

## 1 Introduction

During gasification, a calorific gas is created via several reactions of the original fuel with a gasifying agent at high temperatures. This gas can be used for combined production of heat and power (CHP) or for the production of alternative fuels. In the case of autothermal gasification, the gasifying agent consists of oxygen, whose reactions are exothermic, and of a moderator [1], whose reactions are endothermic. In the case of allothermal gasification, the gasifying agent is composed only of a moderator, and the heat needed for endothermic processes has to be supplied from an external source. The term 'moderator' expresses well the nature of this part of gasifying agent, as it moderates the process by consuming heat generated by exothermic reactions of oxygen. In the same time, it introduces additional (bound) oxygen, which is needed for the higher conversion of fuel carbon into gasses (CO, CO<sub>2</sub>) and, in the case of fluidized bed reactors it acts also as an additional fluidizing agent.

Nowadays, in most cases, steam is used as the moderator for gasification, but carbon dioxide can play a very similar role and should be considered for three main reasons: a) The CO<sub>2</sub> from carbon capture technologies [2] can become waste and its re-use will be preferred over its disposal [3]. b) Inert N<sub>2</sub> needed for technological purposes can be substituted with CO<sub>2</sub> [4] c) The products of oxyfuel combustion (with predominant CO<sub>2</sub> content and with the temperature of about 500 °C) can be recycled into the gasification chamber in order to improve the overall process efficiency [4,5]. However, the substitution of H<sub>2</sub>O with CO<sub>2</sub> affects the gas composition and the overall process behaviour.

When CO<sub>2</sub> was used under **non-catalytic conditions**, it acted mainly as a diluent of the producer gas, but also slightly higher carbon conversion and lower tar release was observed. Namely, Svoboda *et al.* [6] (in our previous article) compared the effect of CO<sub>2</sub> and H<sub>2</sub>O during the gasification of coal-oil and coal-water-oil slurries in a sand fluidized

### Abbreviations:

daf – Dry and ash free  
 CEM – Controlled evaporation and mixing system  
 CHP – Combined heat and power  
 ER – Equivalence ratio  
 LHV – Lower heating value  
 MFC – Mass flow controller  
 MSD – Mass spectrometric detector  
 NDIR – Nondispersive infrared sensor  
 PTFE – Polytetrafluoroethylene (Teflon)  
 SNG – Synthetic natural gas  
 WGS – Water gas shift reaction  
 $\Delta H_r^0$  – Standard enthalpy of reaction at 25 °C

bed at temperatures between 800 and 925 °C (ER  $\approx$  0.2). When gasifying with CO<sub>2</sub>+O<sub>2</sub> mixture, the concentration of C<sub>2</sub>-C<sub>5</sub> hydrocarbons, benzene and tar compounds were moderately or slightly lower than those in gasification by steam-oxygen mixture. Heating values of dry, N<sub>2</sub>-free producer gas were lower in comparison with gasification by steam-O<sub>2</sub> mixtures at comparable conditions, due to the diluting effect of CO<sub>2</sub> in the producer gas. [6] Spiegl *et al.* [4] investigated fluidized-bed gasification of coal under non-catalytic conditions at high partial CO<sub>2</sub> pressures. They found that tar release decreased and carbon conversion mildly increased when the CO<sub>2</sub>/fuel ratio increased. Butterman *et al.* [5] investigated the impact of a CO<sub>2</sub> co-feed on steam non-catalytic gasification of biomass. They report that the presence of CO<sub>2</sub> improved char conversion compared to gasification solely with steam.

Some authors investigated gasification with CO<sub>2</sub> under **catalytic conditions**. García *et al.* [7] studied allothermal fluidized-bed gasification of biomass by CO<sub>2</sub> with a special Ni catalyst in the fluidized bed. They state that, when the CO<sub>2</sub> is used as a gasifying agent, it is converted into valuable gases. The gas composition was close to the corresponding thermodynamic equilibrium because of the presence of the catalyst [7]. Simell *et al.* [8] compared the effect of CO<sub>2</sub>, H<sub>2</sub>O and their mixture on the decomposition of a model tar compound (toluene) in an environment of simulated producer gas at a pressure of 2 MPa, 900 °C and on different catalysts. They found that, with both dolomite and nickel catalysts, steam and CO<sub>2</sub> reforming types of reactions took place at a high rate, CO<sub>2</sub> reforming being faster than steam reforming.

