Influence of Pressure and $CO₂$ in Fluidized Bed Gasification of Waste Biomasses

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Abstract

An autothermal fluidized bed reactor was used to carry out research on the influence of pressure on gasification process of different types of biomasses. The gasified feedstocks were bark, lignin and softwood pellet as a reference material. The gasification was done with a mixture of $O_2/CO_2/H_2O$. The impact of the application of CO_2 on yield of H_2 in syngas was determined. Resulting high content of CO makes use of the syngas in chemical synthesis applications very difficult without pretreatment. On the other hand, the $CO₂$ proved to improve Carbon Conversion Efficiency of the gasification and to be an option for its chemical sequestration (negative carbon footprint). Moreover, a slight variation of conventional indices used to evaluate efficiencies of gasification systems (Carbon Conversion Efficiency and Steam/Carbon ratio) was proposed to take into account the impact of the additional source of carbon. Increasing system pressure led to syngas changes in line with predictions of the Le Chatelier's principle. The changes were seen primarily by higher yields of CH₄ and lower overall production of syngas. For higher hydrocarbons (C_xH_y) the trend was unclear. For each pressure level and a standard 850°C gasification temperature, a set of stable gasification parameters were achieved with the exception of lignin at 2 bar_{φ} .

Keywords: $O_2/CO_2/H_2O$, gasification, biomass, biogenic residues, pressure, ash agglomeration

1.Introduction:

Pressurized gasification is the state-of-art technology for highly-efficient production of chemical intermediates or fuels from primary sources of energy. However, when the feedstock is changed to renewable sources like biomass, the need for use of pressurized reactors is highly debated.

The impulse for development of pressure systems for gasification of biomass has been recognized by many influential agencies. For renewable production of fuels and chemicals, International Renewable Energy Agency and Internal Energy Agency have prioritized the

following goals:

1) to develop BtL routes for the production of biodiesel and DME from black liquor gasification;

2) to maturate pressurized gasification plants to produce bio-SNG, as in the Bio2G project;

3) to study hybrid biochemical and thermochemical conversion routes.

The first two goals are directly related to development of pressurized biomass gasification systems.

Noteworthy, from the principle for thermodynamics gasification of biogenic feedstocks at higher operating pressures may be beneficial from several perspectives. Firstly, biomass gasification at elevated pressures provides higher reaction efficiencies and kinetics. Secondly, when the syngas is produced for the purpose of chemical synthesis, the overall process efficiency can be increased by avoiding the step of gas compression, which always incurs energy and exergy loses. Nonetheless, drawbacks are operational challenges related to complexity of the system, its construction and control.

To assess the effect of pressure on kinetics of gasification reactors often thermogravimetric (TG) approaches are applied. Currently, TG lack the possibility to exactly map the process conditions of a fluidized bed (FB), where volatilization and gasification happen quickly one after the other at the same temperature and pressure conditions. For most biomasses 4-7 bar is said to be the maximum gasification pressure which provides an optimum ratio of kinetic-gain to processcomplexity-loss. Thus, it is often suggest that operation at 4-5 bars should be optimal for biomass (1-2, 5).

Another approach is thermodynamic equilibrium calculations and modelling. With equilibrium models it has been shown that rising pressure and temperature leads to lower $H₂$ and CO production, while yields of $CO₂$ and $CH₄$ increase [4-5].

Looking into syngas changes, contradictory results of FB pressure gasification can be found. Generally it is agreed that with increasing pressure also overall gas yields and tar yields increase. The subject of char production remains disputable. In allothermal steam blown gasification studies it has been proven that methane yield increase by up to 38% with pressure increase from 2-10 bars [15]. This indicates higher needs for catalytic syngas shift and conversion after pressurized gasification. The changes in yields of gaseous compounds with pressure can be partly explained by the influence of pressure on gas phase reactions (acceleration of water–gas shift kinetics and change in hydrocarbon reactions) that act in line with the Le Chatelier's principle. The increase of methane yield with pressure is suggested also to be partially linked to a change in secondary pyrolysis reactions scheme that takes place under high pressures.

