



The positive effects of bed material coating on tar reduction in a dual fluidized bed gasifier

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ABSTRACT

The utilization of biomass for the substitution of fossil fuels to reduce greenhouse gas emissions in biomass steam gasification plants is a promising technology for the production of electricity, heat, and fuels for transportation. Experience from industrial scale dual fluidized bed steam gasification plants showed a modification of the bed material due to the interaction of the bed material (olivine) with biomass ash components and additives. In this paper the influence of bed material modification on the gasification properties of used olivine from an industrial scale plant in Güssing is compared with the case of fresh olivine. The trials were carried out under similar conditions in a pilot plant at the Vienna University of Technology. The pilot plant trials showed an increase in hydrogen and carbon dioxide in the product gas with the used bed material while the content of carbon monoxide in the product gas decreased. The exothermal water–gas shift reaction is enhanced by the used bed material, resulting in a lower energy demand for the gasification. Tar content was decreased by around 80% for tars detected by gas chromatography–mass spectrometry (GCMS) and the composition of the tar showed less components during the trial with used bed material.

The results obtained with the used bed material at the 100 kW pilot plant are in good agreement with those for the 8 MW industrial plant in Güssing, confirming good scale-up properties from the 100 kW plant to industrial scale plants.

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1. Introduction

Biomass can play a significant role by substituting for fossil fuels which cause greenhouse gas emissions in the production of electricity and second generation biofuels [1]. Biomass is a renewable source and releases the same amount of carbon dioxide during energy usage or natural decomposition as it aggregates during the growth period. Using woody biomass for steam gasification is a promising technology that has been successfully demonstrated since late 2001.

The basic principle of biomass gasification is the thermal decomposition of biomass using a gasification agent such as steam, air, or carbon dioxide to produce a combustible gas consisting mainly of hydrogen, carbon monoxide, carbon dioxide, and methane. If air is used as a gasification agent a high amount of nitrogen is present in the producer gas, which reduces its heating value. The gas can be utilized for electricity production, fuel synthesis or synthetic natural gas.

Dual fluidized bed (DFB) steam gasification for biomass was developed by the Institute of Chemical Engineering, Vienna University of Technology [2]. A pilot plant (100 kW) is in operation at the Institute of Chemical Engineering, Vienna University of Technology, with various research activities concerning bed material [3–5] or different fuels [6,7]. This process was brought to the market by the first plant in Güssing (Austria; 8 MWth) in 2001, followed by plants in Oberwart (Austria; 8.5 MWth), Villach (Austria; 15 MWth), Ulm (Germany; 11.5 MWth), Göteborg (Sweden; 32 MWth), which commenced operation recently or are currently in the realization phase [4]. Various research activities concerning further utilization of the product gas in addition to production of heat and electricity are ongoing at the plants in Güssing and Oberwart [8,9].

The advantage of DFB steam gasification is the usage of steam as a gasification agent to avoid the introduction of nitrogen into the producer gas. It results in a producer gas with a high calorific value of 12–14 MJ/Nm³ (referred to as dry gas) and a high hydrogen content. To supply the thermal energy that is required for the endothermic gasification reactions in the bubbling bed a separate combustion zone with a fast fluidized bed is used. The bed material, which is heated up in the combustion zone, is transferred to the gasification zone.

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The main gasification reactions are shown in Table 1. These reactions are considered as equilibrium reactions with variable equilibrium conditions according to Le Chatelier's principle depending on gas concentrations, temperature and pressure. Since various reaction paths are possible, an enhancement of reaction paths is possible through the use of catalysts.

Undesired by-products of biomass gasification are described by the collective term "tars". Tars are defined as follows: "The organics, produced under thermal or partial-oxidation regimes (gasification) of any organic material, are called 'tars' and are generally assumed to be largely aromatic" [10].

These tars cause operational problems when cooled down and condensed at heat exchangers, plugging pipes, and so on. Various research activities focus on reduction of these tars before further utilization of the product gas. The chemical reactions concerning tar reduction are described in Table 2 for toluene as a model component. Similar reactions can be described for the other tar components. These chemical equations allow a wide range of reaction schemes and show the complexity of the topic.

To decrease the amount of tar in the product gas, catalytic material is used in the fluidized bed.

The use of olivine as a bed material has become state of the art in industrial scale DFB steam gasification plants. Additionally calcium-rich additives such as calcite or dolomite are used for further reduction of the tar content in the producer gas. Experience from the industrial scale plant in Güssing, Austria, showed that biomass ash and additives interact with bed material, building calcium-rich layers around the particles. The inner layer is homogeneous, composed mainly of calcium and silicate, while the outer layer has a similar composition to the fly ash of the plant [13]. Fig. 1 shows a micrograph of a used bed material particle and the results of energy-dispersive X-ray (EDX) spectroscopy are shown in Table 3. The positive effects of this calcium-rich layer on the tar reduction and the influence on the gas composition are known from the experience of the plant in Güssing. Experience also showed that the catalytic properties of the bed material improve with a higher retention time of the bed material in the system. This effect has not yet been described in detail or quantified.

The significant increase in calcium in the surface layer of the bed material leads to the assumption that the catalytic properties of the used bed material are dominated by the calcium-rich surface. Small amounts of potassium are also detected.

The positive effect of olivine on tar reduction has been reported by various authors with regard to various fuels [4,14–21]. A better catalytic activity of the olivine can be achieved by calcination of olivine [14,22]. Even better conversion is achieved by the use of modified olivine such as Ni-olivine, Fe-olivine [4,20,23–26] or synthetic catalysts [27–29].

Dolomite also showed good results with regard to the catalytic activity for reducing tars [3,4,18,30–33].

A comparison of dolomite and inert bed material was carried out by Ruoppolo et al. [27]. They reported a 50% higher tar conversion in a fluidized bed using dolomite as bed material compared to quartzite as well as a simplification of tar components.

Table 1
Typical equilibrium reactions of the main gas components [11,12].

Name of reaction	Chemical equation	ΔH (kJ/mol)	
Water-gas shift	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	-40.9	Formula (1)
Methane reforming	$\text{CO} + 3 \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$	-225	Formula (2)
Water-gas (i)	$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$	118.5	Formula (3)
Water-gas (ii)	$\text{C} + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2 \text{H}_2$	103	Formula (4)
Boudouard	$\text{C} + \text{CO}_2 \leftrightarrow 2 \text{CO}$	159.9	Formula (5)
Methanation	$\text{C} + 2 \text{H}_2 \leftrightarrow \text{CH}_4$	-87.5	Formula (6)
Oxidation (i)	$\text{C} + \text{O}_2 \leftrightarrow \text{CO}_2$	-393.5	Formula (7)
Oxidation (ii)	$\text{C} + 0.5 \text{O}_2 \leftrightarrow \text{CO}$	-123.1	Formula (8)

Corella et al. [18] reported that the tar removal efficiency with dolomite was ~1.4 times better compared to olivine in a fluidized reactor. In a previous publication the authors concluded [34] that the introduction of dolomite into the fluidized bed gives better results compared to a down-stream usage of dolomite in a second reactor. The polymerization of tars is suspected to take place when using a gasification reactor with silica sand and a down-stream reactor with dolomite.