From the literature survey and our previous experiences with non-catalytic gasification (Svoboda *et al.* [6]), we concluded that the use of CO<sub>2</sub> is rational under **catalytic conditions**; however, a comprehensive study focused solely on the comparison of CO<sub>2</sub> and H<sub>2</sub>O as moderators under catalytic conditions is missing. Only García *et al.* compared results obtained by CO<sub>2</sub> catalysed gasification [7] with the results obtained by steam gasification [9] under the same conditions, but they focused primarily on the effect of the concentration of Ni-catalyst in the fluidized bed and they did not publish the concentration of tar compounds and the overall conversion of solid fuel into producer gas.

To bridge this knowledge gap, we designed and performed gasification experiments on our semi-autothermal reactor with catalytically active dolomitic limestone in the fluidized bed. We thoroughly compared the effect of the gasifying agent composed of O<sub>2</sub> with H<sub>2</sub>O or CO<sub>2</sub> or N<sub>2</sub> at atmospheric pressure and at a temperature of 850 °C.

## 2 Materials and Methods

### 2.1 Fluidized bed gasifier

The main part of the reactor (see Fig. 1), the reaction zone, is an electrically heated 2200 mm high tube with an inner diameter of 51.1 mm in the lower section and 99.0 mm in the upper section (freeboard) made of high-temperature resistant stainless steel with the maximum operating temperature of 980 °C at reductive conditions. The lower section was filled with dolomitic limestone, which was fluidized by a preheated (500 °C) gasification agent passing through the grate. The grate is made from a high-temperature-resistant stainless steel plate 8 mm thick and it distributes the fluidizing and gasifying agent through holes with a diameter of 3 mm in the lower part (6 mm high) and 1 mm in the upper part (2 mm high) drilled in 7 circles around the axis of the reactor. The 24 mm high size reduction area between the lower and higher section is placed in the height of 545 mm above the grate.

The electrical heating with the maximal output of 10 kW consists of three independent stoves along the height of the reactor, which are regulated separately according to actual temperature inside the reactor. The temperature inside the reactor is measured by two K-type thermocouples. The first one is immersed in the centre of the fluidized bed and the second one is placed at the central part of the freeboard. The thermocouples are placed vertically in the axis of the reactor and they enter the reactor from the top in order to prevent thermal conduction from the heated walls of the reactor to the sensor of the thermocouples, thus, to eliminate possible temperature measurement errors. Other additional two K-type thermocouples are used to measure the temperature of the fluidizing (gasifying) agent below the grate and the temperature of the producer gas at the upper end of the reactor (headspace).

The fuel feeding line (its detail is in Fig. 1) consists of a two-chambers PTFE slide feeder with downstream consecutive pneumatic transport to the reactor by means of N<sub>2</sub>. The flow of nitrogen is maintained at 1.35 m<sup>3</sup> h<sup>-1</sup> by MFCs (El-flow® F-201 AV by Bronkhorst). The fuel-feeding rate can be controlled by varying the frequency of the sliding plate and by installing plates with different dimensions of the cylindrical chambers. A detailed description of the fuel feeding device can be found elsewhere [10,11]. The feeding line is cooled by a water cooler at the entrance into the gasifier in order to prevent fuel sintering. The axis of the fuel feeding pneumatic transport tube at the entrance to the gasifier is about 88 mm above the grate.

A mixing device supplied by Bronkhorst prepares and supplies the fluidizing/gasifying medium of precise composition. This medium consists of N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O<sub>g</sub> and CO<sub>2</sub>. The individual gases are fed from gas cylinders by means of MFCs (El-flow® F-201 AV) and the distilled water is fed from a pressurized tank (pressurized by N<sub>2</sub>) by MFC Liqui-Flow™ L23. All the gas and liquid streams are heated up to 200 °C and mixed in CEM W303A. The mixture is then heated up to 500 °C in an electrical pre-heater and enters the reactor below the grate.

