore, during the continuous steam gasification process with sand, more alkalis will accumulate in the system than for the AER process.

B) AER gasification of alkali-rich biomass

The behaviour of alkalis were investigated not only theoretically (thermodynamics), but also experimentally by AER gasification of mineral-rich biomass in batch mode. As alkali enriched feedstock, wheat straw was used with a potassium content of 6000mg/kg. The sodium content is very low; therefore the main alkali component is potassium. The CaO bed material was freshly calcined before starting gasification experiment.

Main achievements

The measured gas composition of the raw product gas (dry basis) is shown in the next diagram for both bed materials, CaO and sand. Also using straw as fuel, the product gas quality is significantly higher in case of AER gasification.

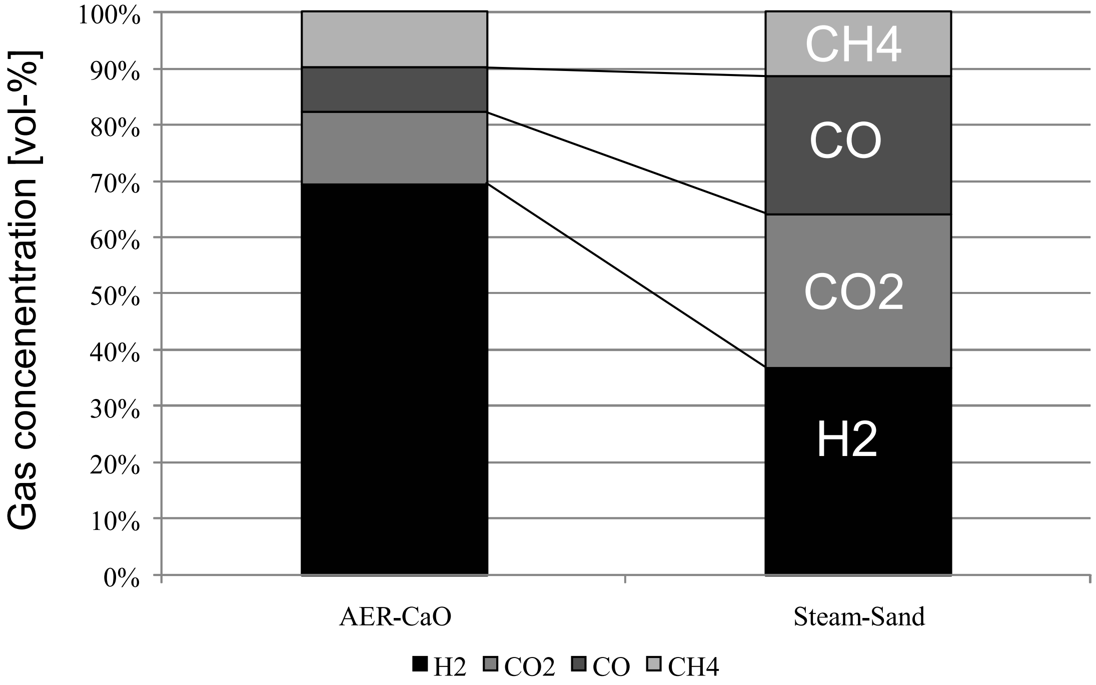


Fig. 3.38: Measured product gas composition during wheat straw gasification at 650°C using CaO (AER) and sand as bed material.

Agglomeration occurred not in the gasification, but in the combustion step. The flue gas was slightly enriched in potassium in case of the CaO-based bed material.

Summary and conclusion

Thermodynamic considerations could be confirmed by experimental investigations. Under AER conditions, alkalis leave the system via the flue gas. The main results in detail:

Thermodynamic simulation of the alkali behavior during gasification and the subsequent combustion/regeneration of the bed material produced:

- During gasification and combustion/regeneration more alkalis are released into the gas phase with increasing temperature.

- During AER gasification at 650°C, 98mol-% of the alkalis remain in the solid phase.
- There is no difference between sand and CaO with respect to the alkali gas concentration at 650°C during gasification.
- During combustion, 45mol-% of the alkalis are released to the gas phase when CaO is used as bed material, twice the amount released during the combustion with sand as the bed material.

The main results of the performed experiments were:

- During combustion, significantly more alkalis are released in the gas phase when CaO is used as bed material, than compared with sand.
- More and softer agglomerates were created when sand is used as the bed material during gasification and subsequently combusted than compared to when CaO is used as the bed material.

3) AER gasification of S-rich biomass sources (USTUTT)

Methodology / approaches

To investigate the sulphur behaviour, rapeseed was used with a high amount of sulphur. The experiments where conducted in a DFB at USTUTT. The gasification temperature was set to standard AER conditions at 650°C. The experiments were conducted with freshly calcined bed material. Limestones C1 was used as bed material. The goal of the experiments was to measure the sulphur concentration in the product gas of the gasifier and in the regenerator. For the investigation of the sulphur behaviour in the calciner, it was expected that sulphur is just as SO_2 stable in the gas phase. Therefore, an infrared photometer from ABB was installed in the flue gas line of the calciner. This measurement technique works continuously within a measurement range from 1 to 1000 ppm. The analyzer was calibrated with test gas (750ppm). To get detail information about the sulphur behaviour, thermodynamic simulations were done related to the experiments.

Main achievements

The experimental investigation results in:

The hydrogen content was stable about 2 hours and constant around 75 $vol\%_{dbN2free}$. The CO_2 and CO content was below 7 $vol\%_{dbN2free}$ while methane was over 12 $vol\%_{dbN2free.}$ Compared to the wood gasification experiments, the content of the non condensable hydrocarbons are higher (about 5 $vol\%_{dbN2free}$) as well as the methane content. Nevertheless, the results for the gas composition of the main gas components shows that very high hydrogen concentration can be achieved with the AER-process also in case of a problematic feedstock like rapeseed. Under normal conditions, no SO_2 was measured. This means that the transported sulphur from the gasifier is bounded into the CaO-based bed material. This leads to $CaSO_4$ accumulation and deactivation of the CO_2 sorbent bed material in long term runs.

FactSage™ simulations were carried out to obtain phase equilibrium information about the sulphur behaviour in the DFB gasification system. The gasification process was simulated for different AER operating conditions between 600°C – 700°C with lime based bed material.

The thermodynamic investigation of the sulphur behaviour during steam gasification shows: The sulphur releases the gasifier mainly as H_2S. Only 5 mol-% of the rapeseed sulphur release the DFB system into the product gas phase. 95% of the sulphur remains in the solid phase. In the gasifier, the sulphur is bounded into the CaO-based bed material as CaS. CaS is transformed in the regenerator to SO_4^{2-}, for example ($CaSO_4$). The sulphur remains in the solid phase. This leads to an accumulation of sulphur in the solid phase. Therefore, depending on the S-content of the fuel, a make-up flow of fresh bed material might be necessary to keep the CO_2 capture - activity high enough.

Conclusion suitability of alternative fuels (TUV, USTUTT)

The AER process is a suitable technology for steam gasification of various biomass resources, including alkali-enriched and S-rich sources. However, due to the low ash melting point of alkali rich fuels, agglomeration must be considered in the combustion zone. On the data basis generated in this work package, we therefore recommend to mix alkali-rich fuels with woody biomass in order to reduce the resulting ash content. Both, the experiments at TUV and at USTUTT were done with pure fuels. Sulphur from biomass is released partially as H_2S in the product gas but it is mainly transported in the solid phase (CaS) into the riser (regenerator). Here, $CaSO_4$ is formed, which remains stable. Thus, the bed material partially deactivates, depending on the amount of S, transported into the system. Possible activity losses of the CO_2 sorbent bed material are compensated by a continuous purge of the sorbent bed material, which is necessary due to losses by attrition.

3.4 WP 4: Experimental run with the 8 MW plant in Güssing

(BKG, TUV, GEJ)

Introduction / Motivation and goals

In work package 4 the results from the other work package were used to run experimental campaigns under AER conditions at the industrial wood gasifier in Güssing. The overall goal in this work package is to prove the feasibility of an AER Gas process in industrial scale. Furthermore, AER operation provided useful information / data not only for the project but also for the engineering of the planned AER demonstration plant.

1) Preparation of test campaign

a) TUV: cold flow model

As the actual circulation rate of the bed material in the biomass CHP Güssing is optimised for normal steam gasification, this circulation rate is much too high for the AER process. In an existing cold flow model of the biomass gasifier as installed at the CHP Güssing several aspects are investigated:

- Bed material solid circulation in dependence of the particle size
- Bed material solid circulation in dependence of the overall volume flows and the air staging (bottom/primary/secondary air)
- Fuel circulation rate in dependence of operational parameters (air staging, bed material size, bed material circulation, etc.)

Methodology / approaches

In **Fig. 3.39** the basic design of the cold flow model can be seen. It is very similar to the gasifier in Güssing in a scale four times smaller than in reality. Instead of steam which is used at the CHP Güssing air has been used in the cold flow model to fluidise the bed material.

The amount of bed material which has been used in the cold flow model was about 130 kg. This amount result from the condition that a pressure drop of 97 mbar should be adjusted in the gasification zone. This value is calculated based on the Glicksman – criteria in relation to the pressure drop at the CHP Güssing which is about 108 mbar. All other parameters have been scaled according the Glicksman – criteria. Details on the scaling calculations can be found in literature[1,2].

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[1] Pfeifer, C., Kreuzeder, A., Hofbauer, H., 2008, “Fluidy-dynamic Investigations in a Cold Model for a Dual Fluidized Bed Biomass Steam Gasifer: Solid Circulation and Fuel Residence Time”, Proceedings of the Circulating Fluidized Bed Technology IX Conference, Hamburg, Germany, May 13-16, 2008, p 123-128

[2] Kreuzeder, A., Pfeifer, C., Hofbauer, H., 2007, "Fluid-Dynamic Investigations in a Scaled Cold Model for a Dual Fluidized Bed Biomass Steam Gasification Process: Solid Flux Measurements and Optimization of the Cyclone", International Journal of Chemical Reactor Engineering: 2007, Vol. 5: A31

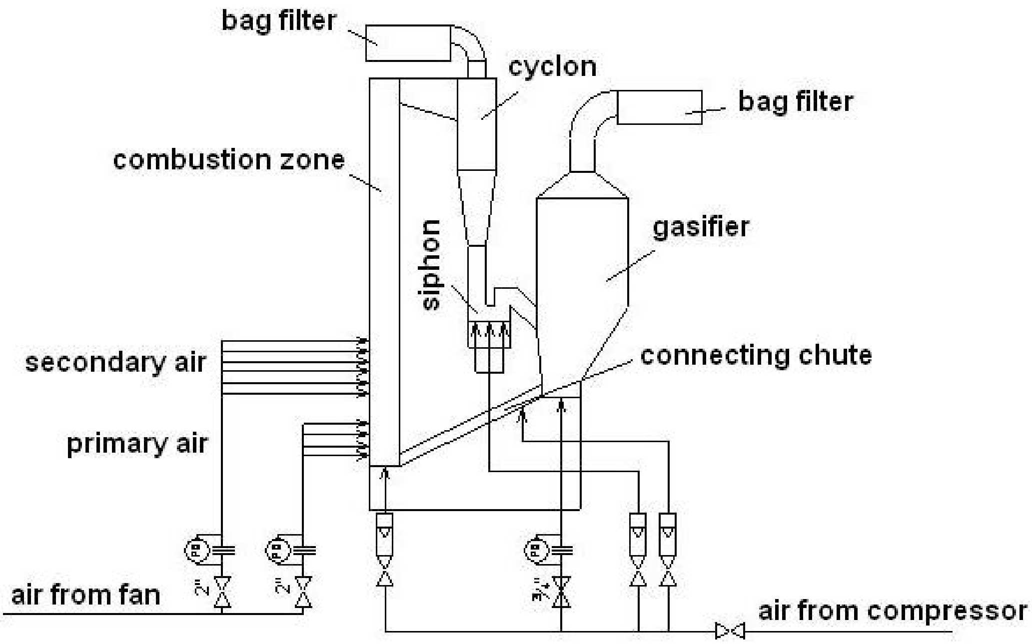

Figure 3.39: Basic design of the cold flow model

Procedure

An important figure for the scale up of circulating fluidized beds is the bed material solid mass flux per area. To determine this value for the hot rig mass and energy balances need to be done. At the cold model it can be directly identified according the following procedure. The fluidization of the siphon is closed abruptly. Thus, the bed material accumulates in the down comer pipe from the cyclone separator to the siphon. The time of the rising bed material level passing marks on the down pipe is measured. Subsequently the solid mass flux can be calculated taking the accumulated volume, the measured time value, and the bulk density of the bed material (bronze 5370 kg/m³) into account.