Another aspect of biomass gasification is utilization of $CO₂$ as a gasifying agent. $CO₂$ can take part in gasification systems similar to steam and thus act as both fluidizing and active gasification agent. Usage of $CO₂$ shifts equilibrium of both Boudouard's reaction as well as gas-shift reaction in favour of CO . $CO₂$ also has higher specific heat capacity and hence tendency to lower temperature of gasification, hence higher equivalence ratios (ER) are needed. The concept of using $CO₂$ for increasing C conversion and lowering C footprint is known and has been subjected to research in coal gasification and oxy-combustion studies. For biomass, use of $CO₂$ can make a unit C negative which is very interesting for the future. To this point only limited amount of data can be found on $CO₂$ gasification of biomass [18-21].

The article presents results of experimental research on pressurized gasification of wastes biomass in FB reactor. Two waste feedstocks (wood bark and lignin from production of bio-ethanol) were compared with a reference fuel (softwood pellet, SWP) for their gasification efficiency figures. The tests were performed in autothermal mode with use of $O_2/CO_2/H_2O$ mixture as gasifying agent. The operational data on FB gasification of waste biomasses, process efficiency and syngas quality figures were validated with mass and energy balances.

For good design of gasification experiments it is necessary to set a precise range of control variables that can be followed. For O_2 /CO₂/H₂O gasification process the encountered opposing action of $CO₂$ and H2O makes the use of conventional indices problematic. Thus, few validated process and efficiency indices are presented here in order to help to describe the $CO₂$ gasification runs. Analysis of obtained results provides answers in the field of production of FT fuels from $CO₂$ gasification of waste biomasses.

2. Concept and methodology: Research installation

The experiments were carried out on a bench-scale experimental stand presented in Fig. 1. Main part of the unit is a fluidised-bed gasifier with an in-bed feeding system. The reactor is electrically heated during start-up. Its upper part is a water-jacket design which is used for

excess heat removal. This design enables quick start-up as well as long term stable operation with good control of process temperature. The internal part of the reactor is made of a heat-resistant steel tube with internal diameter of 105 mm and height of 1500 mm. Bottom part of the reactor is 300 mm long and has conical shape which tapers to the diameter of 75 mm at the distributor level. Fluidization medium is distributed within the reactor with use of a perforated plate of ca. 4% open area. Temperature measurements inside the reactor and the freeboard are carried out with use of five vertically mounted K-type thermocouples. Three bottom thermocouples are placed within the bed while the remaining two indicate temperature profile of the freeboard.

The fuel feeding system consists of three storage tanks. Two of them are equipped with knife gate valves which enable fuel

Fig. 1: Process scheme of the lab scale gasification installation

loading while the experiments are conducted in over pressure. The biomass flow is regulated by changing rotational speed of the upper screw feeders. From the fuel dosing tanks, the fuel is fed into a drop tube. The drop tube ends with a high capacity in-bed screw feeder which is equipped with an additional water jacket. This technical solution prevents heating-up of the stored fuel and its uncontrolled pyrolysis during intermittent phases of reactor's operation. For safety reasons, the feeding system is continuously purged with small quantities of nitrogen.

Downstream of the reactor, syngas reaches a cyclone where particles of the entrained char, ash and bed material are recovered. Syngas after dedusting is directed through a pressure relief valve towards a flare. After reduction of pressure, the syngas is sampled for analyses.

Gasification agent mixture is prepared from gas cylinders (arranged into bundles with separate pressure regulators) containing technical grade O_2 , N_2 , CO_2 . The flow rate of each agent is measured independently by means of a dedicated Bronkhorst EL–FLOW SELECT mass flow controller. The gas mixture flow lines are electrically heated up to 320°C. The steam flow rate is regulated by FWT di Tommaso Commonara water dosing pump (max. flow - 4dm³/h) positioned upstream of the steam generator and steam preheater.

Feedstocks

The conducted research was focused on the use of two waste biomass feedstocks of high ash content and demanding chemical composition. Feedstocks before use were pelletized (6mm diameter) to improve their density and homogeneity. However, due to small size of screw feeders used in this small-scale unit, the fuel pellets needed to be crushed and sieved before use. Average particle size

Tab. 1: Physicochemical characteristic of gasified feedstocks

distribution and bulk density of the feedstocks after size reduction were measured. Physicochemical properties of the gasified biomasses are shown i[n Tab.](#page-3-0) 1.

The feedstocks ashes were analysed with visual method against their thermal behaviour in half-reducing atmosphere. The procedure followed CEN/TS 15370-1.

Primary bed material used in the research was olivine, obtained from Magnolithe GmbH.