A laboratory scale quartz tube reactor was used by Simell et al. [11] to study the decomposition of toluene, which was used as a model component for tar over dolomite and nickel catalyst. They concluded that the dry reforming reaction (Formulas (15) and (16)) and steam reforming reaction (Formulas (9) and (10)) take place with both catalysts. The presence of steam inhibits the dry reforming reaction but tar decomposition is carried out with steam reforming. The presence of CO on dolomite strongly inhibited the tar decomposition on dolomite.

Alarcón et al. [35] studied the catalytic activity of a mixture of CaO with MgO for naphthalene steam gasification in a fixed bed. While pure MgO and CaO achieved carbon conversion of 54% and 62%, respectively, a mixture of 10% CaO and 90% MgO showed the highest carbon conversion, 79%. A catalytic synergy between the two oxides was described.

Similar results were published by Delgado et al. [36]. The authors studied the catalytic activity of calcined dolomite, calcite, and magnesite in a fixed bed reactor reforming product gas of a fluidized bed gasification reactor. The fixed bed reactor was loaded with the examined catalyst. They reported better gas yields and tar reduction with dolomite followed by calcite and magnesite.

Kyotani et al. [37] investigated the mechanism of calcium catalysis of carbon gasification with oxygen. They found that calcium enhances the formation of CO₂ in carbon gasification with O₂. The process was explained as follows: O₂ dissociatively chemisorbs on CaO particles to form CaO(O). The active oxygen from CaO(O) quickly migrates to the carbon surface to form C(O). When active sites around CaO are occupied by C(O), oxygen reacts with the C(O) at the active site to CO₂ which is released leaving an active site on the CaO.

Nair et al. [38] studied the tar removal of biomass-derived fuel gas by pulsed corona discharge with respect to the decomposition scheme of naphthalene. They concluded that the most favorable pathway for tar decomposition is the direct attack of oxygen radicals.

This theory is also confirmed by studies by Chen and Yang [39] on alkali and earth alkali metals where the authors catalyzed gasification reactions of graphite by CO₂ and H₂O. They reported the formation of C–O–M groups, where M denotes for the metal. Oxygen radicals have their origin in CO₂ and H₂O. In earlier studies they found that particles are more active than single C–O–K groups [40].

However, the usage of bed materials with better catalytic activity than olivine is desired. Alternative bed materials to olivine often face problems with attrition (e.g. dolomite [4,19]) or their preparation is expensive (e.g. synthetic catalysts). The disposal of wastes of alternative bed materials such as nickel coated bed material is also problematic.

An exact statement about the influence of the formation of a calcium-rich layer on the catalytic properties of the bed material is not available. To study this effect, used bed material from the industrial scale gasification plant in Güssing, Austria, was used in the 100 kW DFB steam gasification pilot plant at the Institute of Chemical Engineering, Vienna University of Technology, and compared with the results of the utilization of unused olivine under the same conditions.

This paper summarizes the latest investigations of the catalytic properties of used olivine with a calcium-rich layer with regard to

Table 2
Possible reactions of hydrocarbons in hot gas cleaning conditions, with toluene as model hydrocarbon[11].

Name of reaction	Chemical equation	ΔH kJ/mol	
Steam reforming	$C_7H_8 + 7 H_2O \rightarrow 7 CO + 11 H_2$	876	Formula (9)
	$C_7H_8 + 14 H_2O \rightarrow 7 CO_2 + 18 H_2$	647	Formula (10)
Steam dealkylation	$C_7H_8 + H_2O \rightarrow C_6H_6 + 2 H_2 + CO$	123	Formula (11)
	$C_7H_8 + 2 H_2O \rightarrow C_6H_6 + 3 H_2 + CO_2$	90	Formula (12)
Hydrocracking	$C_7H_8 + 10 H_2 \rightarrow 7 CH_4$	-713	Formula (13)
Hydrodealkylation	$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$	-104	Formula (14)
Dry reforming	$C_7H_8 + 7 CO_2 \rightarrow 14 CO + 4 H_2$	1105	Formula (15)
	$C_7H_8 + 11 CO_2 \rightarrow 18 CO + 4 H_2O$	1236	Formula (16)
Thermal cracking	$nC_7H_8 \rightarrow m C_6H_6 + p H_2$	-	Formula (17)
Carbon formation	$C_7H_8 \rightarrow 7 C + 4 H_2$	-73	Formula (18)

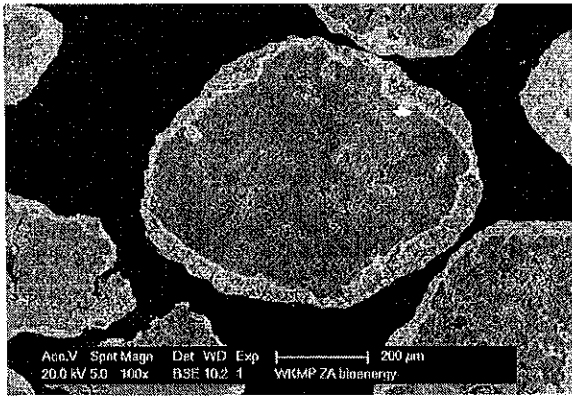


Fig. 1. Layer formation on used olivine [13].

Table 3
EDX: Comparison of unused and used olivine [13].

Olivine	Unused olivine		Used olivine	
	Particle inside (wt.%)	Particle inside (wt.%)	Inner layer (wt.%)	Outer layer (wt.%)
C	n/a	n/a	5.3	9.8
O	15.2	14.2	12.9	13.7
Mg	37.4	30.3	8.6	18.5
Al	0.1	0.7	0.1	0.1
Si	35.5	32.2	17.3	15.4
P	n/a	0.0	n/a	0.3
K	n/a	8.5	2.6	3.2
Ca	n/a	1.8	46.5	33.5
Cr	n/a	n/a	2.7	0.4
Mn	n/a	0.0	0.9	1.2
Fe	11.8	12.5	3.0	3.7

n/a = not applicable.

gas composition and tar reduction, and the results from an industrial scale plant are compared with results from the pilot plant.

2. Experimental section

Two trials were carried out at a 100 kW pilot plant, one using fresh olivine as a reference and one using used olivine from the industrial plant in Güssing. The results of these trials were compared with the results of the industrial scale plant in Güssing.