The mean residence time of the model fuel particle is determined according to the following method. The model function F(t) Model is fitted to the measured accumulated residence time distribution by adjusting the parameters a and b with a least square algorithm.

$$F(t)_{Model} = 1 - \exp[-a \cdot (t - b)] \qquad \text{(eq. 3.3)}$$

With the gained parameters a and b the residence time can be calculated with

$$\bar{t} = \int_{0}^{\infty} t \cdot dF(t) = \frac{1}{a} \cdot \exp(a \cdot b) \qquad \text{(eq. 3.4)}$$

The total amount of fluidization air of the riser (primary air, secondary air and bottom air) was kept constant for all experiments at 450 Nm³/h. This value corresponds to the scaled riser volume flow of the CHP plant. With increasing secondary air/total fluidization air ratio, the solid mass flux per area decreases.

Main achievements

The cold flow model has been used to measure circulation rates of bed material and biomass in the gasifier and to identify the influence of the particle size on these figures. For the experiments three different medium diameters have been chosen: 253 µm, 205 µm and 126 µm (126µm is equivalent to the annualized diameter of Olivine particles used at the CHP Güssing for standard gasification).

Bed material circulation rate

There are several possibilities to decrease the bed material circulation rate compared with the process parameters for normal steam gasification:

One possibility is to change the conditions in the combustion zone. First of all an increase of the secondary air and a decrease of the primary air causes a decreasing circulation rate (see next diagram).

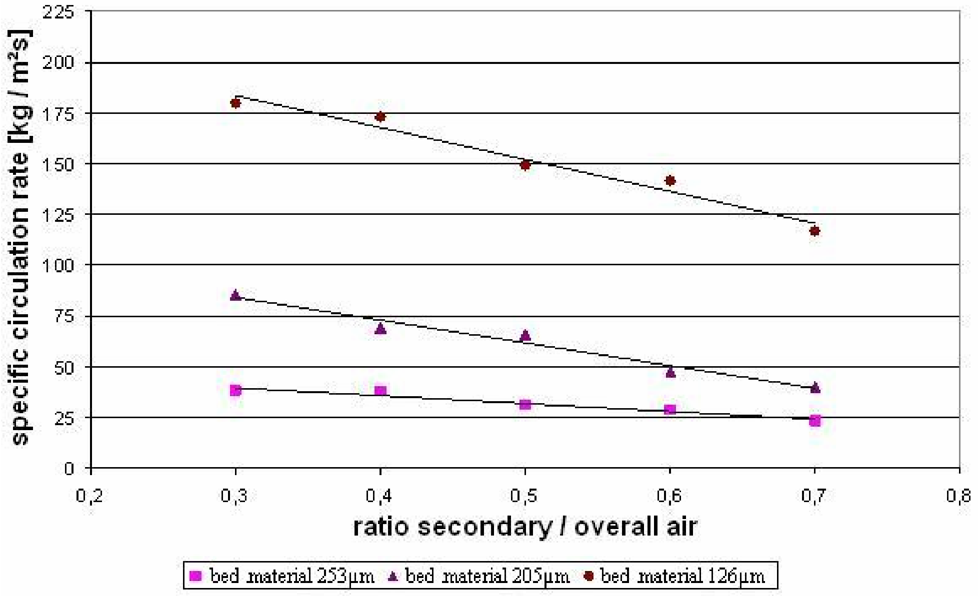

Figure 3.40: Variation of the medium diameter of the bed material and the amount of primary and secondary air

Another opportunity is to lower the volume flow of the bottom air. Generally a lower overall volume flow causes a decrease of the superficial velocity and consequentially a decrease of the circulation rate. A reduction of the overall air at the CHP Güssing is only conditional possible because a certain amount is needed for the combustion of the biomass. The overall air amount of 340 Nm³/h is equivalent to 75% of the overall air amount normally used during standard gasification at the CHP Güssing, **Fig. 3.41**.

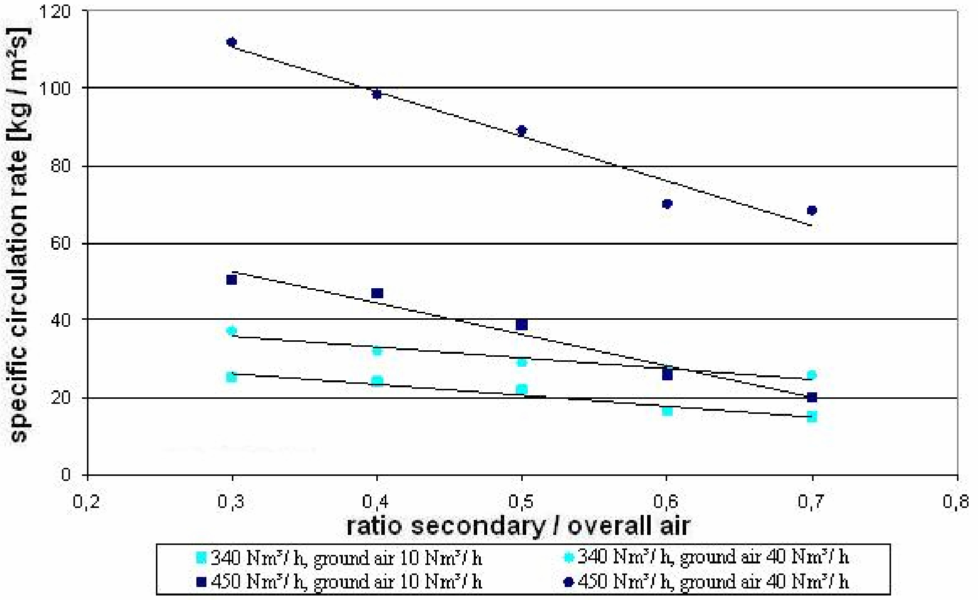

Figure 3.41: Comparison: reduced overall air amount (340 Nm³/h)/ normal overall air amount (450 Nm³/h)

Another alternative is to variegate the fluidisation conditions in the connecting chute between gasifier and combustion zone. With a lower fluidisation the circulation rate can be decreased.

Of large effect is the selection of the bed material size. With increasing particle diameters the bed material circulation rate is reduced substantially. So for the 1st test campaign at the CHP Güssing a medial diameter of 0.9 mm is recommended (calculated based on the Glicksman – criteria; the medial diameter of 253 µm in the cold flow model is equivalent to the medial diameter of 0.9 mm at the CHP Güssing). The 1st test campaign in Güssing verified the results displayed above.

Fuel circulation rate

The model biomass particles are spherically like the bed material. The diameters of these particles are 3 and 6 mm that correspond to spherical biomass particles in the hot rig with diameters of 12 resp. 24 mm. The volume of the spheres is equivalent to the wood chip volumes which are gasified in Güssing. The density of the model particles are calculated according scaling laws[3]. The properties of the fuel used in Güssing are displayed in **Tab. 3.6**. **Tab. 3.7** shows the model particle materials and notation. The densities of the used particles cover the calculated range of densities very well.

Table 3.6: Biomass properties

timber	water content [wt%]	density [kg/m³]
fir	11	0.46
beech	11	0.71
beech	20	0.76

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[3] Ake T., Glicksman, L R., Scale Model and full scale test results of a circulating fluidized bed combustion, Seminar of fluidized bed combustion technology for utility applications, Paolo Alto, California, (1988)

Table 3.7: Model particle properties and corresponding densities

material	notation	particle size [mm]	density (cold model) [kg/m³]	density (hot rig) [kg/m³]
plastic	6a	6	1.04	0.30
plastic	6b	6	1.82	0.52
plastic	6c	6	2.60	0.74
aluminium	6d	6	2.70	0.77
glass	3a	3	1.35	0.39
plastic	3b	3	2.56	0.73

In the following the main findings are presented. Figure 3.42 displays the summary of all experiments. To cover a large solid mass flux region, bed material with different mean particle diameters were chosen. Independent from the mean bed material diameter and model particle diameter a tendentious characteristic is visible. Thus, this figure can be used for an estimation of the residence time. The bed material solid mass flux has a strong influence on the model particle mean residence time. If the settling velocity is higher than the superficial velocity of the particle the transport of the model particles in the combustion zone is determined by the solid flux of the bed material. The curve can be divided into two ranges, more or less than 100 kg/m²s solid flux. Above the 100 kg/m²s the influence of the solid flux on the mean residence time is low compared to the range below. Due to the increasing void age with decreasing solid mass flux the model particle mean residence time increases in the combustion zone.

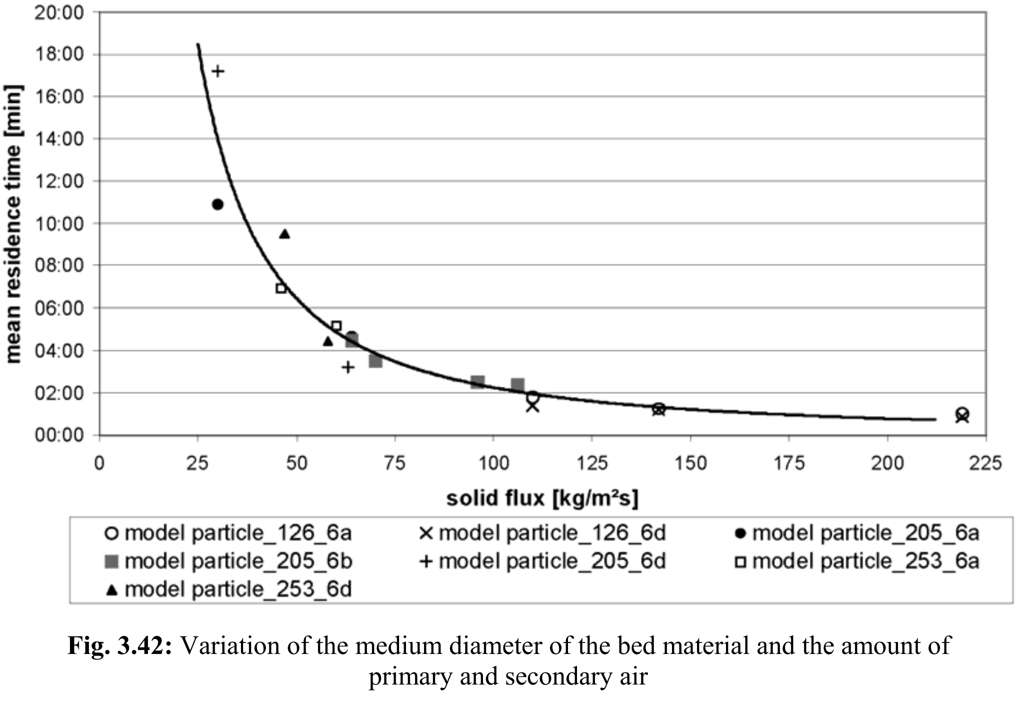

Fig. 3.42: Variation of the medium diameter of the bed material and the amount of primary and secondary air

Moreover, as can be seen in **Table 3.8**, the residence time in the gasification zone decreases for heavier particles due to the decreased solid circulation from the gasification to the combustion zone. The gasification zone can be seen simplified as steady-state mixed flow reactor whereas the combustion zone can be seen as steady state plug flow reactor. For the siphon no significant trends are noticeable.