Determination of syngas composition and content of contaminants

Samples of the syngas were collected in Tedlar bags and analysed with GC in order to determine the exact composition. The GC analyses were done using a Varian CP3800 coupled with Flame Ionization Detector and Thermal Conductivity Detector and Pulse Flame Photometric Detector. The qualitative and quantitative analyses were performed using the external gas standard method.

Moreover, syngas was sampled to determine its content of water, tar and solid particles. The sampling system consisted

of a probe, two impinger bottles and a tube filled with cotton wool. The probe was introduced axially into syngas line after the pressure relief valve. The end of the probe was connected to two impinger bottles containing about 50 ml of isopropanol at ambient temperature. In these two bottles most tar and dust is collected. The glass tube filled with cotton wool, fitted at the end of the probing set, acts as a droplet collector. The syngas was sucked by a pump coupled with a flow regulator.

For determination of water content in syngas, Karl-Fischer method was applied. Mass of gravimetric tars was measured after evaporation of solvent under reduced pressure (0.1 bar, 80°C) and final drying until constant mass was reached. Conditions of the above mentioned treatment, stand for definition of tars adapted for this research.

Dust particles collected in the isopropanol solution were filtered off, washed with additional portion of isopropanol and dried until constant mass was reached. The total amount of solids after the gasifier was determined by addition of the weight of solids from the isopropanol probing and from the stream of solids separated in the cyclone. For mass balancing and efficiency calculations the recovered solids were used for proximate and ultimate analysis.

Method and operating conditions of the reactor

After initial electrical preheating of the reactor up to 700 °C, combustion process was started with air and small amount of steam. When temperature in the bed reached 750 °C the air was replaced by carbon dioxide and oxygen mixture. Flowrates of gas and fuel were adjusted to obtain steady combustion parameters and good control over heating-up of the bed up to starting temperature of the process (840°C). Usually the longitudinal profile

of temperatures in freeboard zone stabilized between 600°C and 750°C. If the conditions in the reactor/installation (i.e. temperature, pressures etc.) were sufficient, the fuel stream was further increased to initiate the gasification process. Set point of total pressure was regulated manually by adjusting the pressure-relieve valve.

For all feedstocks a baseline gasification temperature has been set to 850°C. The temperature was controlled by adjusting the flowrate of oxygen, fuel and water fed into reactor' jacket. Reactor pressure has been varied between 0, 1 and 2 bar $_{\circ}$.

The influence of steam added to the process was determined in the range $0.55 - 1.2$ H₂O/C, where the index can be calculated as:

$$
\frac{H_2O}{C} = \frac{\dot{m}_{Steam,fa} + \dot{m}_{H2O,fuel}}{\dot{m}_{C,fuel}} \tag{1}
$$

In terms of fluidization number, the tests were conducted at the level of $U/U_{\text{mf}} =$ 8.5 ± 1.5 , with the exception of lignin.

FB gasification indices

In conventional gasification systems where air/ H_2O or O_2/H_2O mixtures are used as gasifying agent the conversion efficiency indices are well established and successfully allow comparing different reactors and process conditions. Primary attention has been paid here towards Cold Gas Efficiency (CGE), Carbon Conversion Efficiency (CCE) and $H_2O/Carbon$ $(H₂O/C).$

CGE gives direct information about the amount of useful chemical energy of fuel transformed into syngas. It can be calculated based on either higher or lower heating values and is not sensitive for the composition of gasifying agent. In the article Eq. 2 was used to calculate reactor' CGE.

$$
CGE = \frac{(HHV_{syn} + i_{syn})m_{syn}x100\%}{(HHV_{fuel} + i_{fuel})m_{fuel}}
$$
 (2)

CCE is an index that gives information regarding the efficiency of a process/reactor in conversion of feedstock's carbon into syngas rather than to tars or chars. It is based on C balance of the system and can be calculated through the use of the following equation:

$$
\phi_{C, fuel \to C, syn} = \frac{x_{C, syn} m_{syn} x 100\%}{x_{C, fuel} m_{fuel}}
$$
 (3)

Eq. 3 does not take into account the additional source of C introduced in feed with CO2. Hence, it evaluates process efficiencies of over 100%. To counteract this fact the CCE needs to be fitted with additional term related to the fed $CO₂$. For this reason equation Eq. 4 was devised. It is a direct C balance equation which takes into account the additional substrate - $CO₂$. Part of the $CO₂$ reacts with fuel and influences the CO and H_2 yields in syngas, while rest leaves as a ballast gas which influences the composition of syngas.

$$
\varphi_{C,in \to C, syn} = \frac{X_{C, syn} \dot{m}_{syn} x 100\%}{X_{C, fuel} \dot{m}_{fuel} + \dot{m}_{C, CO2 fa}} (4)
$$

Eq. 4 is proposed as the best simple approximation of the logic behind the conventional CCE index for later studies on $CO₂$ gasification.