2.1. DFB biomass gasification

The DFB biomass-steam gasification plant in Güssing, Austria, has a thermal power of 8 MW and an electrical power of 2 MW. The plant went into operation in late 2001 and had an operation

time of 60,000 h at the gasifier and 54,500 h at the gas engine up to September 2011. Wood residues harvested in the local area are used as fuel. Various literature is available about the plant [2,41,42].

A basic flow sheet of the plant is shown in Fig. 2. Biomass is fed into the gasifier via a screw system and is gasified in a bubbling bed in the gasifier at 850 °C using steam as a gasification agent. Bed material also containing char is transferred to the combustion zone, where char is combusted in a fast fluidized bed at 930 °C. Air is used for fluidization in the combustion zone. The bed material is separated from the flue gas in the cyclone and transported back into the gasifier, providing the heat for the gasification. The flue gas is further cooled down and the fly ash is separated in the flue gas filter. A part of the fly ash is circulated into the gasifier due to its positive effects on tar reduction and to save bed material consumption.

The product gas is cooled down after leaving the gasifier and particles are separated from the gas stream in the product gas filter. The fly coke from the product gas filter contains inorganic matter such as biomass ash, additives, and products of bed material abrasion as well as unconverted char and tar. To utilize the remaining combustible substances, the fly coke is burnt in the combustion zone. After the separation of the particles from the product gas in the product filter, the gas is washed in a rapeseed methyl ester (RME) scrubber to remove water and tars. The cleaned gas is then utilized in a gas engine to produce electricity and heat. A small amount of the product gas is used to control the temperature of the combustion zone.

2.2. Description of the pilot plant

At the pilot plant at the Institute of Chemical Engineering, Vienna University of Technology, the basic design parameters of the gasifier in Güssing, Austria were developed. The basic principal of the gasifier is the same as that of the industrial scale plant in Güssing but due to its size some details are different. The pilot plant shown in Fig. 3 is well-described in literature [4,6,7].

However, the gasifier consists of a gasification zone with a bubbling bed, which is fluidized by steam, and a combustion zone with a fast fluidized bed, which is fluidized by air. The bed material is circulated between the two zones to carry the heat from the combustion zone to the gasification zone. The separation of the bed material and the flue gas after the combustion zone is carried out using a gravity separator. Siphons are located between the gasification zone and the combustion zone to avoid leakage of gases from the combustion zone such as air or flue gas into the gasification zone.

The fuel is dosed into the fluidized bed of the gasifier where water and volatile components of the fuel are released. The remaining char is gasified with steam. A part of the char is trans-

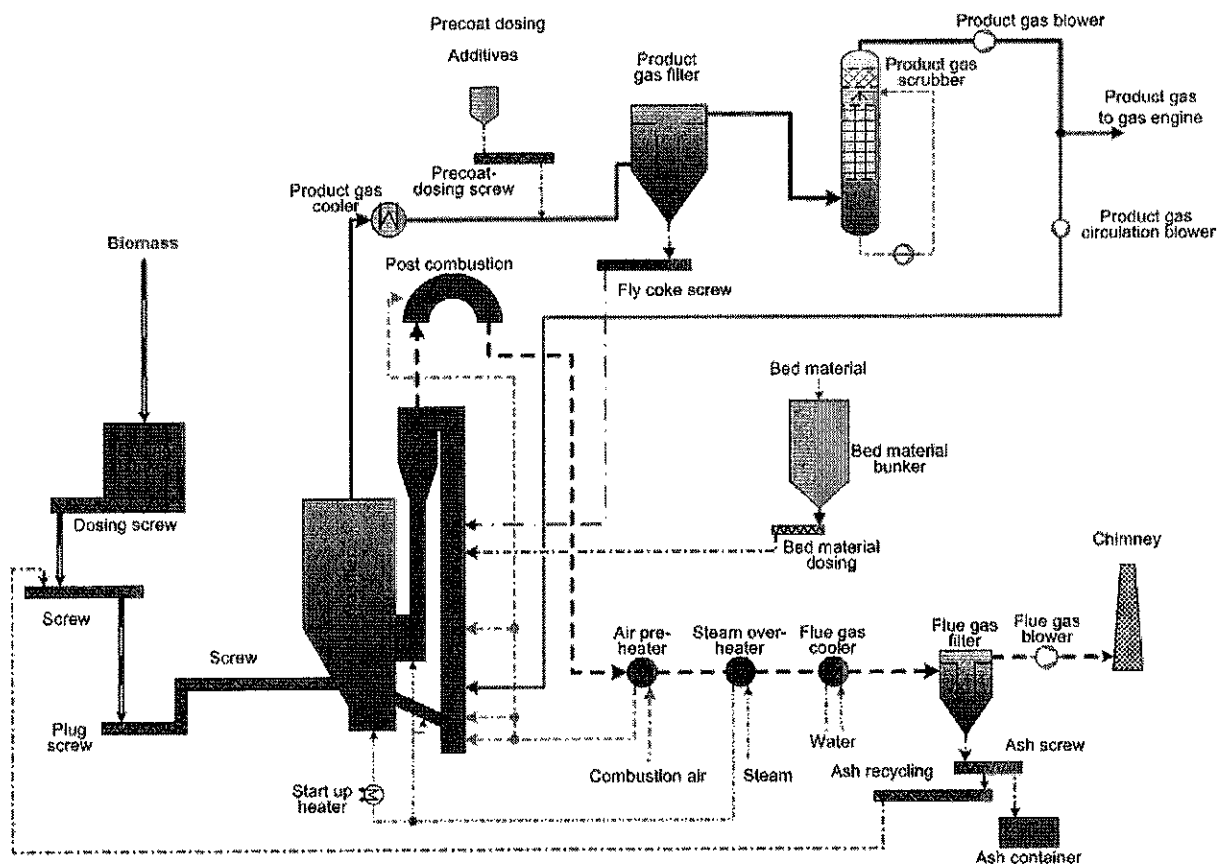


Fig. 2. Basic flow sheet of the DFB gasification in Güssing, Austria [13].

ported with the bed material to the combustion zone, where the char is burnt.

In contrast to the industrial scale plant the pilot plant is designed to add fuel into the combustion zone to provide a part of the required heat to the gasification not via transport through the chute but from outside the system. Light fuel oil is used in the pilot plant. The amount of fuel in the combustion zone with constant gasification temperatures allows a qualitative evaluation of the gasification properties of the fuel or a comparison of the bed material using the same fuel. In the industrial scale gasifier, fly coke from the filters, tar, saturated RME, and a small quantity of product gas are injected into the combustion reactor. The product gas is used to control the temperature.

The pilot plant is equipped with gas measurement in the product gas stream and in the flue gas stream.

2.3. Sampling at the industrial scale plant

The required amount of used bed material (150 kg) for the trial in the pilot plant was taken from the plant in Güssing in December 2010. The bed material was taken during regular operation from the bottom of the combustion zone. To avoid impact on the production of the plant, several batches were taken over a period of 2 days.