Table 3.8: Residence times of different parts of the CFM with different model particle densities, fixed bed material size 253 µm, solid mass flux 60 kg/m²s

mean residence time	model particle			
	6a	6b	6c	6d
gasification zone with connecting chute [min]	04:07	03:53	02:36	02:30
combustion zone with cyclone separator [s]	23	28	30	35
siphon [s]	11	8	9	9
total [min]	04:41	04:29	03:15	03:14

Conclusion

Scale-up of reactors is amongst the most important procedures for the development of industrial processes. Apart of heat and mass transfer as well as of chemical reactions, the fluid dynamics are of particular importance for fluidized beds. The determination of solid circulation (bed material as well as fuel) is very important to close the mass and energy balances of the overall process. Obviously, chemical reactions cannot be reproduced in cold flow models. From this it follows that no particle changes, for example diameter and density, can be considered and the transferability of the cold model investigations on the hot rig depends on the volatile matter of the fuel particle. Hence, a good accordance with a low volatile matter (e.g. hard coal) has been given. Summarising, the fuel circulation is mainly dependent on the solid flux and on the particle diameter and less on the density of the fuel particle.

b) Calcite C1 as precoat material at BKG during standard gasification (BKG)

Because of the fact that BKG has no experience with AER bed materials in the 8 MW_{th} gasifier, BKG decided with the other partners to run a preliminary test using calcite C1 as precoat material in the bag filter cycle. This test was done in February 2007.

Methodology / approaches

During this test BKG tried to find out how the bed material reacts concerning the major parts of the plant like product gas cooler, air pre-heater, product gas filter, ect. Therefore, during conventional gasification (with Olivine as bed material and gasification temperatures above 840°C), the standard precoat material was replaced continuously by limestone C1. In **Fig. 3.43** you can see that the material is inserted just before the product gas filter and gets distributed within the whole gasification plant.

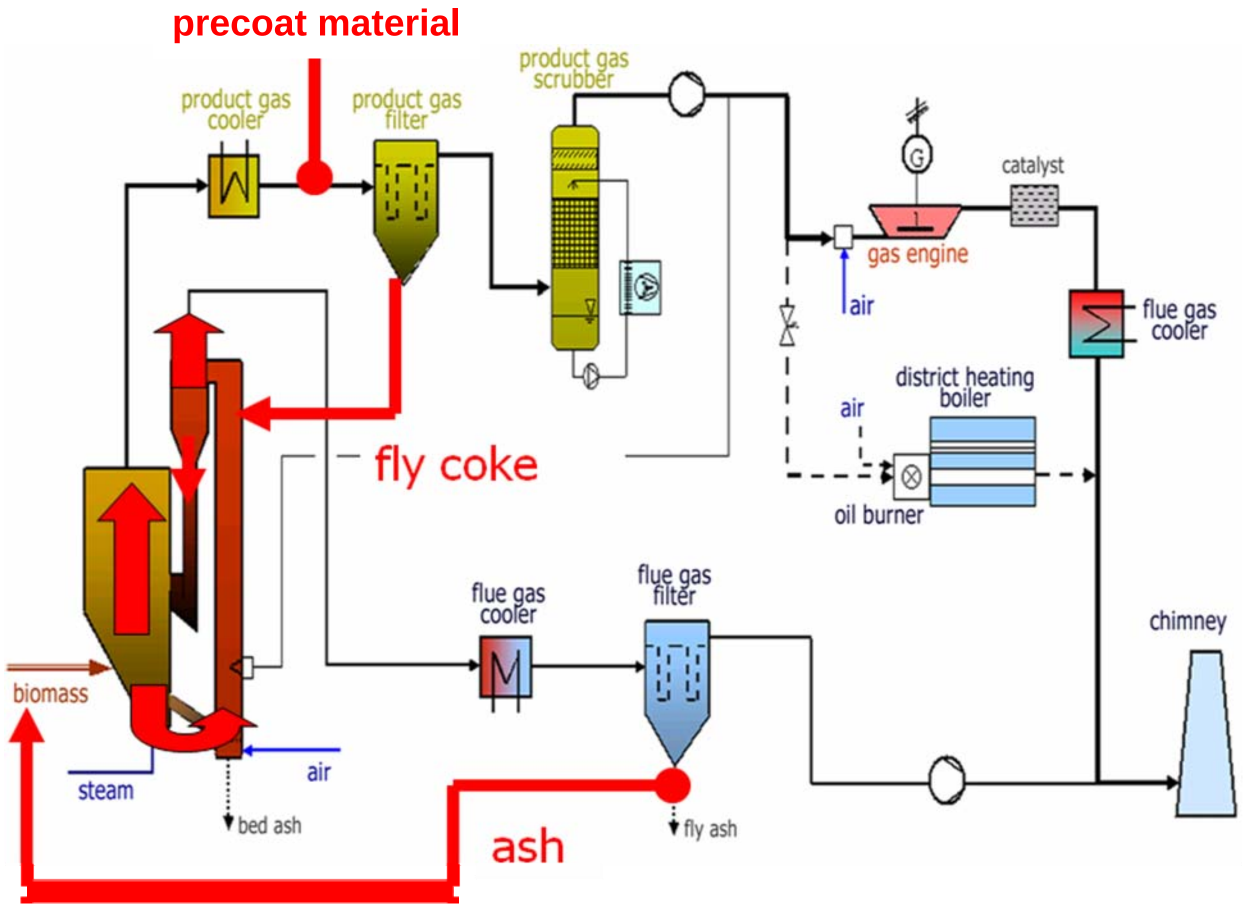

Fig. 3.43: Injection point of limestone C1 as precoat material to replace the standard precoat material. The precoat material is distributed in the whole power plant.

Main achievements and conclusion

The product gas quality was increased due to the catalytic activist of the C1 material towards tar removal. However, already several hours after the first addition of the bed material the air pre heater starts to block. The plant operation had to be stopped in order to remove the deposits. The problem was the mixture of olivine and the AER bed material. If small amounts of one material is mixed to the other one, agglomeration takes place and blocks different parts of the plant.

The main outcome of this test was the know-how that we have to clean all chambers and empty all solid mass flows before we switching from one bed material (e.g., Olivine) to the other one (e.g., limestone). This means that the whole plant needed to be cleaned before and after an AER test campaign.

2) Modification of gas engine *(GEJ)*

Methodology / approaches

Due to the high hydrogen content of an AER product gas, the probability of a backfire into the intake manifold of the engine increases. An uncontrolled ignition of the mixture in the cylinder can cause the ignition of the mixture in the intake manifold, a so called backfire. The result is a pressure peak in the suction manifold that may destroy the weakest part (e.g., the air filter housing). Without counter measures this effect is a serious issue for the safety of the operators.

In addition, a high H_2 content can also lead to a stronger knocking behaviour of the engine also caused by a low auto ignition temperature of the hydrogen. For an optimum engine operation an adequate knocking detection software is mandatory.

Due to the mentioned issues, GE Jenbacher launched initiatives to develop an appropriate engine configuration for AER gas including the following modifications:

- Special software to reduce the probability of backfire caused by auto ignition (software detects auto ignition and stops it)
- Pressure relief device for preventing the destruction of the intake manifold and a safety issue for human beings.
- Cylinder individual knocking detection system

Main achievements

The developed special software detects an auto ignition of the mixture before the nominal ignition point with the help of several parameters. When the auto ignition occurs counter measures are set by the engine controller to stop auto ignition.

Due to the detection and the extinction of the auto ignition the probability of a backfire has been reduced. This results in a higher availability of the engine as well as an increased safety.

Although the probability of a backfire has been reduced due to the software it can not be avoided totally. Therefore a pressure relief device was developed and mounted on the air filter housing of the engine to release the undesired pressure peak that results from a backfire in a safe way. If a backfire occurs only the burst disc of the relief device is ruptured and the intake manifold itself is protected. The burst disc can easily be replaced.

Fig. 3.44: Standard air filter housing (left); Pressure relief device mounted on air filter housing on the Güssing gas engine (right)

Conclusion

Due to the accomplished modifications a safe engine operation was proven during the 1st test campaign in Güssing with the usage of AER gas with a load of 970 kW electrical output.

Additional tests on a single cylinder engine of the same type have proven the possibility to operate the engine with full load (1970 kW).

Additionally the developments like the special software are now state-of-the-art for Jenbacher gas engines and are useful for entering the market with gases characterised by a high H_2 content.

3) 1st Test Campaign (BKG, TUV, GEJ)

The 1st test campaign of the AER process at the biomass CHP in Güssing (BKG) was accomplished from July, 16th to 18th 2007. The experiment in total lasted approximately 35 hours.

Experimental

The experiment is divided into start up, steady state (concerning AER conditions) and cooling down. A flow sheet of the combined heat and power plant in Güssing is given in the following figure.

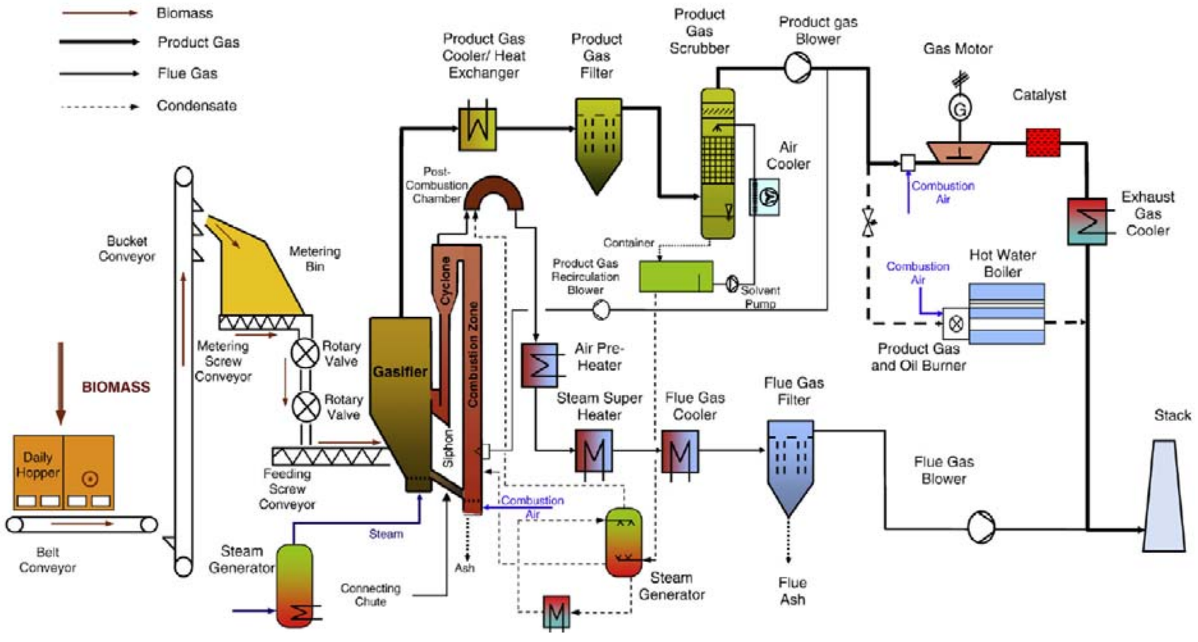

Figure 3.45: Flowsheet of the biomass CHP in Güssing, Austria

Start up procedure

Before the experiment the whole plant was cleaned and all the Olivine was removed from the gasifier. The bed material dosing system has been modified in that way that bed material could be fed continuously via the fly ash circulation device. At the beginning of the test campaign about 3 t of bed material (pre - treated calcite C1) were filled into the gasifier. Due to the fact that this material is easily flowing some bed material was transported into the tubes and nozzles of main fluidization of the gasification zone. Thus, a short break of the start up procedure occurred to clean these tubes.