The top part ('the head') of the gasification reactor is equipped with vertical outlets to monitor pressure and to sample the gas for **off-line** analysis and tar determination. After leaving the reactor, the hot raw producer gas is de-dusted in a hot cyclone (with the operational temperature of 400–500 °C) and then the gas is fed into the exhaust. The sample point for **on-line** analysis is in the wall of the exhaust tube downstream the cyclone.

## 2.2 Materials

As fuel, we used wood chips supplied by J. Rettenmaier & Sohne GmbH commercially available under the trademark 'Räuchergold HBK 750–2000'. This blend of oak and beech (without bark) is normally used for smoking meat and fish. It is well suitable for experimental purposes for its homogenous composition and favourable particles distribution with the absence of needle-like particles, which could cause problems in the feeding system. For the gasification experiments, the size fraction 0.25–2.00 mm of wood was prepared. Its loose poured bulk density was  $273 \pm 25 \text{ kg m}^{-3}$  and the apparent density of wood particles was  $645 \pm 25 \text{ kg m}^{-3}$ . Results of the proximate and ultimate analysis (of this fraction of the wood) are in table 1.

As the material of the fluidized bed, we used the Italian dolomitic limestone. Its properties are summarized in table 2. This limestone is marketed under the trademark 'Franchi'. The elemental composition was measured by an X-ray fluorescence spectrometer 9400 XP made by THERMO ARL and the contents are expressed in the form of oxides. More information about this material can be found in Hartman *et al.* [12].

The carbonate materials are generally known for their brittleness in calcined state, which leads to a high level of attrition and carry-over from the fluidized bed. However, their catalytic activity [13,14], together with low price and a lack of environmental problems, makes them a suitable choice for a gasification catalyst. The use of catalytically active materials during biomass gasification promotes char conversion, changes product gas composition and reduces tar yield. Besides these,

addition of active bed materials also prevents agglomeration tendencies and subsequent choking of the bed. [15] To make the use of dolomite in the fluidized bed possible, we had to overcome **two basic problems**.

**Primarily**, we had to secure that the dolomite is in calcined state, because in carbonated state its catalytic activity can be substantially lower [8] or even totally lost [16]. The equilibrium of decomposition of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  depends on the temperature and on the partial pressure of  $\text{CO}_2$  in the reactor [16]. Hence, we have chosen the constant temperature of 850 °C in the fluidized bed, because, even for the highest partial pressure of  $\text{CO}_2$ , this temperature is about 30 °C above the re-carbonation point of the calcite part of the dolomitic limestone.

The **second** complication was the attrition of the material and its carry-over from the reactor. This causes not only a high concentration of fines in the gas stream, but also the loss of dolomite mass from the reactor, which can cause a change in experimental conditions. Prior to our experiments, we measured the carry-over of this specific dolomitic limestone from the reactor at the same experimental conditions as in this article and we developed a model, which serves us to estimate the mass of material that is carried from the reactor in a specific time-period and that needs to be replenished. [12] The construction of our experimental facility enables us to add the material of the fluidized bed during the experiment by a two-valve tube through the head of the gasification reactor. Hence, after finishing a steady-state sampling for a defined gasifying agent mixture, we replenished the corresponding amount of dolomite to secure similar conditions for another measured steady state. Moreover, because of high amount of fines in the gas, the capacity of the flying ash container below hot cyclone had to be extended.

### 2.3 Gas sampling and analysis

The producer gas was analysed both on-line and off-line. The on-line analysis served for monitoring and controlling the gasification process; the off-line analysis supplied data for a detailed study of gasification products.