To have a similar particle size distribution compared to fresh olivine, the used bed material was sieved and the fractions smaller than 400 μm and bigger than 1 mm were removed to avoid the presence of fine ash or nails and broken refractory lining in the pilot rig.

Gas analyses at the industrial scale plant were carried out with a Clarus 500 gas chromatograph (GC) made by Perkin Elmer. The GC is equipped with three different columns: one molecular and two non-polar (Porapak) sieves, connected with two automated valves and an injection loop of 500 μl . Helium is used as the carrier gas. Two types of detectors are used: a thermal conductivity detector (TCD) for the permanent gases (O_2 , N_2 , CO , CO_2) and a flame ionization detector (FID) for hydrocarbons up to a carbon number of three. The hydrogen concentration is calculated as 100 minus the sum of the gas concentration given by the two detectors.

The average values of various measurements taken over the period from the beginning of October until the middle of January were calculated and used for comparison.

2.4. Sampling at the pilot plant

Wood pellets were used as a fuel in the trials in the pilot plant. A wood pellet sample was taken before both trials in the pilot plant and analyzed. The same batch of wood pellets was used for both trials. To obtain representative values the samples were taken on the basis of DIN 51701. Ash content was determined according to DIN 51719 but at 550 $^{\circ}\text{C}$. The content of volatile matter was determined using DIN 51720 and the higher and lower heating values according to DIN 51900 T2.

The elemental composition of the unused and used bed material was determined by X-ray fluorescence (XRF) and calculated as oxides. Samples for XRF were melted in a Merck Spectromelt at 1050 $^{\circ}\text{C}$ and dumped on a 400 $^{\circ}\text{C}$ stainless steel plate. The analyses were carried out with a PANalytical Axios Advanced analyzer under a vacuum atmosphere with a rhodium anode, an excitation

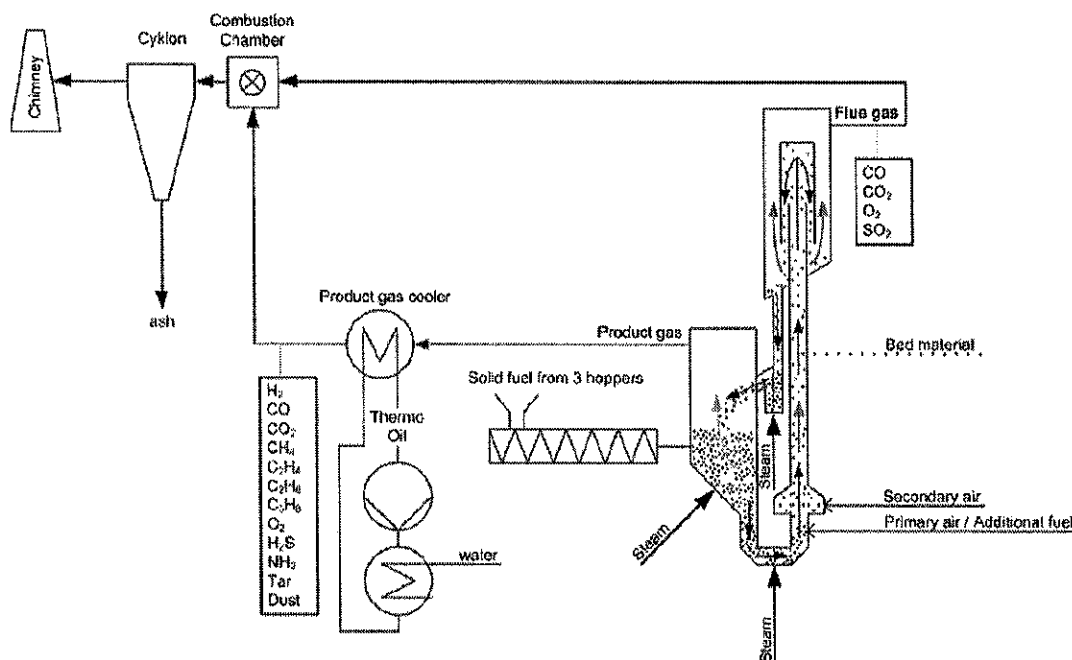


Fig. 3. 100 kW pilot plant [7].

voltage of 50 kV, and a tube current of 50 mA. The results indicate the elemental composition of the total sample calculated in oxides.

Gas and tar analysis of the product gas of the pilot plant is well-described in the literature [4–7]. Carbon monoxide, carbon dioxide, methane and hydrogen were measured by a Rosemount NGA2000. The components nitrogen, ethylene, ethane, and propane were measured by a gas chromatograph (Syntech Spectras GC 955). For the calculation of average values a stationary phase of the plant was taken into consideration. The stationary phase for the trial with unused bed material lasted for 2:25 h, while the one for the trial with used bed material lasted for 1:05 h. Tars are absorbed in toluene and measured similarly to the tar protocol. Detailed descriptions of the tar measurement are given by Wolfesberger et al. [43] and Aigner et al. [44]. Gravimetric tars represent the heavy tars while GCMS tars represent the smaller tar molecules. As the measurement ranges of both tar analyses overlap, they cannot be added. Three samples of tar were taken during each trial and averages were calculated.

The simulation software IPSEpro was used to calculate mass and energy balance to determine gas yields. The software and model library is described by Proell and Hofbauer [45].

2.5. Used materials at the pilot plant trials

To ensure similar fluidization and gasification conditions with used and with unused bed material, a similar particle size distribution is required for both bed materials. Fig. 4 shows the particle size distribution of both bed materials and Table 4 shows the characteristic values for the particle size of the bed material.

Due to variations in the operating conditions at the industrial plant in Güssing, the used bed material that was used for the trial in the pilot plant was analyzed to determine the elemental composition. The results are shown in Table 5. The main difference between the elemental compositions of the unused and the used bed material is the content of calcium and potassium. From earlier investigations it is known that calcium occurs mainly in the layers on the surface of the particle [13].

Wood pellets were used as fuel in both trials in the pilot plant. The composition of the fuel used in both trials is shown in Table 6. Wood pellets were chosen because they have better conveying properties in the screw feeder of the pilot plant and because their composition is similar to that of the used fuel in the industrial plant. The water content of the pellets (6.74%) is significantly lower than the water content of the wood chips used in the plant in Güssing, which is 20–30% [22].

3. Results and discussion

The operational parameters at the pilot plant were chosen to be similar to those of the industrial scale plant in Güssing. Table 7 shows a summary of important operational parameters. The marked values are the measurements of set points. The other values are given by the operating conditions. The chosen operating temperature of the gasifier is 850 °C because experience at the plant in Güssing has shown that this gasification temperature ensures safe production. A higher steam-to-carbon ratio was required in the pilot plant compared to the plant in Güssing to reach fluidization properties.