The bed material circulation could be accomplished at about 2am and then the system was heated up to the desired temperature of about 900°C to calcinate the whole bed material (see next diagram). It can be seen that during the calcination step (beginning at about 10am) the pressure drop is slightly decreasing (due to ongoing calcination of $CaCO_3$) and the temperatures remain more or less stable (see **Fig. 3.46**).

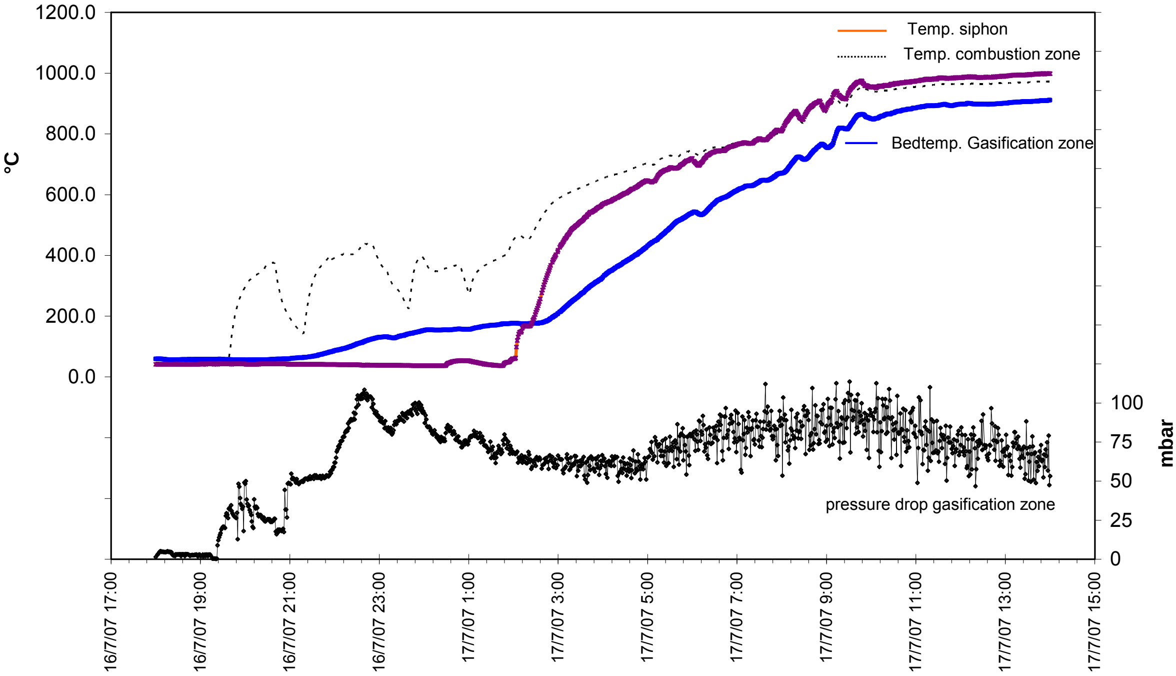

Figure 3.46: Temperatures in the gasifier and pressure drop of the gasification part during the start up procedure

Steady state period

After reaching the desired temperatures and full calcination of the bed material, the biomass feeding was started and the fluidization of the gasification zone was switched to steam. Thus, the temperature in the gasification zone decreased to the desired range from 650 to 690 °C (see next figure). It can be clearly seen that it needed about 4 hours to stabilize the system according to the temperatures.

Fig. 3.48 shows the gas composition of the producer gas during the steady state period. As expected the CO_2 absorption worked well after reaching temperatures below 690 °C. The gas engine was in operation for nearly the whole steady state period. Hydrogen contents in the producer gas of more than 50 vol%$_{db}$ could be reached.

Surprisingly the CO content was measured higher than the CO_2 content in contradiction to results from the 100kW$_{th}$ pilot plant at TUV. This effect needs more investigations as well as the fact that more ungasified char was produced due to the low temperatures and as a result thereof, more char was transported to the combustion zone.

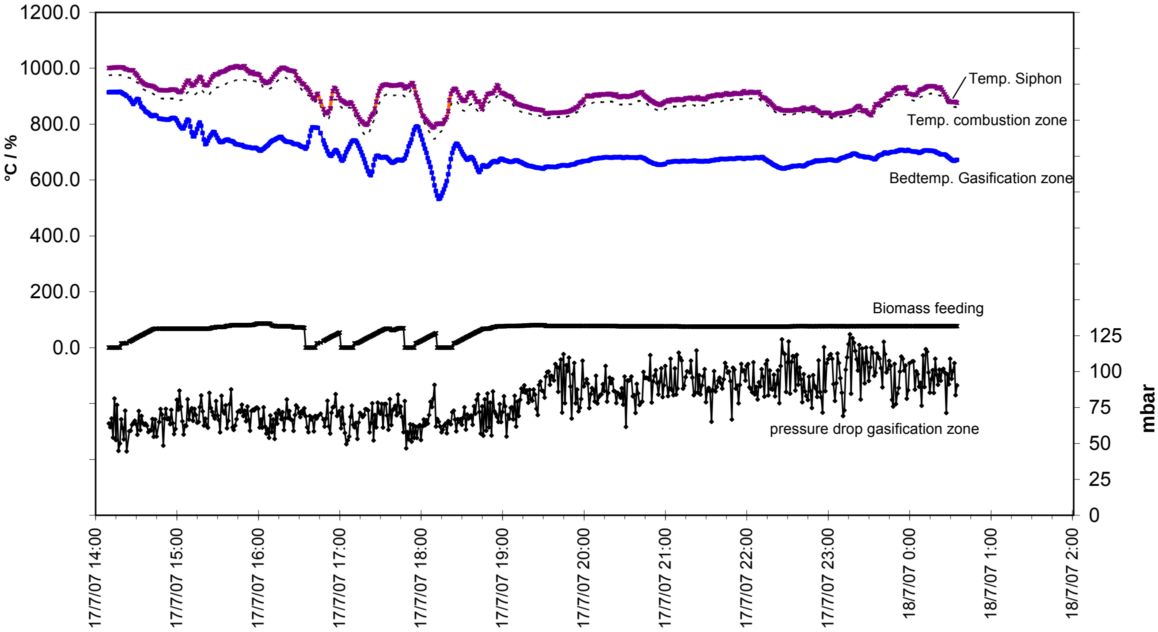

Figure 3.47: Temperatures in the gasifier and pressure drop of the gasification part during the steady state period as well as speed of the biomass feeding screw.

The experiment has been stopped because the combustion zone was temporarily operated under-stoichiometric. Thus, unburned char was transported out of the combustion chamber into the flue gas line and separated in the flue gas filter. To avoid damages of the flue gas filter and to ensure safety conditions the operation of the plant was stopped.

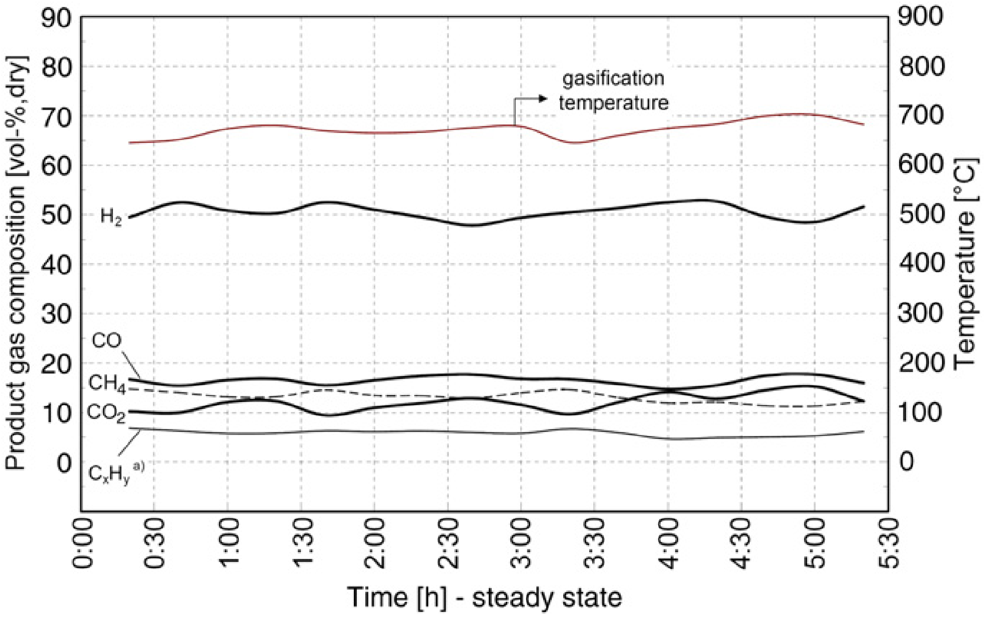

Figure 3.38: Product gas composition, gasification temperature during steady state;

a) sum of C2–C3 hydrocarbons (C_2H_4,C_2H_6,C_3H_8)

Cooling down procedure

The biomass feeding was stopped and the fluidisation of the gasification zone was switched back to air. Thus, the re-carbonation of the bed material should be accomplished. No problems occurred during the cooling down of the plant. Directly after the experiment the yearly revision started and all parts of the plant were inspected. No damages have been caused by the AER test campaign.

Main achievements

Obviously, the CO_2 content is directly effected by the gasification temperature (see **Fig. 3.48**): the higher the temperature, the higher the CO_2 content. The opposite is observed for the H_2 and the CH_4 content, which decrease for increasing gasification temperatures.

During the steady state period, the following mean product gas composition was achieved at an average gasification temperature of ~675 °C (see **Fig. 3.51**). The amount of H_2 in the product gas increased up to ~50 vol.-%dry.

The tar content of the product gas was measured. The measuring method has been developed at the Institute of Chemical Engineering (Vienna University of Technology), and is based on the tar protocol Gravimetric Tars developed by Neeft and co-workers[4]. During AER operation the tar content of the raw product gas before product gas scrubber (see **Fig. 3.45**) was determined to about 1 g/Nm³db, which is much lower than under standard conditions.

Fig. 3.49 indicates the CO_2 partial pressures (at wet basis) in the gasifier and in the combustion zone during steady state operation, comparing AER gasification with standard gasification. Furthermore, the CO_2 equilibrium partial pressure is displayed, to point out the corresponding zones of carbonation and calcination. Within **Fig. 3.49** two main differences between AER and standard operation are illustrated: the expanded temperature difference between the reactors aswell as the changed CO_2 partial pressures or CO_2 contents due to the selective CO_2 transport by the bed material. In addition, the measured CO_2 partial pressure of the AER product gas is close to the equilibrium partial pressure. In technical processes, one must consider the difference of the CO_2 partial pressure in the gasifier and CO_2 equilibrium partial pressure of the carbonation reaction ($p_{CO2,gasifier}-p_{CO2,eq}$), effecting the rate of the CO_2 sorption reactions.