The **on-line** sampling point was placed behind the cyclone. The gas was sampled through a PTFE tube with an inner diameter of 4 mm. First, it passed through two impingers, where it was cooled down, water and tars condensed and rough dust was captured, then the gas was filtered by glass wool filters and dried by cooling down to 4 °C. The gas was polished on a paper filter and a ceramic filter, and finally a pump pushed it to the analysers.  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  contents were analysed by means of NDIR

and H<sub>2</sub> by a thermal-conductivity analyser. To verify that the sampling line was well sealed, the absence of air in the sampled gas was checked by an O<sub>2</sub> magneto-mechanic analyser (H&B Magnos 4Gex). The on-line analysers were supplied by ABB.

The gas for **off-line** analysis was captured into gas-sampling bottles at a sampling point at the end of the reactor and it was analysed after the experiment using a gas chromatograph HP 6890 equipped with two analytical channels with a flame-ionization detector and a thermal-conductivity detector. This analysis is described in detail in our previous article [17]. The relative error measured during this experiment on 6 samples was less than 2%. This relative error includes also the natural variation of the fluidized bed process.

For **tar collection**, we used a standard sampling procedure according to the corresponding norm [18]. Our sampling line consisted of a steel tube, which leads the sampled gas directly from the gas stream at the end of the reactor. The tube is connected to a PTFE tube, which leads the gas into three absorption bottles with acetone (150 ml). The first one was kept at a normal temperature; the other two were cooled in a bath with solid CO<sub>2</sub> (– 70 °C). Downstream to the absorption bottles, the flow regulator and the wet gas meter were placed. The gas flow rate was regulated to 2 dm<sub>n</sub><sup>3</sup> min<sup>-1</sup> and the gas volume collected was 71–94 dm<sub>n</sub><sup>3</sup>. We analysed tar components absorbed in acetone using a gas chromatograph HP 6890 with a mass selective detector (GC-MS). The analysis is also described in detail in the above-mentioned article [17]. The relative error of this measurement is difficult to statistically express, because the collection of samples takes app. 30–50 min; however, the error should be minimal because a big amount of gas is collected. We measured good repeatability of this method during several experiments.

## 2.4 Experimental procedure

The reactor tube was heated up to 700 °C by external electrical furnaces with low flow of nitrogen through the reactor. Then, the material of the fluidized bed was added (2.1 kg) through the tube at the top of the reactor and it was fluidized by nitrogen (2 m<sub>n</sub><sup>3</sup> h<sup>-1</sup> through the grate and 1.43 m<sub>n</sub><sup>3</sup> h<sup>-1</sup> through the fuel transport line). The volume of the limestone bed was 1.5±0.1 dm<sup>3</sup>, which corresponds to the height of the fluidized bed of 60–90 cm and the gas-retention time of 0.5–2.5 s. The dolomitic limestone was heated up to the temperature of calcination and after the calcination (with finished release of CO<sub>2</sub> after about one hour) the reactor was heated up to the desired temperature of 850 °C.

The corresponding amount of dolomitic limestone, which was carried out of the reactor during the heating stage ( $250 \text{ g h}^{-1}$ ), was replenished. After the calcination of the newly added material of the fluidized bed, inputs of the gases were set to the conditions of the first planned steady state ( $\text{H}_2\text{O}+\text{O}_2$  according to the table 3) and fuel feeding ( $1380 \text{ g h}^{-1}$ ) started.

After about one hour of fuel feeding, steady state conditions were reached. Again, new material of the fluidized bed was added and calcined, after which the collection of off-line samples (corresponding to the first steady state) began. The calcination under fuel feeding was monitored by the increase in  $\text{CO}_2$  concentration above steady-state conditions and by temperature measurement in the fluidized bed. When new limestone is added, the temperature of the fluidized bed decreases down to  $750\text{--}800 \text{ }^\circ\text{C}$ , then rises quickly up to the temperature of calcination, where it remains as all the inserted and generated heat is consumed by the endothermic process of decomposition of  $\text{CaCO}_3$  to  $\text{CaO}$  and  $\text{CO}_2$ . Only after the calcination has finished and all the  $\text{CO}_2$  has been released, the temperature can rise again to the desired value of  $850 \text{ }^\circ\text{C}$ .