The same reasoning was applied towards determination of a correct way to define an index based on H_2O/C , which would serve the purpose of relating the amount of steam used as a fluidizing agent, to the amount of carbon fed with fuel and $CO₂$. Similarly to CCE, usefulness of H_2O/C finds limits when $CO₂$ is introduced into

a gasifier. In a gasifier, $CO₂$ acts as a substrate in $CO₂$ related reforming reaction while being a product of water-gas shift reactions. The most important steam and CO² gasification reactions were collated in Tab. 2. Boudouard's reaction is the main pathway through which $CO₂$ influences gasification systems. This reaction

Tab. 2: Collation of most important gasification reactions impacted by partial pressure of H2O and CO2.

is more endothermic then water-gas shift and produces CO which pushes the watergas reaction towards the side of substrates. In equilibrium models, $CO₂$ addition increases yields of CO with simultaneous drop in production of $H₂$. To follow the combined influence of $CO₂$ and H_2O a number of indices have been analysed. The most reliable and clear to evaluate results have been found when the index $H_2O/(C+CO_2)$ was calculated:

$$
\frac{H_2O}{(c + C_2)} = \frac{m_{Steam,fa} + m_{H2O,fuel}}{m_{C,fuel} + m_{CO2,fa}} \tag{5}
$$

The expression can be calculated with both mass and molar values. However, usefulness of the obtained results differs.

Design of experiment

When conducting gasification experiments in FB reactors it is vitally important to keep similarity of process conditions alike between each test (U/U_{mf}) , ER, CO_2/C , H_2O/C , \dot{m}_{fuel} etc.). This goal becomes difficult to reach in situations when reactor pressures are varied. The level of complexity rises even further when mixture of $O_2/CO_2/H_2O$ is used for gasification. To simplify the amount of strategies, which can be used to design a FB research, two most commonly applied strategies are described below. For any FB research, the fundamental condition is to keep hydrodynamic parameters of the bed constant. Following is the stream of fuel which can either be kept constant (constant heat input) or rise with increasing pressure in a linear or exponential function (varying heat input). For biomasses the rise in reactor's output power can be approximated to change linearly with increasing pressure (up to 8 bar). In the constant heat input case, it is impossible to keep the relations between the amount of H_2O/CO_2 and the feedstock (carbon in fuel) constant. Either H_2O or $CO₂$ needs to be used as the excess fluidizing gas needed to keep the hydrodynamic conditions of the bed stable between different pressures. On the other hand, when a variable heat input is applied, the relations between fluidizing gas composition and the feedstocks can be kept constant, but in this case another source of problem stems up from the increasing amount of ash material present in the system. On one hand ash agglomerates can influence the gasification kinetics while on the other it can leads to severe agglomeration problems. In this research the variable heat input strategy has been applied.

3. Results and discussion

Goal of this research was to perform screening tests in order to search for optimal gasification conditions and to set limits for tests that will be carried out in later stages of the project. Results of the gasification runs where stable process conditions were achieved are presented in Tab. 3. For each pressure value, at standard 850°C FB temperature, a set of stable gasification parameters were achieved with the exception of gasification of lignin at 2 barg. For lignin also experiments at 2 bar _s and temperatures of 830°C and 800°C always led to quicker or slower defluidization of the bed.

From all the feedstocks, lignin stood out as the most difficult one for gasification. Its atmospheric gasification showed that high amount of fuel stayed in the bed and that it did not fluidize well (high temperatures difference in FB). Here also the freeboard temperatures were lower than for other feedstocks. On the other hand, when at 1 bar fluidization number was slightly reduced, lignin exhibited high tendency for fragmentation, and large portion of the fuel was elutriated from the bed. Hence, higher freeboard temperatures were noticed. To assess if this property is characteristic for lignin, bark was also gasified at higher in-bed gas velocities. However, no signs of feedstock fragmentation, heterogeneous bed behaviour, or tendencies for defluidization were noticed. For bark and SWP the variable heat input design of experiment was successful and gave good comparison of obtained results. Also, no conditions were determined when the FB would defluidize.