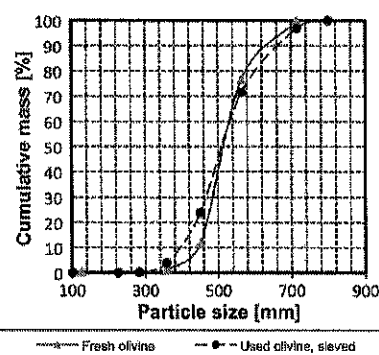


Fig. 4. Particle size distribution of the bed material.

Table 4
Particle size of the bed material.

	Unit	Fresh olivine	Used olivine, sieved
d_{p10}	μm	445	395
d_{p50}	μm	514	510
d_{p90}	μm	630	662

Table 5
Elemental composition of the bed material.

Metal oxide	Fresh olivine (wt.%)	Used olivine (wt.%)
Na_2O	0.43	1.67
MgO	46.76	40.52
Al_2O_3	0.40	0.44
SiO_2	39.84	33.60
P_2O_5	0.03	0.19
SO_3	0.06	0.08
K_2O	0.32	3.89
CaO	0.90	10.71
Cr_2O_3	0.28	0.38
MnO	0.15	0.24
Fe_2O_3	10.32	7.45
NiO	0.31	0.33
Cl	0.10	0.27
Others	0.11	0.23

Table 6
Fuel analysis of the fuel for the pilot plant.

Parameter	Value	Unit
C	51.07	mass% db
H	5.79	mass% db
N	0.13	mass% db
S	0.005	mass% db
Volatile matter content	86.12	mass% db
LHV (dry base)	19.0	MJ/kg db
HHV (dry base)	20.3	MJ/kg db
Ash	0.32	mass% db
Water content	6.74	mass%

db – dry base with ash.

Table 8 shows the performance parameters of the pilot plant for the trial with fresh olivine and used olivine. The gasification conditions in the gasifier were similar and performance difference is indicated mainly by the oil consumption. To get a good comparison of the efficiency the total gas yield is referred to the total fuel input which consists of fuel to gasifier and fuel to combustion zone.

The gas composition of the two trials in the pilot plant and the industrial scale plant is shown in Fig. 5. While the trial with the used olivine in the pilot plant shows similar results compared to the industrial scale plant, the results for fresh bed material in the pilot plant show a significantly higher CO content and significant lower CO₂ and H₂ contents. The values from the industrial scale plant show a higher deviation compared to the pilot plant due to

Table 8
Performance parameters of the pilot plant (results from mass and energy balance).

	Unit	Reference trial at the pilot plant with fresh olivine	Pilot plant with used bed material from Güssing
Gas yield	$\text{Nm}^3/\text{kg wood (db)}$	1.06	1.09
Total gas yield	$\text{Nm}^3/\text{kW total fuel input (db)}$	0.157	0.172

varying fuel quality (moisture content) and instability of inorganic flows (e.g. bed material consumption and ash circulation).

Comparison of the trials from the pilot plant with fresh and used bed materials reveals an enhancement of the water–gas shift reaction, Formula (1), with used bed material, which leads to higher H₂ and higher CO₂ contents, while the CO content decreases. Additionally, the water–gas shift reaction is slightly exothermic, which explains the lower fuel consumption in the combustion chamber in the trial with the used bed material, as shown in Table 7, considering a similar bed material circulation. The pressure profile of the pilot plant is shown in Fig. 6 indicates similar operating conditions in the trials. The pressure difference at the combustion zone can be explained by the slightly higher mean particle size for the used bed material shown in Table 4. This pressure difference may indicate a lower circulation rate, which should cause a higher temperature in the combustion chamber when the same energy demand is assumed in the gasifier. However, the temperature in the combustion zone is significantly lower with used olivine at the same gasification temperature, indicating again a lower energy demand for gasification.

The tar content of the product gas in the pilot plant is shown in Fig. 7. It indicates that substantially lower tar content was found with the used olivine from Güssing independently of the method of analysis. The GCMS measured tars decreased by 82% and the gravimetric tars decreased by 65%.

Fig. 8 shows the detailed GCMS analyses of tar components for both trials including the chemical structure of the components. The concentrations are presented on a logarithmic scale. The trial with used bed material showed fewer components in the tar composition. Various components mostly large multi-ring hydrocarbons, were not detectable. This reduction in tar species due to gasification with calcium-rich bed material was also described by Ruopolo et al. [27].

The tar component with the highest content in both cases was naphthalene. Anthracene was the component with the second highest concentration in the trial with the unused olivine but due to a better reduction rate with used bed material it had the third highest content in the trial with used bed material, while acenaphthylene had the second highest content. Acenaphthylene showed a lower relative reduction rate than the average of the

Table 7
Operational parameters at the industrial scale plant and the pilot plant.

	Unit	Reference trial at the pilot plant with fresh olivine	Pilot plant with used bed material from Güssing	Industrial scale plant in Güssing
Gasifier bed temperature	°C	852 ± 2 ^a	850 ± 1 ^a	850 ^a
Riser temperature	°C	897 ± 2	872 ± 1	~930
Fuel input	kW	97 ^a	97 ^a	8 000 ^a
Fuel into the combustion zone	kg/h	3.23	2.54	–
Total fuel input	kW	135 ^b	127 ^b	–
Steam to carbon ratio	– (kg/kg)	1.8 ^a	1.8 ^a	1.2–1.6

^a Set points and target values respectively.

^b Results from mass and energy balance.

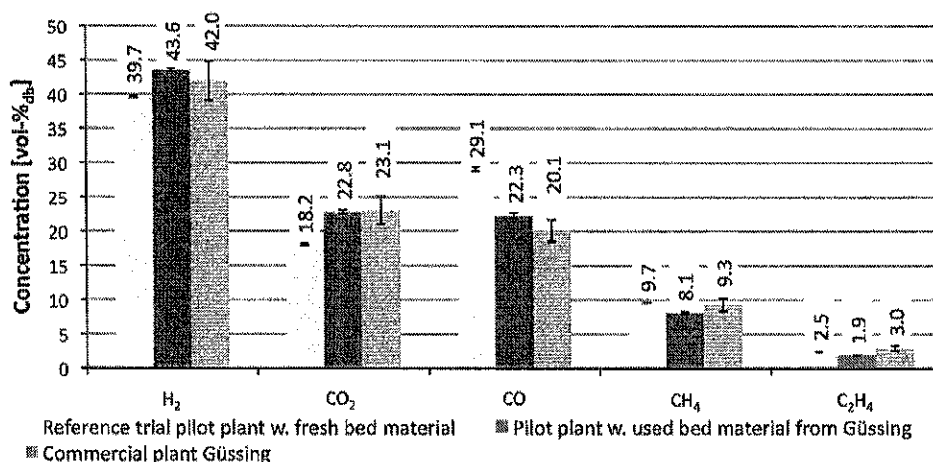


Fig. 5. Product gas composition of unused and used bed material at the pilot plant compared with the industrial scale plant.