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[4] J.P.A. Neeft, H.A.M. Knoef,U. Zielke, K. Sjöström, P.Hasler, P.A. Simell,M.A. Dorrington, N. Abatzoglou, S. Deutch, C. Greil, G.J. Buffinga, C. Brage, M. Soumalainen, Guideline for Sampling an Analysis of Tar and Particles in Biomass Producer Gas, Version 3.1; Energy project EEN5-1999-00507 (Tar protocol), 1999

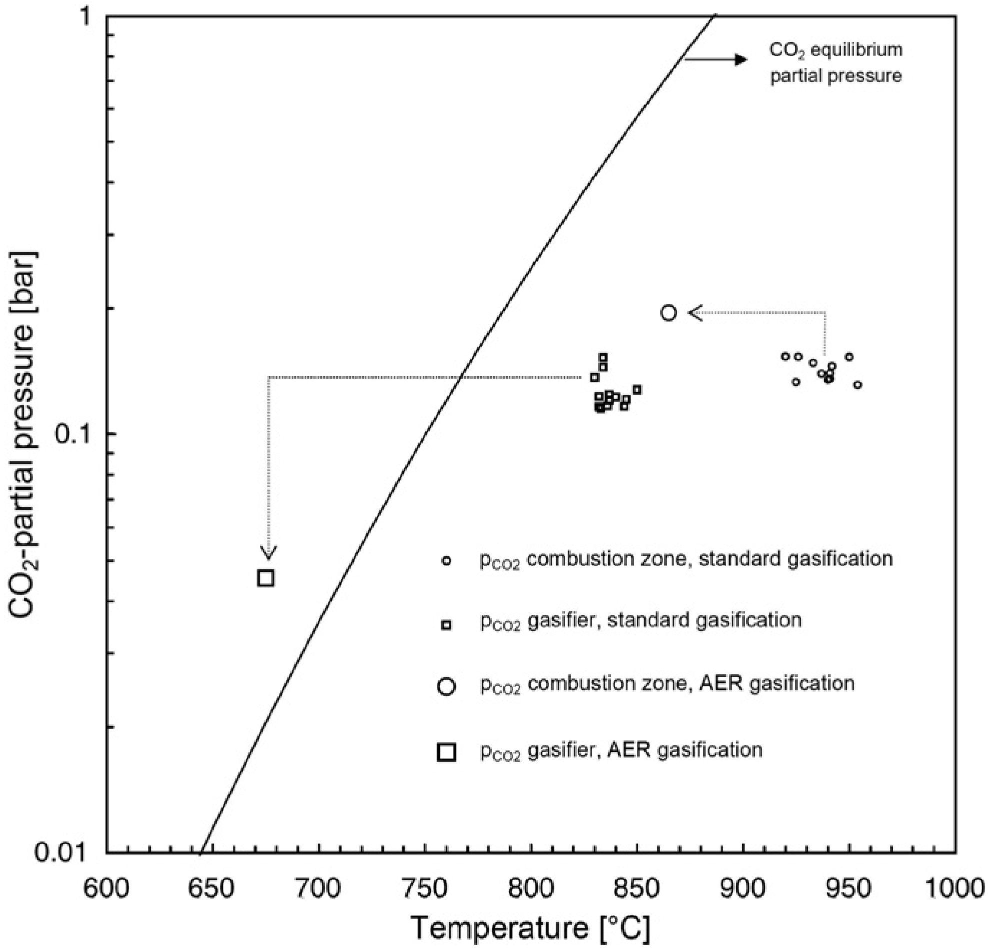

Figure 3.49: CO_2 partial pressure vs. temperature

Fig. 3.50 depicts the gasification temperature versus the H_2, CO, and CO_2 content in the product gas. Below temperatures of 690 °C, the CO_2 content in the product gas decreases significantly due to improved selective CO_2 removal in the gasifier. Thus, the required difference of $p_{CO2,gasifier}-p_{CO2,eq}$ is sufficient to enable the carbonation of the bed material, the CO_2 uptake. The CO content decreases and the H_2 content increases with decreasing CO_2 content, since the removal of the reactant CO_2 enhances the CO shift reaction.

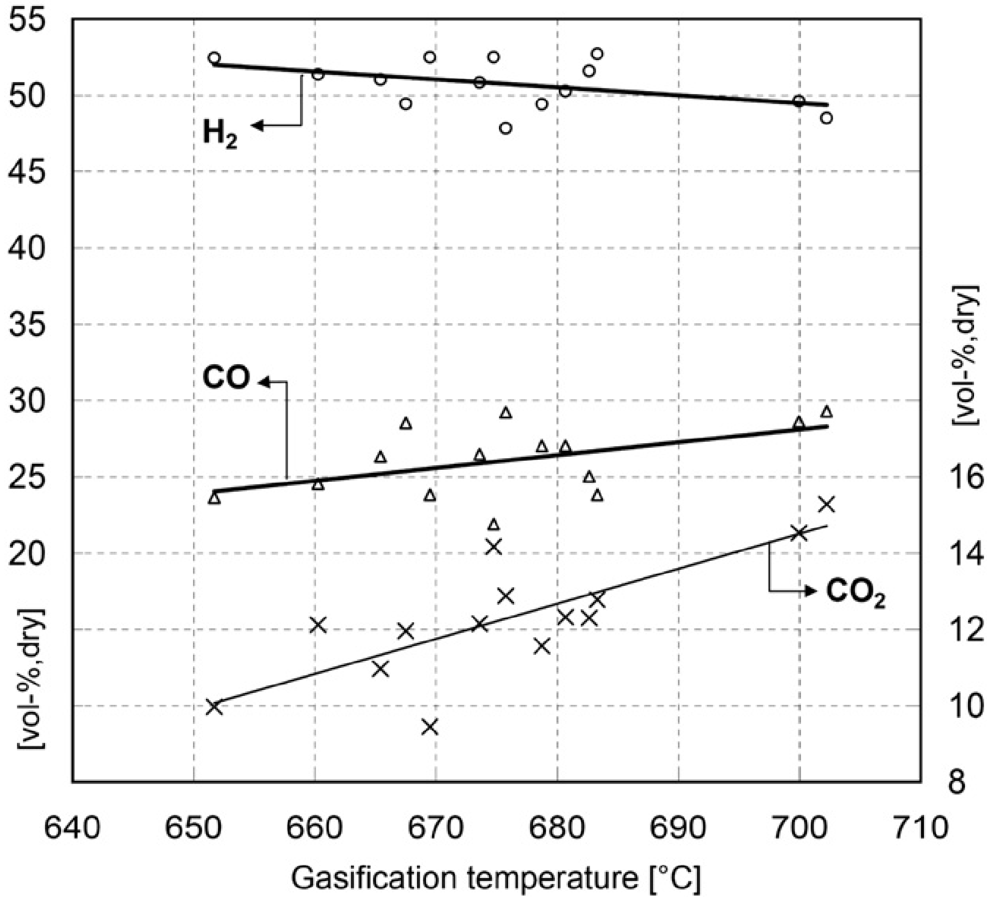

Figure 3.50: Effect of gasification temperature on composition of AER product gas

Fig. 3.51 depicts a comparison of standard gasification with AER test campaign at the CHP Güssing concerning the product gas composition. The product gas composition for standard gasification is displayed in typical ranges for each component. Thus, it appears that CO_2 removal enhances the CO conversion towards a higher H_2-yield. The amount of CH_4 and higher hydrocarbons is slightly greater, since hydrocarbons are rather formed at lower gasification temperatures. The low gasification temperature of about 675 °C compared to gasification temperatures of 850–900 °C results in lower reaction rates for the gasification reactions. However, as the AER process is operated at lower bed material circulation rates to accomplish the increased temperature difference between gasification and combustion zone (enabling CO_2 removal and release), the residence time of the solid matter is consequently increased in the gasification zone, compensating the disadvantage of lower reaction rates. Typical tar contents in the raw product gas (measured before product gas scrubber) for standard gasification at CHP Güssing are about 2–5 g/Nm³db. The lower tar content of about 1 g/Nm³db in the raw product gas suggests a catalytic impact of the bed material concerning tar reforming. Limestone as a possible catalyst for tar reforming has been investigated by several authors and is pointed out as a suitable catalyst.

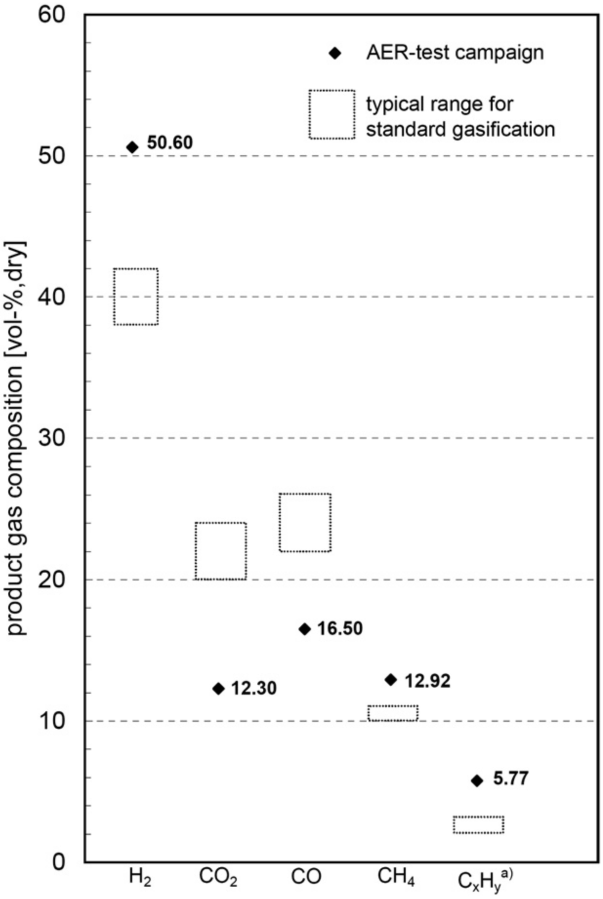

Figure 3.51: Product gas composition: standard gasification and AER test campaign;
a) sum ofC2–C3 hydrocarbons (C_2H_4,C_2H_6,C_3H_8)

Results of the investigations in pilot scale are presented in chapter 3. At the pilot plant the influence of various parameters (fuel water content, different bed materials) has been studied.

Fig. 3.52 shows the typical ranges of the AER product gas components, obtained in the pilot plant, in comparison to the product gas of the AER test campaign. At the pilot plant, H_2 contents of up to 65 vol.-%dry were achieved, when the pre-treated limestone C1 was used as bed material. The CO_2 content of the AER test campaign is in the range achieved at the pilot plant, proving again the sufficient CO_2 reactivity of the sorbent bed material used. The lower CO contents as well as the higher H_2 contents indicate an increased CO conversion at the pilot plant. The CH_4 content and the content of higher hydrocarbons is slightly greater compared to the pilot plant. The steam to fuel ratio has been balanced to about 0.83 $kg_{steam}/kg_{fuel,dry}$ for the steady state operation during AER test campaign at CHP Güssing. The steam to fuel ratio amounts 1.24–1.62 $kg_{steam}/kg_{fuel,dry}$ at the pilot plant in AER operation. Hence, a higher amount of steam in the reaction atmosphere enhances significantly the conversion reactions toward the desired products, since steam is the main reactant.

For further analysis and assessment of the first test campaign concerning mass and energy balances and key data, the validation of measurements has to be accomplished. In order to carry out this task a process simulation has been set up using the simulation tool IPSEpro. A detailed overview over the results is given in the following chapter (Results of WP5).