In relation to gas yield, lignin produced much higher amounts of gas species in relation to other feedstocks, mainly with regard to CO. Furthermore, a general trend was noticed where for all tested feedstocks, increase in pressure led to

 $*$ syngas in dry state with $CO₂$ ** tar measurement and definition described above

Tab. 3: Results experimental test runs CO² gasification, Process efficiency parameters, Process indices.

subsequent increase in yield of CH4. For higher hydrocarbons (C_xH_y) the trend was unclear.

To perform synthesis of chemicals from syngas it is necessary to assure a certain ratio of $H₂/CO$. For FT the ratio should reach values in excess of 2. With conventional O_2/H_2O gasification and with use of mildly catalytic bed material such as olivine this goal is often attainable without use of additional water-gas shift reactors. However, in the performed experiments it has been shown that addition of even small amounts of $CO₂$ into a gasification system has a detrimental effect on the yield of $H₂$. The highest ratio of $H_2/CO = 0.78$ was obtained for gasification of bark when the $H_2O/(C+CO_2)$ was equal to 0.51 (H_2O/C $= 1.03$). For lignin the same tend was

noticed where the ratio of $H_2O/C=1.2$, yielded only $H_2/CO=0.69$ (here $H_2O/(C+CO_2) = 0.53$).

When process efficiency is concerned, the highest CGE of over 76% has been reached for bark. Consecutively lignin and SWP gave lower CGE, yet still above the level of 70%. Recurrent picture can be seen where gasification of lignin was done with lower CGE and higher CCE in relation to bark. No clear information could be determined as to the impact of pressure on CCE. However, for bark a stable rise in CGE was noticed.

Bed agglomeration propensity

Even though for all tested feedstocks, the gasification runs were conducted at the same temperature level the amount of observed bed agglomeration differed greatly. For all SWP tests no signs of bed agglomerations could be found. Gasification of bark led to formation of a small amount of very fine agglomerates in the bed (sieve analysis >1mm). However, for no process conditions did the agglomeration of bark ash led to the point of bed defluidization. Finally, even though many experiments were performed, no stable operation at 2 bar_g could be reached for lignin. From equilibrium calculations it is known that pressure should have little or no effect on agglomeration behaviour of the tested biomasses. Still, performed tests show that when the amount of fuel fed into a FB is increased, situations where the bed does not fluidize stably are encountered often. Origins of this behaviour may lie in maldistribution of the fluidizing gas due to the increasing amount of char material present in FB or reaching the critical concentration of ash.

4. Conclusion and Outlook

The presented experimental research was conducted for 3 pressures, changing rate of fed fuel (variable heat input) and similar fluidization conditions. This mode of experiment design gave good comparability of results between tests conducted at very broad spectrum of gasifying agent compositions and feedstocks. Hence, it is proposed for future research on pressure gasification with use of $CO₂$. Important though is to take into consideration the impact of increasing ash material present in bed to avoid its defluidization.

For the tested waste biomasses, bark was determined to give the best overall gasification behaviour with good yields and quality of syngas, high CGE and CCE. Connecting this with the fact that for bark' gasification runs were very stable, makes the feedstock very promising for future research. SWP used here as reference material provided worse characteristics of produced syngas and CGE to both bark and lignin. However, it was also the only feedstock which showed no signs of ash agglomeration in FB.

On the other hand, it was found that lignin gasification was prone to lead to bed defluidization with increasing stream of fuel and system pressure. It can be argued that bed fluidization occurred here through a mechanism which involves a combined influence of the chemical characteristic of lignin's ash material as well as a certain limiting amount of the ash that is possible to be present in a FB. Experience gained during the trials

indicates that lignin is a difficult, but promising feedstock for gasification. Due to its abundance, waste character and stable annual availability, it should be treated as a viable choice for diversification of the group of applicable waste feedstocks.

The conducted experiments show that the concept of chemical sequestration of $CO₂$ is technically feasible option in biomass gasification reactors. However, influence of the applied $CO₂$ on the composition of yielded syngas is very high and may deem its utilization for the purpose of chemical synthesis impractical.

Due to the fact that addition of $CO₂$ into a gasification system changes the usefulness of commonly applied process efficiency indicators it is important to adapt them in a way which would not influence highly their original meaning. For this reason the adapted CCE (Eq. 4) and $H_2O/(C+CO_2)$ (Eq. 5) indices were proposed.

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