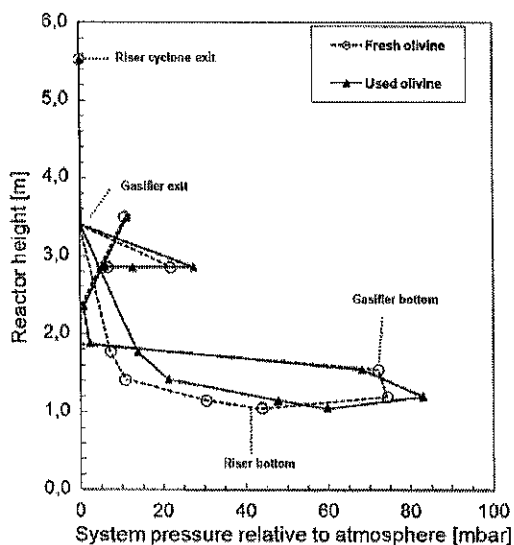


Fig. 6. Pressure profile over the DFB pilot plant.

GCMS tars. Anthracene showed the highest absolute reduction from the components which were detected in both trials, followed by naphthalene and acenaphthylene. Styrene had the lowest relative reduction rate (45%) and had the fourth highest absolute concentration in the trial with the used bed material. Multi-ring hydrocarbons with four or more rings such as benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, and indeno(1,2,3-c,d)pyrene were detected in the trial with the fresh bed material but not in the trial with used bed material. One exception was pyrene, which could be detected in the trial with used bed material but showed a higher relative reduction rate (91%) compared to the total tars. Phenol and phenylacetylene were detected in the trial with fresh bed material but not detected in the trial with used bed material. Methyl-naphthalene showed low relative reductions, with 2-methyl-naphthalene achieving better reduction. Benzofuran and dibenzofuran showed above average relative reduction rates of 88% and 92% respectively. Fluorene also had a high relative reduction rate of 95%. Phenanthrenes showed similar contents; 73 mg/Nm³ for phenanthrene and 71 mg/Nm³ for 4,5-methylphenanthrene. The relative reduction rate of phenanthrene was significantly high-

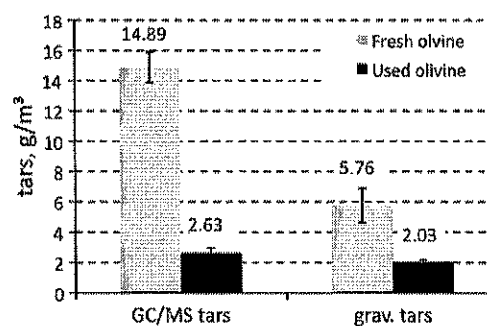


Fig. 7. Tar contents with fresh and used olivine in the pilot plant.

er (97%) compared to that of 4,5-methylphenanthrene (66%). The reduction rate of 1H-Indene was above average at 87%, while that of biphenyl was slightly below average at 80%. Fluoranthene showed a reduction rate of 85% which was slightly above the average.

The decrease in multi-ring polycyclic aromatic hydrocarbons with the usage of calcium-rich bed material is in accordance with experience from the literature. Longwell, summarized by Milne et al. [10], states that thermal treatment with CaO in coal gasification removes newly formed pyrolysis tars and pure aromatic compounds such as multi-ring polycyclic aromatic hydrocarbons and benzene respectively. Devi et al. [16] suggest the reaction scheme of naphthalene decomposition. In agreement with this reaction scheme these trials confirmed the theory that the recombination of cyclic hydrocarbons into multi-ring hydrocarbons is inhibited. The tar composition of the trial with used bed material showed no multi-cyclic hydrocarbon with more than three rings. The decomposition products of naphthalene seem to react with small molecules to form small single-ring hydrocarbons such as styrene, methyl-naphthalene, and acenaphthylene.

Milne et al. [10] summarize examinations by Alden et al., stating that almost all components of tar are non-polar after catalytic cracking with dolomite. This is confirmed by this study. Phenol was not detectable in the trial with the used bed material.

While phenanthrene was reduced in the trial with used bed material to close to the detection limit, anthracene is available in significant amounts and has the second highest concentration after naphthalene.

Summarizing the tar analyses, it can be concluded that the layer formation on the bed particles shows very positive effects on tar reduction.