After the collection of all required samples of the corresponding steady state, the dolomite was replenished, the inlet gas composition was changed to the next desired set of conditions, and the second steady state was achieved. The experimental conditions for the three compared steady states are reported in table 3.

After finishing all the experiments, the fuel feeding was switched off and, at the same time, the gasification medium was substituted by  $\text{N}_2$  in order not to burn the carbon, which remained in the fluidized bed. Then, the heating of the reactor was turned off. This enabled us to do further analyses and state proper mass and elemental balances.

## 2.5 Nomenclature and basic assumptions

All volume units of the gas and other relevant values are reported at **101.325 kPa and  $25 \text{ }^\circ\text{C}$** .

**Reactor temperature** is the average of the temperatures measured by the thermocouple in the fluidized bed and in the freeboard (the difference was at maximum  $15 \text{ }^\circ\text{C}$ ).

**Dry gas yield** is the volume of the gas (at  $101.325 \text{ kPa}$  and  $25 \text{ }^\circ\text{C}$ ) related to mass flow of dry fuel (1). Total gas yield was calculated from the  $\text{N}_2$  balance (known volume in the inlet and known concentration in the dry gas at the outlet). The yields of

specific gases were calculated from the total gas yield multiplied by their concentrations in the dry producer gas.

$$gas\ yield = \dot{V}_{dry\ gas} / \dot{m}_{dry\ fuel} \quad (1)$$

**Steam yield** is the yield of steam that is created in the reactor as a product of gasification (steam in the gasifying agent is not included – eq. 2).

$$steam\ yield = steam\ output - steam\ input \quad (2)$$

Steam yield was calculated as the average of two values – first one from the elemental H balance and the second one from the O balance (the elemental balances are depicted in the appendix). The closeness of the steam yield values from the two balances indicates the level of correctness of the measurements of inputs and outputs (ideally they should be equal).

**Moist gas yield** is the sum of **dry gas yield** and **steam yield**.

**Lower heating value (LHV)** was calculated as the sum of products of heating value of measured gas components ( $LHV_i$ ) and their concentrations ( $\varphi_i$ ) in the producer gas, according to the equation (3). The lower heating values of the gas components were adopted from the norm EN ISO 6976. The tarry compounds weren't included in the computation.

$$LHV = \sum_{i=1}^n \varphi_i \cdot LHV_i \quad (3)$$

**Cold gas efficiency** is the ratio of the chemical energy of the dry producer gas (based on  $LHV^d$ ) to the chemical energy stored in the dry fuel ( $LHV^d$ ).

**Tar yield** is calculated from the concentration of tar in the dry gas ( $g\ m^{-3}$ ) multiplied by the dry gas yield ( $m^3\ kg^{-1}_{dry\ fuel}$ ).

**Equivalence ratio (ER)** is the molar ratio of the total input of  $O_2$  by the gasifying agent related to  $O_2$  theoretically needed for total combustion of the fuel into  $CO_2$  and  $H_2O$  (and  $SO_2$  etc.; the real oxygen demand will be higher because of thermodynamic and kinetic limitations). For example, the ER of 0.2 means that 20 % of the oxygen theoretically needed for total combustion is fed into the reactor.

**Steam to fuel carbon ratio ( $H_2O/C$ )** is the molar ratio of steam fed into the reactor by gasifying agent and/or as the fuel moisture related to the elemental carbon in the fuel.



**Carbon dioxide to carbon ratio ( $\text{CO}_2/\text{C}$ )** is the molar ratio of carbon dioxide fed into the reactor by gasifying agent related to elemental carbon in the fuel.

**Elemental oxygen to carbon ratio ( $\text{O}/\text{C}$ )** is the molar ratio of elemental oxygen present in the gasifying agent (in the form of  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) and in the fuel related to the elemental carbon in the fuel. This ratio can serve as a basic overview on how much of carbon can be gasified into oxidized form. For example the value  $\text{O}/\text{C}=1$  means that theoretically all the carbon can be gasified into  $\text{CO}$ . Practically, the value has to be considerably higher because of the thermodynamic and kinetic limitations (other oxidized forms will be formed as well –  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , *etc.*).