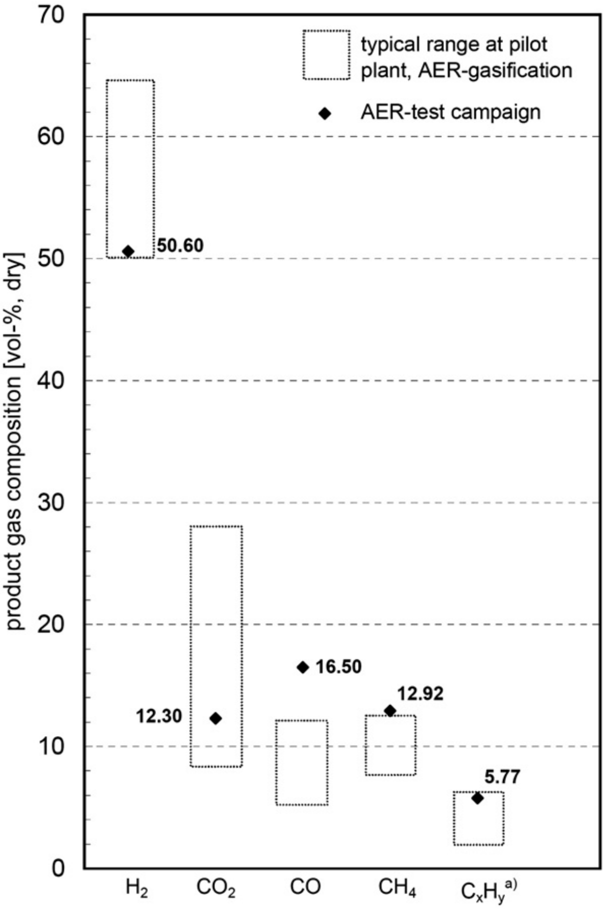

Figure 3.52: Product gas composition: AER pilot plant and AER test campaign;

[a] sum of C2–C3 hydrocarbons (C_2H_4,C_2H_6,C_3H_8)

Conclusion

Within the test campaign, the first experimental approach to apply the absorption enhanced reforming process at industrial scale was accomplished. The test campaign demonstrates the principle feasibility of the AER process at industrial scale. Steady state conditions were achieved and the gas engine was started for CHP generation. For security reasons, it was operated at partial load (ca. 1 MWel).

A significant CO_2 removal from the producer gas resulting in an increased conversion of CO toward H_2 has been detected. The product gas composition has been upgraded with an increased H_2 content of about 50 vol.-%dry. The tar content was quantified to about 1 g/Nm³db. Hence, it could be proven that both operation modes, standard and AER, are possible in the same power plant.

However, further investigation of the AER process are necessary to vary important process parameters, e. g. temperature, steam to fuel ratio, bed material circulation with regard to a higher H_2 content respectively to adjust a proper H_2/CO ratio for synthesis processes. Main focus of process control will be the connection of bed material circulation, residence time, temperature, CO_2 removal and CO conversion. Furthermore the capability of bed material concerning tar reforming will be an aspect to be observed, since a low tar content increases the gas yield as well as the heating value of the product gas. The option of primary tar reforming or elimination by catalytic active bed material will contribute to an increased overall performance of the biomass gasification with less efforts for the product gas cleaning.

3.5 WP 5: Economic, technical and market analysis of the 8 MW_{th} plant with AER process

(TUV, BKG, ZSW)

Introduction / Motivation and goals

This work package focussed on the technical and economic assessment of the AER process to quantify the efficiency and the cost reduction potential. In addition suitable product gas applications were pointed out and a strategy for market implementation was elaborated.

Methodology / approaches:

Process simulation with IPSEpro

The technical analysis of the process is done by process simulation, using the commercial software IPSEpro. The steady state simulation software IPSEpro has been used for processing of the assessment. IPSEpro allows process simulation with regard to determination of mass- and energy balances. The software is commonly used in chemical and process engineering. For the purpose of comparison, two process flow sheets have been set up.

The flow sheet structure is based on the process structure of the combined heat and power plant Güssing. Hence, the process comprises the entire gasification process as well as the gas cleaning unit and the gas utilisation for power and heat production. The process flow sheets enables calculations according to the FICFB standard gasification process as well as calculation related to FICFB process in conjunction with the AER process. The topological structure of the flow sheet, which is common for the FICFB standard process and the AER process is display in **Fig. 3.53** main units are highlighted.

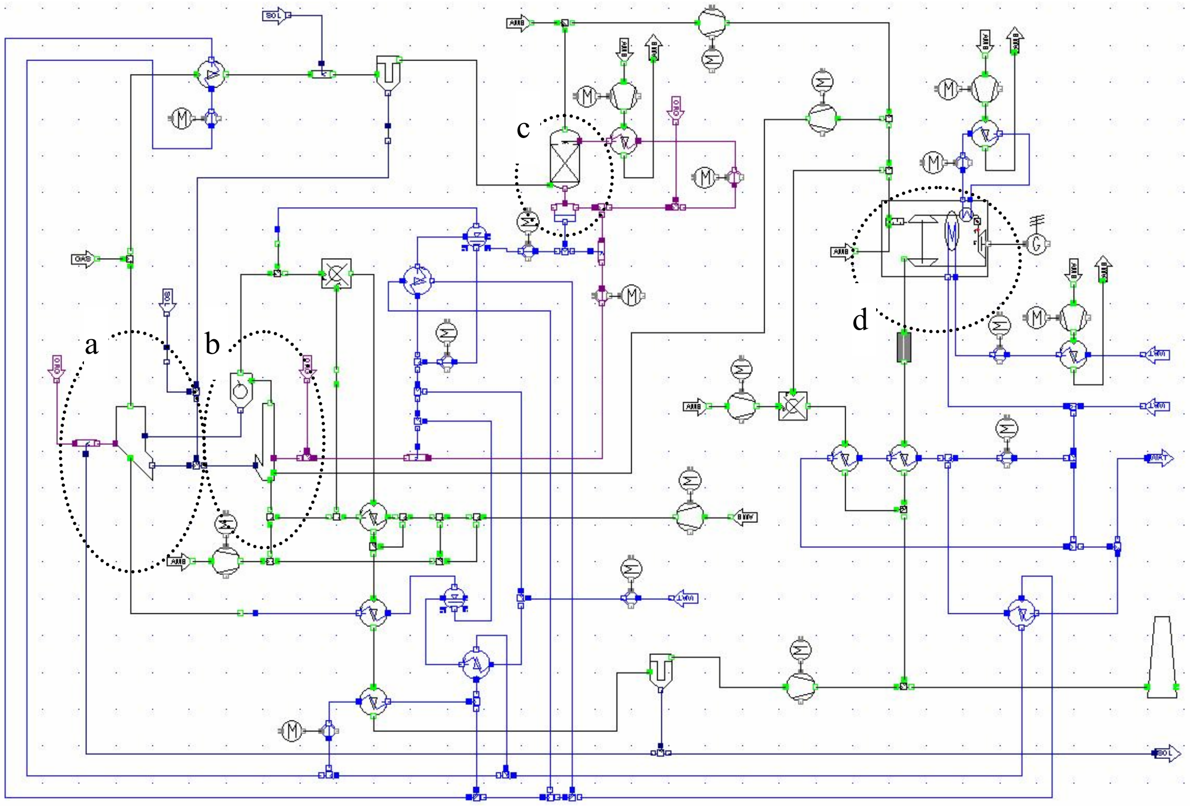

Fig. 3.53: process flow sheet for analysis and assessment, main units are highlighted: a: gasifier model, b: riser model, c: producer gas scrubber, d: gas engine

The flow sheet for analysis of the AER process comprises the feature of selective CO_2 absorption in the gasifier, subsequent transport and CO_2 desorption in the riser, which is caused by the bed material (calcite). This constitutes the main difference to the FICFB standard gasification process model. **Table 3.9** summarizes the main features of product gas generation unit (gasifier and riser) implemented into the AER process flow sheet to allows calculations according to the AER process.

Table 3.9: Parameters of the AER process flow sheet

Parameter regarding:	Unit	Gasifier	Riser
amount of CO_2 capture and release	kg/h	CO2_capt	CO2_release
CO_2 load of bed material	kg_{CO2}/kg_{CaO}	phi_CO2_CaO	non existent
temperature of CO_2 absorption	° C	T_bed_ads	non existent
logarithmic deviation of reaction equilibrium	-	pd_eq_CO2capt	pd_eq_CO2release
CO_2 partial pressure	bar	p_CO2	p_CO2
CO_2 equilibrium partial pressure	bar	p_eq_CO2	p_eq_CO2
heat of reaction	kW	Q_carb	non existent

These parameters allow a detailed examination of the AER process so that the CO_2 transport from the gasifier to the riser can be reproduced in terms of simulation with determination of mass- and energy balance.

Main achievements

Based on the measurement of the 1st test campaign, the progress of the process has been simulated according to the AER process flow sheet. This enables a detail analysis of the process behaviour of the 1st test campaign. The analysis has been carried out stepwise, whereas the steady state period of the test campaign has been split into 12 sections. Figure 3.54 displays the progress of carbon-conversion, bed material circulation, and bed temperature in gasifier during the steady state operation.

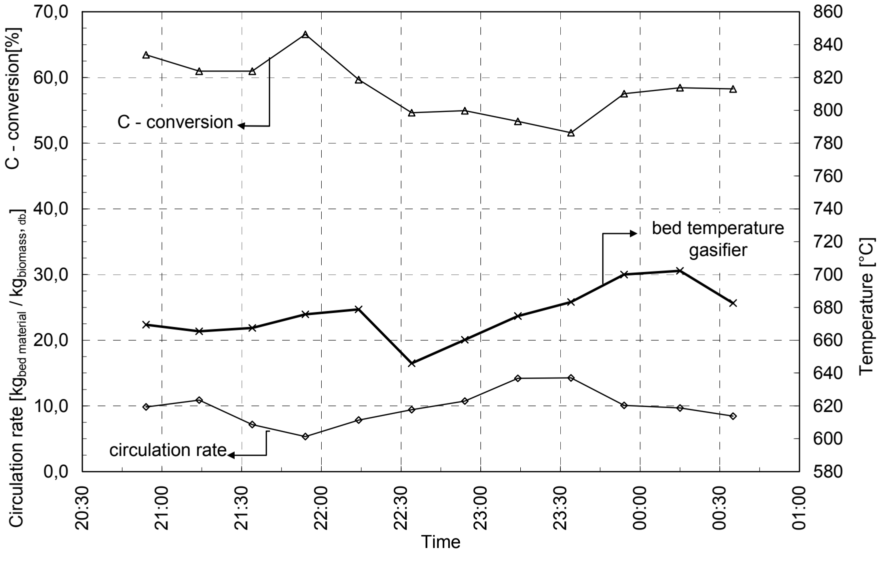

Figure 3.54: C-conversion, bed material circulation, and bed temperature in gasifier at BKG during 1st test campaign

Figure 3.54 points out the fuel conversion into the gasifier, which is expressed as C-conversion. Stable correlation can not be read off but tendencies are visible. The higher the temperature, the higher is the carbon conversion. The temperature is directly influenced by the circulation rate of the bed material, since the heat demand of the gasification process is supplied by the circulation of the bed material. Increased circulation rate, increases the temperature in the gasifier.