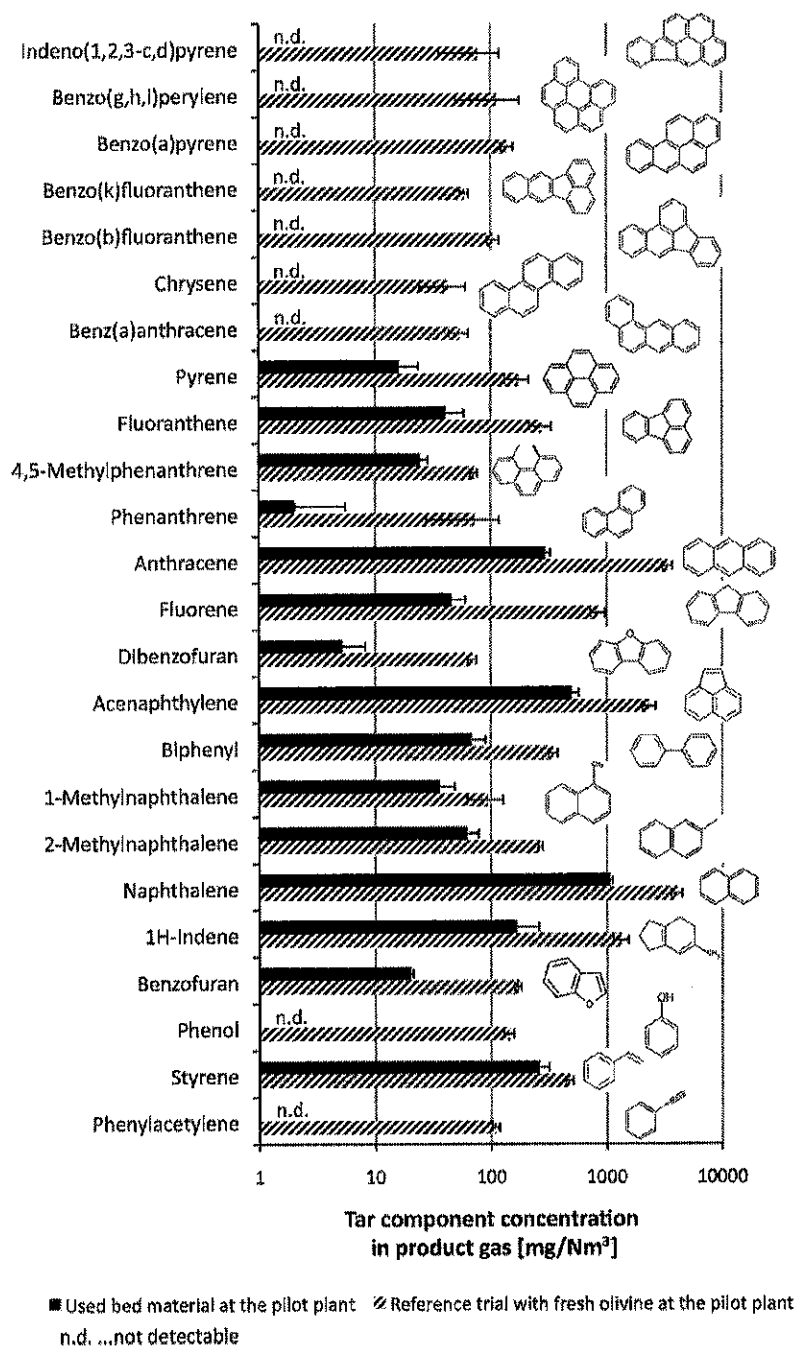


Fig. 8. Comparison of tar components in the pilot plant.

Considering the main components of the layer on the bed material the following elements have to be considered catalytically active: calcium oxide, magnesium oxide, and potassium oxide.

Potassium is available in concentrations of about 4% in bed material and fly ash but not detectable in crystal structures [13]. The catalytic activity of potassium is lower compared to dolomite [46]. According to Thy et al. [47], potassium is forced out of the crystal structure with high CaO concentration and is mainly present in gasified form. Considering this along with the finding of Chen and Yang [40] that the catalytic activity of clusters (particles) is significantly higher than that of C–O–M groups, the catalytic

activity of potassium can be considered to be insignificant in this case.

The catalytic properties of olivine are well-proven. Since the results of the trial with used bed material showed these significant improvements in the catalytic activity, calcium and probably the mix of calcium and magnesium are considered to be the component that causes the catalytic improvements.

The comparison of the gas composition from the industrial plant in Güssing and the trial with the used bed material from Güssing presented in Fig. 5 shows very similar gas compositions of the pilot plant and the industrial scale plant with the same bed mate-

rial. Also, the results of tar analyses of the trial with the used olivine are in the range of published values of the plant in Güssing. Rauch et al. published values of around 1–2 g/Nm³, assuming that the only reason for the tar reduction was the calcination of the olivine [22]. Results from the plant in Güssing published recently by Aigner indicate GCMS tar values of around 2 g/Nm³ and gravimetric tars values of around 1.8 g/Nm³ for wood as a fuel [48].

As shown with these results, the performance of the pilot plant can be easily transferred to the industrial scale plant. A good scale-up of the 100 kW pilot plant to industrial scale plants seems to be possible when the long term interaction of ash and additives with the bed material is considered.

4. Conclusions

The comparison of fresh olivine and used olivine from an industrial scale plant showed significant influence on the gas composition and catalytic effects on tar reduction. The difference between the effects of fresh olivine and the used olivine on the gasification properties is caused by the formation of a calcium-rich layer on the used bed material due to the interaction of bed material with biomass ash and additives.

The calcium-rich catalytic bed material promotes the exothermic water–gas shift reaction, which increases the hydrogen and carbon dioxide content of the product gas while the carbon monoxide content is decreased. The lower energy demand for the gasification confirmed the assumption of the promotion of the water–gas shift reaction.

The comparison of the results of the trial with used bed material from Güssing in the 100 kW pilot plant with data from the industrial scale plant in Güssing showed good scale-up properties.