### 3 Theory

When the fuel biomass is fed into the hot fluidized bed, the fuel pyrolyses into three basic types of products: solid char, permanent gases ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{C}_x\text{H}_y$ ) and condensable hydrocarbons referred to as tars. In order to set a clear boundary between the tars and the hydrocarbons in the form of permanent gases, tar is considered to be all organic contaminants with molecular weight higher or equal to toluene.

Subsequently, pyrolysis products react with the gasifying agent to give permanent gases and lesser quantities of hydrocarbon gases [19]. The **char** reacts mainly with steam by Water-gas reaction (4) and with carbon dioxide by Boudouard reaction (5) stated in table 4. The Methanization reaction (6) (table 4) becomes important under higher gasification pressures. The reaction rates of the heterogeneous reactions with carbon are the slowest and these reactions become the rate-controlling step of the gasification process. [20] From these reactions, it can be assumed that the higher the partial pressure of  $\text{H}_2\text{O}$  and/or  $\text{CO}_2$  will be, the **higher conversion of solid char** can be expected.

The most abundant **gases** in the producer gas ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) react in the reactions (7)–(9) stated in table 4. The free oxygen in the system reacts most readily with carbon monoxide and hydrogen by the reactions (7) and (8). These reactions are very quick, complete and they provide heat for the pyrolysis and other endothermic reactions. Oxygen can, as well, react directly with the carbon molecule in the char, if the oxygen is still available in the system, but probably most of it will be consumed by homogeneous reactions (7) and (8). The Water-gas shift reaction (WGS) (9), which balances the concentration of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , is very important for gas composition. In a

catalysed environment, this reaction is very sensitive to the partial pressures of the reactants.

The condensable hydrocarbons (**tars**) are being decomposed into permanent gases by the reactions (10)–(15) listed in table 4. Not all the tars from the pyrolysis step are completely converted due to the physical or geometrical limitations of the reactor and the chemical limitations of the reactions involved. This gives rise to contaminant tar compounds in the final product gas. [19] It can be supposed, that higher partial pressure of H<sub>2</sub>O and CO<sub>2</sub> in the reactor will lead to **lower tar content** in the producer gas, because the chemical equilibrium of the reactions (10)–(15) will be shifted towards products, according to Le Chatelier's principle.

## 4 Results and discussion

The measured data are presented and discussed with the focus on major gas components and cold-gas efficiency (first subchapter), then on carbon conversion (second subchapter), and, finally, on minor organic compounds and tars (third subchapter).

To present and discuss the results, the yields (in m<sub>n</sub><sup>3</sup> kg<sup>-1</sup> or g kg<sup>-1</sup> of dry fuel biomass) were selected instead of more traditional concentrations, because they enable better comparison of the gasification products when different gasifying agents are used. The elemental balances (C, H and O) present a very interesting point of view on the results. They are depicted in the supplement, together with basic technological parameters of the gas, such as lower heating value, concentrations of individual gases and individual tar-compounds' concentration and yield.

### 4.1 Gas yield and cold gas efficiency

The yields of CO<sub>2</sub>, CO, H<sub>2</sub> and H<sub>2</sub>O (Fig. 2) change accordingly to the thermodynamic expectations mainly by means of the WGS reaction (9). The yield of methane and minor organic compounds (C<sub>2</sub>-C<sub>7</sub>, labelled as 'minorities' in Fig. 2) was very similar when both moderators (H<sub>2</sub>O and CO<sub>2</sub>) were introduced into the gasifying agent, and it was the lowest when N<sub>2</sub> was used instead. These organic compounds are mainly the remainders of the pyrolysis that weren't entirely decomposed by the reforming reactions (13) and (14). The individual minor gases are depicted in Fig. 5 and they are discussed together with tars in chapter 4.3.

The cold gas efficiency (Fig. 3) reflects how much of the chemical energy stored in the fuel is transformed into the chemical energy of the producer gas. The presented values are rather high compared to a real autothermal reactor, where a substantial part of the fuel energy is consumed to cover the heat losses of the reactor and to provide the heat needed for endothermic reactions (mainly 4 and 5). However, most of the heat needed for maintaining the temperature of 850 °C inside our reactor is provided by external electrical heating; hence, the only limitations, of how much of the fuel energy is converted into the chemical energy of the gas, consist in thermodynamics and kinetics of the process.