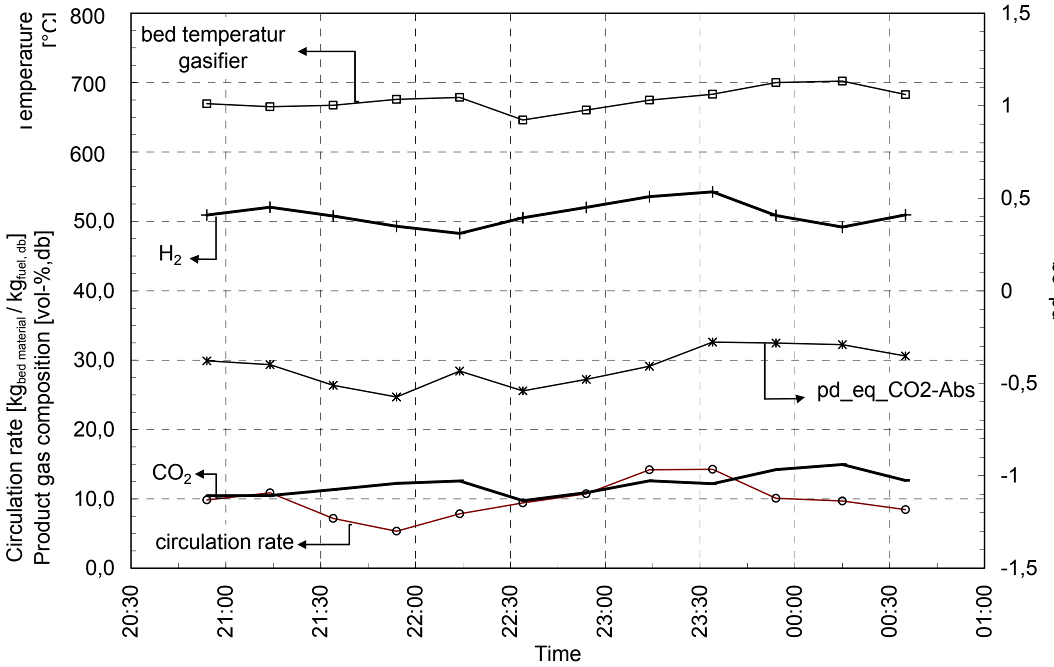

Figure 3.55: H_2 and CO_2 content in product gas, temperature gasifier, circulation rate and logarithmic deviation of water gas shift reaction (during 1st test campaign at BKG)

Figure 3.55 displays the correlation of the product gas components H_2 and CO_2 with the reaction conditions. The parameter pd_eq_CO2-Abs points out the deviation of the equilibrium of the carbonation reaction. The carbonation reaction is located at the educts side at temperatures of 600 – 700 °C. The closer the value at 0, the closer is the reaction in equilibrium.

Based on these experimental data from the 1st test campaign at Güssing, further dependencies are displayed within the following figures, which are results of the simulation with IPSEpro. **Figure 3.56** displays carbon conversion versus the bed material circulation. **Figure 3.57** displays the CO_2 load on the bed material versus the circulation rate of the bed material.

According to **Figure 3.56** the carbon conversion is decreased with increased bed material circulation. The bed material circulation influences the residence times of the solid matter into the gasifier. Hence, a lower circulations rate corresponds to a higher carbon conversion, since the residence time of the fuel is much longer in the gasifier.

Figure 3.57 shows the CO_2 load of the bed material, whose amount depends on the residence time of the bed material in the gasifier. The lower the circulation rate the higher the CO_2 load of the bed material. Since the carbonation of the particle is a function of the (residence) time, the degree of carbonation, the CO_2 load respectively, is influenced by the circulation rate of the bed material.

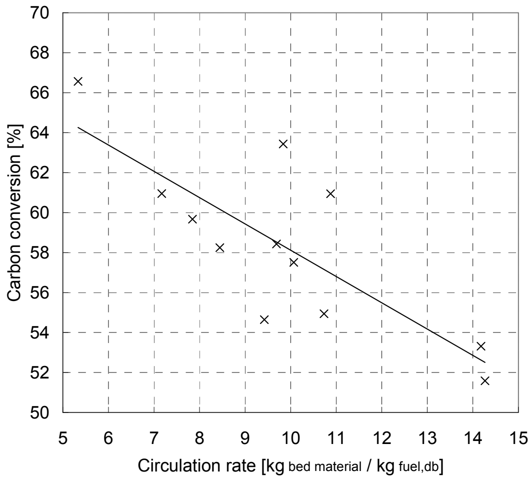

Figure 3.56: Carbon conversion versus bed material circulation during 1st test campaign at BKG

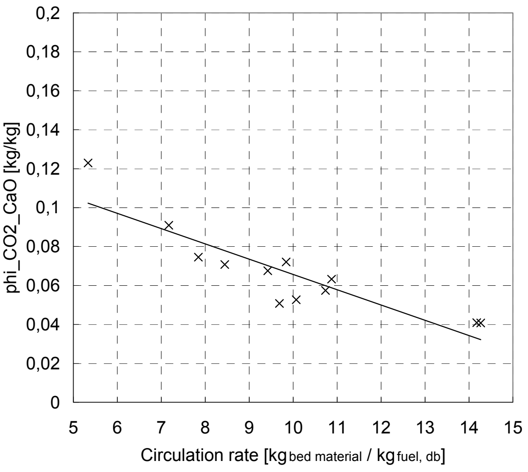

Figure 3.57: CO_2 load versus bed material circulation during 1st test campaign at BKG

Figure 3.58 displays the CO_2 transport versus the bed material circulation. It appears that the amount of CO_2 which is transport by the bed material is almost constant. The amount of CO_2 is a product of bed material circulation and CO_2 load of the bed material. Hence, low circulation rates with high CO_2 load effects the same CO_2 transport as high circulation rate with low CO_2 load.

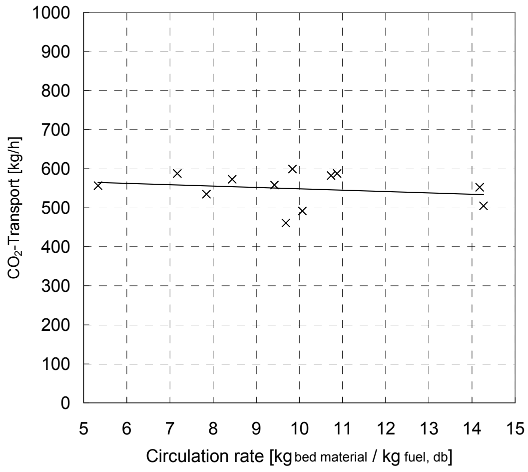

Figure 3.58: CO_2 transport versus bed material circulation during 1st test campaign at BKG

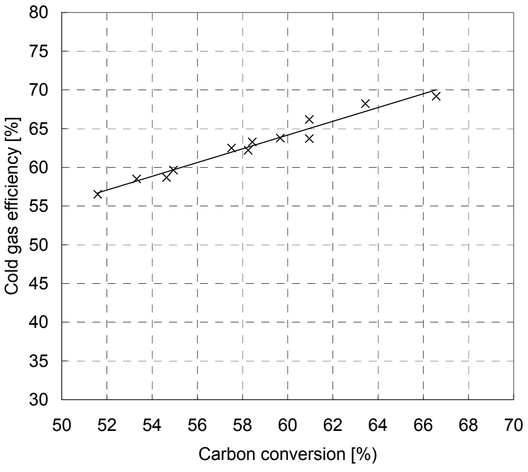

Figure 3.59: Cold gas efficiency versus carbon conversion during 1st test campaign at BKG

Figure 3.59 depicts the cold gas efficiency versus the carbon conversion. The higher the carbon conversion the higher is the cold gas efficiency. The carbon conversion expresses the quantity of carbon as gaseous component (e.g., CO, CO_2, CH_4) in relation to the solid carbon of the fuel.

Based on the analysis of the process data by means of simulation, general performance data have been finalised. **Table 3.10** summarises the performance data of the 1st test campaign in the Güssing gasifier.

Table 3.10: General performance data of the 1st test campaign (steady state operation)

Parameter	Unit	Value
CO_2 load on bed material	$[kg_{CO2}/kg_{CaO}]$	0.0642
Bed material circulation rate	$[kg_{bed\ material}/kg_{fuel,\ db}]$	9.4
CO_2 capture	[kg/h]	545.0
CO_2 partial pressure	[bar]	0.0455
CO_2 equilibrium partial pressure	[bar]	0.0176
Heat of carbonation	[kW]	585,0

In comparison to FICFB standard gasification, the AER process necessitates different process conditions. The bed material circulation is the main difference and is significantly lower for AER process. A low circulation rate of the bed material corresponds to high residence times in the gasifier. High residence times enables a higher CO_2 load of the sorbent bed material and sufficient CO_2 transport. The bed material circulation in FICFB standard operation is at values of 50 – 90 $[kg_{bed\ material} / kg_{fuel,db}]$.

It is assumed that in the Güssing gasifier, a CO_2 load of the bed material of about 0.06 $[kg_{CO2}/kg_{CaO}]$ was the upper limit during the 1st test campaign. At pilot plant scale, CO_2 loads of 0.001 to 0.038 $[kg_{CO2}/kg_{CaO}]$ have been achieved, whereas different residence times are present.

Comparison FICFB standard gasification to AER process

For detailed analysis of the AER process at industrial scale, a process simulation for a precise process state has been performed. The input data are based on the analysis of the 1st test campaign in the Güssing gasifier and on results gathered during the experiments at pilot plant scale (100kW DFB gasifier at TUV). Within a further step, the AER performance at FICFB gasification is compared with the FICFB standard gasification. General input data for simulation of the AER process and the FICFB standard gasification are summarised in **table 3.11**.

Table 3.11: General input data for simulation of AER process and FICFB standard gasification

Parameter	Unit	AER	FICFB standard gasification
fuel input	[MW]	10	10
product gas composition	[vol.-%db]		
H_2		66.0	38.0
CO		8.5	25.0
CO_2		9.9	20.6
CH_4		11.5	10.7
C_2H_4		1.2	2.5
C_2H_6		0.6	0.0
C_3H_8		0.2	1.0
circulation rate	[$kg_{bed\ material}$ /$kg_{fuel,\ db}$]	< 10	~50
Gasification temperature	[°C]	650	850

Main difference is the product gas composition as well as the gasification temperature. Beside these items the circulation rate is adapted. AER operation demands a circulation rate below 10 [$kg_{bed\ material}$ / $kg_{fuel,db}$].

As result of the simulation, two performance sheets were generated covering the AER gasification and the standard gasification at the FICFB technology. Results of the performance are displayed in **table 3.12**.

Table 3.12: Performance of AER gasification and standard gasification at FICFB technology

Parameter	Unit	AER	FICFB standard gasification
product gas			
product gas volume flow	[Nm³/h]	2271.0	2618.1
heating value of product gas	[MJ/Nm³]	13.60	13.49
chemical power of product gas	[MW]	7.9	8.2
total el. power	[kW]	3127	3318
el. consumption	[kW]	517.0	517.0
effective heat output	[kW]	4379	4137
cold gas efficiency	[%]	77.4	79.8
el. efficiency brut	[%]	30.5	32.4
thermal efficiency	[%]	40.4	42.7
circulation rate	[$kg_{bed\ material}$ /$kg_{fuel,\ db}$]	6.5	44.5
CO_2 absorption	[kg/h]	1323	-
heat of carbonation in gasifier	[kW]	1423	-

With regard to economical analysis selected items are listed in **table 3.13**, which are of economical interest.