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References

- [1] Bridgewater AV. The technical and economic feasibility of biomass gasification for power generation. *Fuel* 1995;74(5):631–53.
- [2] Hofbauer H, Rauch R, Loeffler G, et al. Six years experience with the FICFB-gasification process. In: 12th European conf biomass and bioenergy. Amsterdam, The Netherlands: self-published; 2002.p. 4.
- [3] Koppatz S, Pfeifer C, Rauch R, et al. H₂ rich product gas by steam gasification of biomass with in situ CO₂ absorption in a dual fluidized bed system of 8 MW fuel input. *Fuel Process Technol* 2009;90(7–8):914–21.
- [4] Pfeifer C, Koppatz S, Hofbauer H. Catalysts for dual fluidised bed biomass gasification – an experimental study at the pilot plant scale. *Biomass Convers Bioref* 2011;1–12.
- [5] Pfeifer C, Puchner B, Hofbauer H. Comparison of dual fluidized bed steam gasification of biomass with and without selective transport of CO₂. *Chem Eng Sci* 2009;64(23):5073–83.
- [6] Wilk V, Kitzler H, Koppatz S, Pfeifer C, Hofbauer H. Gasification of waste wood and bark in a dual fluidized bed steam gasifier. *Biomass Convers Bioref* 2011;1(2):91–7.
- [7] Aigner I, Pfeifer C, Hofbauer H. Co-gasification of coal and wood in a dual fluidized bed gasifier. *Fuel* 2011;90(7):2404–12.
- [8] Rauch R, Hofbauer H, Săcăreanu S, Chiru A. From gasification to synthetic fuels via Fischer-Tropsch synthesis. *Bull Transilv Univ Brasov – Series I – Eng Sci* 2011;3.
- [9] Rehling B, Hofbauer H. Bio-SNG from biomass – first results of a demonstration plant. In: ICPS 09 – Int conf polygeneration strategies. Vienna, Austria: self-published; 2009.
- [10] Milne T, Evans R, Abatzoglou N. Biomass gasifier “tars”: their nature, formation, and conversion. National Renewable Energy Laboratory; 1998.
- [11] Simell PA, Hepola JO, Krause AOI. Effects of gasification gas components on tar and ammonia decomposition over hot gas cleanup catalysts. *Fuel* 1997;76(12):1117–27.
- [12] Kaltschmitt M, Hartmann H, Hofbauer H. *Energie aus Biomasse*. Berlin, Heidelberg: Springer; 2009. p. 1032.
- [13] Kirnbauer F, Hofbauer H. Investigations on bed material changes in a dual fluidized bed steam gasification plant in Güssing, Austria. *Energy Fuels* 2011;110722151257027.
- [14] Devi L, Craje M, Thüne P, Ptasinski KJ, Janssen FJJG. Olivine as tar removal catalyst for biomass gasifiers: catalyst characterization. *Appl Catal A: Gen* 2005;294(1):68–79.
- [15] Devi L, Ptasinski KJ, Janssen FJJG, et al. Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. *Renew Energy* 2005;30(4):565–87.
- [16] Devi L, Ptasinski KJ, Janssen FJJG. Decomposition of naphthalene as a biomass tar over pretreated olivine: effect of gas composition, kinetic approach, and reaction scheme. *Ind Eng Chem Res* 2005;44(24):9096–104.
- [17] Devi L, Ptasinski KJ, Janssen FJJG. Pretreated olivine as tar removal catalyst for biomass gasifiers: investigation using naphthalene as model biomass tar. *Fuel Process Technol* 2005;86(6):707–30.
- [18] Corella J, Toledo JM, Padilla R. Olivine or dolomite as in-bed additive in biomass gasification with air in a fluidized bed: which is better? *Energy Fuels* 2004;18(3):713–20.
- [19] Rapagná S, Jand N, Kiennemann A, Foscolo PU. Steam-gasification of biomass in a fluidised-bed of olivine particles. *Biomass Bioenergy* 2000;19(3):187–97.
- [20] Mastellone ML, Arena U. Olivine as a tar removal catalyst during fluidized bed gasification of plastic waste. *AIChE J* 2008;54(6):1656–67.
- [21] Arena U, Zaccariello L, Mastellone ML. Tar removal during the fluidized bed gasification of plastic waste. *Waste Manage* 2009;29(2):783–91.
- [22] Rauch R, Pfeifer C, Bosch K, Hofbauer H. Comparison of different olivines for biomass steam gasification. In: Proc conf science in thermal and chemical biomass conversion, Victoria, Canada Conference; 2004.
- [23] Rapagná S, Virginie M, Gallucci K, et al. Fe/olivine catalyst for biomass steam gasification: preparation, characterization and testing at real process conditions. *Catal Today* 2011;176:163–8.
- [24] Di Felice L, Courson C, Niznansky D, Foscolo PU, Kiennemann A. Biomass gasification with catalytic tar reforming: a model study into activity enhancement of calcium- and magnesium-oxide-based catalytic materials by incorporation of iron. *Energy Fuels* 2010;24(7):4034–45.
- [25] Swierczynski D, Courson C, Kiennemann A. Study of steam reforming of toluene used as model compound of tar produced by biomass gasification. *Chem Eng and Process: Process Intensif* 2008;47(3):508–13.
- [26] Swierczynski D, Courson C, Bedel L, Kiennemann A, Guille J. Characterization of Ni-Fe/MgO/olivine catalyst for fluidized bed steam gasification of biomass. *Chem Mater* 2006;18(17):4025–32.
- [27] Ruoppolo G, Miccio F, Chirone R. Fluidized bed cogasification of wood and coal adopting primary catalytic method for tar abatement. *Energy Fuels* 2010;24(3):2034–41.
- [28] Miccio F, Piriou B, Ruoppolo G, Chirone R. Biomass gasification in a catalytic fluidized reactor with beds of different materials. *Chem Eng J* 2009;154(1–3):369–74.
- [29] Xie Y, Xiao J, Shen L, et al. Effects of Ca-based catalysts on biomass gasification with steam in a circulating spout-fluid bed reactor. *Energy Fuels* 2010;24(5):3256–61.
- [30] Olivares A, Aznar MP, Caballero MA, et al. Biomass gasification: produced gas upgrading by in-bed use of dolomite. *Ind Eng Chem Res* 1997;36(12):5220–6.
- [31] Florin NH, Harris AT. Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. *Chem Eng Sci* 2008;63(2):287–316.
- [32] Delgado J, Aznar MP, Corella J. Biomass gasification with steam in fluidized bed: effectiveness of CaO, MgO, and CaO–MgO for hot raw gas cleaning. *Ind Eng Chem Res* 1997;36(5):1535–43.
- [33] Myrén C, Hörmel C, Björnborn E, Sjöström K. Catalytic tar decomposition of biomass pyrolysis gas with a combination of dolomite and silica. *Biomass Bioenergy* 2002;23(3):217–27.
- [34] Corella J, Aznar M, Gil J. Biomass gasification in fluidized bed: where to locate the dolomite to improve gasification? *Energy Fuels* 1999;13(6):1122–7.
- [35] Alarcón N, García X, Centeno MA, Ruiz P, Gordon A. New effects during steam gasification of naphthalene: the synergy between CaO and MgO during the catalytic reaction. *Appl Catal A: Gen* 2004;267(1–2):251–65.
- [36] Delgado J, Aznar MP, Corella J. Calcined dolomite, magnesite, and calcite for cleaning hot gas from a fluidized bed biomass gasifier with steam: life and usefulness. *Ind Eng Chem Res* 1996;35(10):3637–43.
- [37] Kyotani T, Hayashi S, Tomita A. Study of calcium catalysis on carbon gasification with molecular oxygen–18. *Energy Fuels* 1991;5(5):683–8.
- [38] Nair SA, Yan K, Pemen AJM, et al. Tar removal from biomass-derived fuel gas by pulsed corona discharges. A chemical kinetic study. *Ind Eng Chem Res* 2004;43(7):1649–58.
- [39] Chen SG, Yang RT. Unified mechanism of alkali and alkaline earth catalyzed gasification reactions of carbon by CO₂ and H₂O. *Energy Fuels* 1997;11(2):421–7.

- [40] Chen SG, Yang RT. The active surface species in alkali-catalyzed carbon gasification: phenolate (C–O–M) groups vs clusters (Particles). *J Catal* 1993;141(1):102–13.
- [41] Bolhar-Nordenkamp M, Hofbauer H, Bosch K, Rauch R, Aichernig C. Biomass CHP plant Güssing – using gasification for power generation. In: Kirtikara K, editor. *Int conf biomass utilisation. vol 1*. Phuket, Thailand: self-published; 2003. p. 567–72.
- [42] Hofbauer H, Rauch R, Bosch K, Koch R, Aichernig C. Biomass CHP plant Güssing – a success story. In: *Pyrolysis and gasification of biomass and waste*. CPL Press; 2003. p. 527–36.
- [43] Wolfesberger U, Aigner I, Hofbauer H. Tar content and composition in producer gas of fluidized bed gasification of wood – influence of temperature and pressure. *Environ Prog Sustain Energy* 2009;28(3):372–9.
- [44] Aigner I, Ute W, Hofbauer H. Tar content and composition in producer gas of fluidized bed gasification and low temperature pyrolysis of straw and wood – influence of temperature. In: *ICPS 09 – Int conf polygeneration strategies*. Vienna, Austria; 2009. p. 1–9.
- [45] Proell T, Hofbauer H. Development and application of a simulation tool for biomass gasification based processes. *Int J Chem Reactor Eng* 2008;6.
- [46] Abu El-Rub Z, Bramer EA, Brem G. Review of catalysts for tar elimination in biomass gasification processes. *Ind Eng Chem Res* 2004;43(22):6911–9.
- [47] Thy P, Leshar CE, Jenkins BM. Experimental determination of high-temperature elemental losses from biomass slag. *Fuel* 2000;79(6):693–700.
- [48] Aigner I. In: Hofbauer H, Pfeifer C, editors. *Co-gasification of coal and wood with steam in a dual fluidized bed gasifier*. Vienna University of Technology; 2010. p. 1–179.