The highest cold gas efficiency was measured when the mixture of CO<sub>2</sub> and O<sub>2</sub> was used as the gasifying agent (third column on Fig. 3). This fact is connected with high carbon conversion in the presence of high partial pressure of CO<sub>2</sub> (the carbon conversion is depicted in Fig. 4). Very interesting is that the measured cold gas efficiency of the neutral case (N<sub>2</sub>+O<sub>2</sub>) was slightly higher than the cold gas efficiency of the case with high partial pressure of steam (H<sub>2</sub>O+O<sub>2</sub>); albeit, from the thermodynamic perspective, higher efficiency of the conversion of chemical energy in the fuel into the chemical energy of the producer gas would be expected with higher partial pressure steam in the reactor.

## 4.2 Carbon conversion

In the chart on Fig. 4, the relative fuel-carbon conversion into producer-gas-components is presented. The highest relative carbon conversion was measured under high partial pressure of CO<sub>2</sub> (third column), which is in accordance with the literature data [5,7,13]. The carbon conversion efficiency higher than 100% can be confusing; nevertheless, this is probably caused by the consumption of the char accumulated in the fluidized bed during the previous measured steady state, despite the fact that the samples were collected after more than one hour after changing the conditions of gasification. From the presented data, it is clear that the Boudouard reaction (5), which is normally very slow under non-catalytic conditions, becomes more potent when catalysed. The different fluid dynamics of CO<sub>2</sub> compared to the fluid dynamics of H<sub>2</sub>O can also play some part in this increase of carbon conversion.

Comparing the case with steam in the gasifying agent with its substitution by inert N<sub>2</sub> (first and second column on Fig. 4), only slightly higher carbon conversion was achieved with high steam partial pressure. This fact is surprising, considering the

kinetics of gasification and our previous experiences with non-catalytic material of the fluidized bed (*e.g.* Svoboda *et al.* [6], Pohořelý *et al.* [17] and Šyc *et al.* [21]). As it is stated in the experimental section (table 3 - Steady states characterization), the ratio O/C is 2.37, when steam is present in the gasifying agent, and it is only 1.25, when the steam is substituted by nitrogen. Such high carbon conversion with such low O/C value is probably caused by the presence of catalytically active material of the fluidized bed, which shifts the real gas composition very close towards the thermodynamic equilibrium [7]. Neither Water Gas reaction (4) nor the Boudouard reaction (5) was favoured by high partial pressure of H<sub>2</sub>O or CO<sub>2</sub>, they proceeded parallel and the combined effect seems to be the most efficient for carbon conversion.

### 4.3 Minor organic compounds and tars

The yield of the individual minor organic compounds is in the next two charts. In the first one (Fig. 5), the yield of individual lighter organic gases (C<sub>2</sub>–C<sub>7</sub>, analysed in gas sample by GC-FID) as well as the sum of tar components is depicted. The yields are stated in g per kg of dry gasified biomass for better comparison with tars.

As was already stated in the discussion related to Fig. 2, the lowest yield of organic compounds was achieved when no moderator (H<sub>2</sub>O or CO<sub>2</sub>) was added to the gasifying agent. On this chart (Fig. 5), it can be seen that the type of moderator differently affects various organic compounds. On one hand, **benzene** yield was higher when high steam pressure was applied (H<sub>2</sub>O+O<sub>2</sub>) and, on the other hand, the yield of **acetylene** was higher when high partial pressure of CO<sub>2</sub> was applied (CO<sub>2</sub>+O<sub>2</sub>). **Other organic compounds** behave relatively similarly as their sum. The yield of every organic compound is the lowest when no moderator was added. The relative **tar** concentration in the gas under various conditions is well connected with the concentration of ‘other’ minor organic compounds.