Table 3.13: Consumption of consumables for AER gasification and standard gasification at FICFB technology

Consumable	Unit	AER	FICFB standard gasification
Bed material		calcite	olivine
consumption	[kg/h]	~100	50 – 60
actual market price (incl. transport)	[€/t]	70 – 100	140
Gas cleaning			
precoat material	[kg/h]	-	15
actual market price	[€/t]	-	40
RME for tar scrubber	[l/h]	5 – 10	15 – 20
actual market price	[€/t]	1	1
Waste materials			
ash	[kg/h]	>100	70 – 100 kg/h
cost for ash dumping	[€/t]	usable as fertiliser	67

Summary and conclusion (TUV)

The analysis and assessment by means of the process simulation have shown the general feasibility of the AER process at FICFB technology. Essential data have been gathered, that identify the performance of the AER process. At the example of the process of the CHP Güssing, the bed material circulation is of high importance. As the temperature is the focus of a proper operation with regard to temperature, the bed material circulation is the most influencing process parameter. Furthermore, a low circulation enables a sufficient CO_2 load of the bed material, since the material residence time is increased in the gasifier. At the example of CHP Güssing, the bed material circulation directly influences the temperatures in the gasifier. This influence of the bed material circulation on the temperatures can be decoupled by constructive measures , e.g., a fluid bed cooler.

In summary, the FICFB technology has the capability to realise the AER process at large scale and commercial realisation, respectively. Specific items, like the material circulation, will necessitate minor process modification compared to FICFB standard gasification. Hence these modifications will focus on precise control of the bed material circulation and heat transport to the gasifier by means of staged fluidisation or e.g., fluid bed cooler. The impact of the heat release by the fluid bed cooler on the overall efficiency is expected to be rather low, since this heat can be used internally for preheating of gas flows or externally as part of the district heating.

As results of the high quality product gas by means of the adsorption process additional benefits are expected with regard to the gas cleaning unit. Since the product gas is characterised by a lower tar content, the gas cleaning unit can be reduced concerning its dimensions. This will directly effect the invest costs and furthermore the cost of operations, since the gas cleaning unit is continuously supplied by a tar solvent.

Promising product gas applications

ZSW evaluated different product gas applications in terms of efficiencies as presented in the following figure. In case (I), the product gas is burnt in a gas engine and the electric output is increased by an ORC cycle. In the second case, H_2 is separated from the product gas via PSA and the off-gas was burnt for CHP generation. In the last case, the product gas is methanated to obtain SNG.

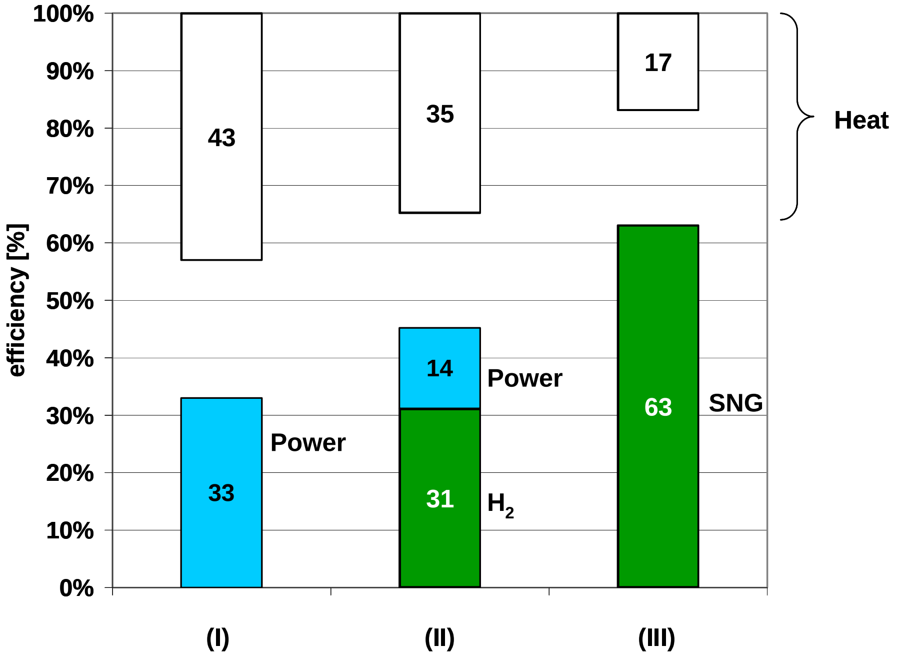

Fig. 3.60 Estimation of the efficiency for different product gas applications by process simulation: (I) CHP generation by gas engine, poly-generation of H_2 (II) via PSA or SNG (III) via methanation.

It is clearly seen that the amount of heat, generated at the gasification plant, is clearly reduced in poly-generation concepts. Therefore, (poly-)generation of fuel, power, and heat increases the over-all efficiency of a gasification plant, especially in periods / cases with a low heat demand.

Final Conclusion

In this project, the AER process was successfully transferred into commercial scale by operating the gasifier at Güssing in AER mode. Thus, it is possible to operate the gasifier in both operation modes, standard (at temperatures above 800°C) and AER (at temperatures below 800°C, which enables *in situ* CO_2 absorption). This minimises the risk for an investor with view to market launch. Even though the biomass conversion in the Güssing gasifier was not as high as during standard gasification, the cold gas efficiency was in the same range.

Regarding the costs of the gasification plant for CHP generation, the investment of an AER gasifier might be higher because the gasification reactor must be larger compared to the Güssing gasifier (due to smaller reaction rates because of lower temperatures). On the other side, the operation costs are reduced, because the CaO based bed material is available at lower costs and it need not be disposed like Olivine. In addition, low-cost biomass resources can be used as fuel in mixtures with wood. Economic advantages concerning investment are expected for poly-generation plants, because downstream gas conditioning (e.g., for SNG production) will not be necessary in case of AER gasification, simplifying the over-all process.

The AER technology has the potential to improve the gasification technology realised at Güssing because of the following important advantages:

- High quality product gas, suitable for various applications (CHP, SNG, H_2, …)
- *In situ* hot gas cleaning and conditioning, simplifying the over-all process for poly-generation
- Multi-fuel compatibility (alternative feedstock besides wood; no competition to food and heating sector)

Therefore, the market potential is increased. Related industrial sectors refer to energy supply (local utilities, gas industry), biomass delivery, plant engineering, construction, and operation.

Similar to the Güssing gasifier, AER gasification contributes to a sustainable energy supply at regional level. It focuses on poly-generation of bio-fuels and CHP in decentralised plants (<50 MW_{th}).

The commercial launch is currently realised in the frame of the AER lighthouse project, in which the first AER gasification plant will start operation in 2011. While the product gas will be used for CHP generation in a first attempt, future product gas applications deal with poly-generation of H_2 or SNG.

4 Final plan for using and disseminating the knowledge

Result 1: AER-DFB gasification process

Description (product(s) envisaged, functional description, main advantages, innovations)

The DFB (dual fluidised bed) gasification technology, commercially realised at BKG in Guessing (A), is adapted to the AER process by (1) replacing the inert bed material by a reactive CO_2 sorbent and by (2) reducing the temperature below 800°C in the biomass gasifier. A H_2 rich product gas with low tar content is obtained to be used e.g. for combined heat and power generation in a gas engine. A further advantage is that also humid and mineral-rich biomass resources are expected to be suitable fuels, having a big potential.

Currently, the first AER power plant (DFB principle) is planned in South Germany (lighthouse project)

Possible market applications

The AER-DFB technology is especially interesting for district energetic biomass utilisation (5-50 MW_{th}) in order to produce a high-quality H_2-rich gas for:

- combined heat and power generation from various biomass resources within 1-2 years
- SNG, H_2, or syngas generation within 2-4 years

Various solid biomass resources are expected to be suitable feedstock (e.g. humid wood, straw).

Stage of development (laboratory prototype, demonstrator, industrial product...)

- feasibility proof in lab-scale AER-DFB reactor (TU Vienna, Austria; Uni Stuttgart, Germany)
- transfer of technology into commercial scale (BKG, Guessing, Austria, 2007)
- construction of first AER-DFB power plant in South Germany (lighthouse project, start 2009)

Collaboration sought or offered (manufacturing agreement, financial support or investment, information exchange, training, consultancy, other)

- financial support for investment sought
- plant engineering and construction sought
- collaboration with utilities (electricity, district heating, natural / micro gas grid, …) sought
- scientific support offered
- bed material for heat transport and / or CO_2 removal in fluidised bed applications offered
- product gas utilisation: methanation unit for SNG production offered
- product gas utilisation: H_2 separation

Collaborator details (type of partner sought and task to be performed)

- investors
- utilities (electricity, district heating, natural gas grid, micro gas grid, …)
- biomass suppliers (forestry, agriculture)
- plant constructors (engineering, control, construction, …)
- plant operator, training on plant operation

Intellectual property rights granted or published

- patents

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Result 2: Physicochemical, Catalytic and Mechanistic Studies (UOC)

Description (product(s) envisaged, functional description, main advantages, innovations)

For the first time various attempts were made in order to correlate the physicochemical with the catalytic activity and H_2 selectivity properties of five (C1-C5) calcite materials (inexpensive, non-toxic) towards H_2 production via steam reforming of phenol. Moreover, important fundamental information on the effects of (a) reaction temperature, (b) water feed concentration, (c) gas hourly space velocity (GHSV, h^{-1}), and (d) the presence of H_2 and CO_2 in the feed stream on the rate of reaction at hand were found. Correlations of H_2 selectivity of reaction with the concentration of active "H-containing" (-OH and/or H) intermediate species participating in the "H-path" of phenol steam reforming using the Steady State Isotoping Transient Kinetic Analysis (SSITKA) technique were derived. This fundamental information will help to design better metal oxide-based materials for the steam reforming of tars into H_2-rich gas.

Possible market applications

- Use of natural CaO-containing materials (cheap, non-toxic) for the selective catalytic conversion of tars derived from biomass and waste-biomass steam gasification into hydrogen rich-gas industrial applications.

Stage of development (laboratory prototype, demonstrator, industrial product...)

- Laboratory prototype

Collaboration sought or offered (manufacturing agreement, financial support or investment, information exchange, training, consultancy, other)

- Financial support sought
- Consultancy offered

Collaborator details (type of partner sought and task to be performed)

- Material suppliers (e.g., companies) sought
- Catalyst manufacturers sought

Intellectual property rights granted or published

- Publications
- Oral and poster presentations

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Result 3: FB coating of particles

Description (product(s) envisaged, functional description, main advantages, innovations)

The coating method developed at IFE for limestone bed materials has shown interesting results. Mechanical properties of C14 materials were increased by 18% while the absorption properties of the materials were not significantly modified. However, results were shown to be strongly influenced by the nature of the coating solution and many process parameters such as residence time in the fluidized bed coating reactor and the calcination temperature. A new research program will start in 2010 sponsored by the Norwegian research council to continue the development of the process. IFE intends to start a patent application on the coating method and publish the results in international journals as soon as the process is optimized.

Possible market applications

In the future, IFE will pursue the research in the field in order to define the ideal process parameters and start an extended screening of coating solutions suitable for industrial processes such as AER gas process, production of H2 by sorption-enhanced steam methane reforming or post-combustion high-temperature CO2 capture applications.

Coating methods are quite commonly used in various industries such as pharmaceutical industry, paper industry and paint industry or for electrochemical applications. Fluidized bed coating is a novel method that can very easily be scaled up for production of large batches of coated particles at a limited cost. This application will open new potential applications for the lime industry.

Stage of development (laboratory prototype, demonstrator, industrial product...)

The coating method was developed using lab scale equipment using a bench-scale fluidized bed agglomerator. Scaling-up of the method is thought to be quite simple.

Collaboration sought or offered (manufacturing agreement, financial support or investment, information exchange, training, consultancy, other)

Once the method will be finalized, external investors and chemical companies will be contacted for licensing and large scale production of sorbents.

Collaborator details (type of partner sought and task to be performed)

- *investors*
- *chemical industries*
- *mineral providers*

Intellectual property rights granted or published

A patent application is thought to be filled up by 2010 on the coating method for improvement of mechanical properties of sorbent materials.

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