The tar is undesirable because of various problems associated with condensation, formation of tar aerosols and polymerization to form more complex structures, which cause problems in the process equipment as well as the engines and turbines (and maybe SOFCs) used in applications of the producer gas. However, the minimum allowable limit for tar is highly dependent on the kind of the end user application requirements. [15]

The chart (Fig. 6) shows the total tar yield and its distribution into four classes according to the methodology, which was described in the article of Devi *et al.* [15]. This classification is mainly based on solubility and condensability of different tar

compounds, rather than reactivity of the compounds. A table with the description of the individual tar classes is provided in the supplement as well as a table with our detailed tar analysis. The tar dew points were calculated by the 'Complete model' by ECN [22]. The tars, which are the most dangerous for smooth operation of the downstream technology and which can be analysed by GC, are the tar compounds of the **type V**. These had, however, very low concentration in the producer gas when compared to the other types of tars. The tars from the **group IV** can be dangerous because they can condense on cooler parts (for example in the pre-cooler of gas motors). The tars of the **class III** can – in some applications – play a beneficial role in the producer gas because they take part in the heating value of the gas, but, on the other hand, if the gas is meant to be used for synthesis reactions, these tars can be harmful due to their potential to create carbonaceous structures, which deactivate the catalyst. The tars of the **class II** can be soluble in water, which can cause problems related to waste water treatment.

The distribution of the tar classes is very similar for all the three cases, with the exception of the heterocyclic tar compounds in the case of  $N_2+O_2$ . Comparing the absolute tar yields, we can conclude the very same fact as for the lower organic compounds: The lowest yields were measured when no moderator was added to the gasifying agent (with the exception of type II compounds).

The possible explanation for the lowest yield of organic compounds (including tars), when no moderator was added, is that the lower partial pressure of both  $H_2$  and  $CO$  shifts the equilibrium of the reactions of steam (13) and dry reforming (14) towards a higher level of decomposition of organic compounds. Other reason can be that the dry reforming (14) reaction on dolomite is inhibited by steam [8] and vice versa (steam reforming reaction (13) is inhibited by carbon dioxide). In the neutral case ( $N_2+O_2$ ), where neither of the two reactions is dominant, the organic compound conversion is the highest because each of the reforming reactions can be more suitable for decomposition of different organic compounds than the other reforming reaction.

Comparing the tar yield when steam was used as a moderator and when the carbon dioxide was used (first and third column of Fig. 6), lower tar yield was measured with the carbon dioxide addition. This fact is in agreement with the literature [9,14] and with the kinetic presumptions (dry reforming is faster at the temperature of 850 °C and when the process is catalysed [8]).

## 5 Conclusions

The use of CO<sub>2</sub> as a moderator, in the process of catalytic biomass gasification, had a significant positive impact on the conversion of biomass fuel into gaseous calorific compounds and on lowering the yield of tarry compounds. In our opinion, higher cold gas efficiency of the gasification with CO<sub>2</sub> will lead to an improved biomass-to-electricity conversion in industrial combined-heat-and-power applications.

For the sake of completeness, we examined also the gasification of biomass without the moderator (it was substituted with inert N<sub>2</sub>). To our surprise, the yield of tar was considerably lower, compared to the use of both examined moderators (H<sub>2</sub>O and CO<sub>2</sub>). We suggest that this phenomenon occurred due to high catalytic activity of the limestone in the fluidized bed. This caused the low (and balanced) partial pressures of H<sub>2</sub>O and CO<sub>2</sub> in the reactor being sufficient for a high degree of carbon and tar conversion.

In this article, we have shown that CO<sub>2</sub> can be an active moderator when limestone is used in the fluidized bed. We suppose, however, that the limestone can still sufficiently catalyse the gasification process while being diluted by a stable inert material; for example, silica sand. Such dilution would lower the carry-over of limestone fine particles from the reactor and would decrease the need of the addition of limestone to the reactor during the operation. Thus, future work is planned to determine the minimal concentration of dolomitic limestone in a fluidized bed of silica sand that would still be active enough to catalyse CO<sub>2</sub> reactions to such a high degree.

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