



Influence of pressure and CO₂ in fluidized bed gasification of waste biomasses

Mateusz Szul¹ · Krzysztof Głód¹ · Tomasz Iluk¹

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Abstract

An autothermal fluidized bed reactor was used to research the influence of pressure (0–2 bar_g) on the gasification process of different types of biomasses. The tested feedstocks were bark and lignin while softwood pellet was used as a reference fuel. A mixture of O₂/CO₂/H₂O was used as a gasification agent. The impact of the application of CO₂ on the yield of H₂ in product gas was determined. Resulting product gas was characterized by a high content of CO which makes its use for applications based on chemical synthesis very difficult without extensive upgrading or supply of H₂ from external sources. CO₂ proved to improve carbon conversion efficiency (CCE) of the gasification process and to be an option for its chemical sequestration (negative carbon footprint). A slight modification of conventional indices used to evaluate efficiencies of gasification systems (CCE and water/carbon ratio) was proposed, to take into account the impact of the additional source of carbon fed into the reactor. The increase of system pressure led to changes in the composition of the product gas in line with predictions of Le Chatelier's principle. The influence was predominantly visible in higher yields of CH₄ and lower overall production of product gas. For higher hydrocarbons (C_xH_y), the trend was unclear. A set of stable gasification parameters were achieved for each pressure level and a standard gasification temperature of 850 °C, except for gasification of lignin performed at 2 bar_g. A proposed explanation for the problem is the combined effect of the increasing concentration of ash in the fluidized bed and its low characteristic melting temperatures. Due to the obtained experimental findings, a new ash agglomeration index was formulated.

Keywords O₂/CO₂/H₂O · 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 energy sources. However, when the feedstock is changed to renewables, like biomass, the need for use of pressurized reactors is highly debated.

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

- 1) To develop BtL routes for the production of biodiesel and dimethyl ether (DME) from black liquor gasification;
- 2) To mature pressurized gasification plants to produce bio-synthetic natural gas (bio-SNG), as in the Bio2G project;
- 3) To study hybrid biochemical and thermochemical conversion routes.

The first two goals are directly related to the development of pressurized biomass gasification systems [1].

Noteworthy, from the principle for thermodynamics, gasification of biogenic feedstocks at higher operating pressures can be beneficial from several perspectives. Firstly, biomass gasification at elevated pressures provides higher reaction efficiencies and kinetics [2–4]. Secondly, when the product gas is produced for chemical synthesis, the overall process efficiency can be increased by avoiding the step of gas compression, which always incurs energy and exergy losses [5]. Nonetheless, the inherent advantages of pressurized gasification are equally counterbalanced by its drawbacks. For many

✉ Mateusz Szul
mszul@ichpw.pl

¹ Instytut Chemicznej Przeróbki Węgla, Zamkowa 1,
41-803 Zabrze, Poland

pressurized gasification projects, the operational challenges related to the complexity of the system, its construction and control have ultimately led to various failures, unstable operation or lack of economical ground for the investment [6]. For coal, gasification at pressures higher than 50 bar is supported by the increase in reaction kinetics and thus the whole installation concept is justified. However, for most biomasses, it is said that the maximum gasification pressure which provides an optimum ratio of ‘kinetic-gain to process-complexity-loss’ is 4–7 bar, which derives from the fact that gasification of biomass produces much less char, and the char it produces is much more reactive than char from gasification of coal. Thus, it is often suggested that operation at 4–5 bar should be optimal for biomass [1, 7, 8]. From the process engineering standpoint, this level of pressurized gasification is too low to completely avoid the syngas compression step before synthesis. Thus, the two syngas-based polygeneration routes most often discussed for biomass are methanation, which is operated between 1 and 10 bar, and Fischer–Tropsch synthesis, which is often conducted at 20–40 bar. Noteworthy, synthesis of alcohols and DME, which is often proposed for coal-to-X concepts, demands elevated pressures of respectively 50–300 bar and 15–100 bar.

Over the past few years, thermogravimetric (TG) and differential scanning calorimetry (DSC) approaches were broadly applied to assess the effect of gasification process conditions (e.g. pressure, temperature, composition of the gasification agent) on the reaction kinetics of a broad range of feedstocks. Both methods can be performed simultaneously and are relatively low work-intense while providing data necessary to determine the intrinsic reaction kinetics parameters with high accuracy and repeatability. Importantly though, to avoid the problems related to condensation of the organic phase (especially pronounced in pressurized TG) or to keep isothermal reaction conditions, and thus good repeatability of produced results, TG experiments on carbonaceous feedstocks often need to be conducted on chars obtained from feedstocks that were devolatilized. Thus, currently, TG lacks the possibility to exactly map the process conditions occurring in a fluidized bed (FB), where volatilisation and gasification of the feedstock occur simultaneously at the same atmosphere, temperature and pressure conditions.

Another approach to assess the impact of pressure and composition of the gasification agent is based on thermodynamic equilibrium calculations and modelling. With equilibrium models, it was shown that rising pressure and temperature lead to lower H₂ and CO production, while yields of CO₂ and CH₄ increase [3, 9, 10]. Similarly, thermodynamic equilibrium approaches inform us that application of CO₂ for gasification, even more, strengthens the trend towards lower yields of H₂ and CO as a result of reversed water–gas shift and Boudouard reactions [11]. Importantly though, no gasification reactor can reach equilibrium conditions and hence the

resulting products of gasification always differ from the ones calculated with equilibrium models.

Several experimental results of FB gasification of biomass are available in the literature on the influence of pressure; however, the reported results are often contradictory. Generally, it is agreed that with increasing pressure increases also the overall gas and tar yields [6, 12]. The subject of char production remains ambiguous. In allothermal, steam-blown gasification studies, it was proven that methane yield increases by up to 38% with pressure increase from 2 to 10 bar [4]. This indicates higher demand for product gas upgrading 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 the equilibrium of reactions concerning the conversion of hydrocarbons) 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 the scheme of pathways of secondary pyrolysis reactions [2].

Furthermore, contrary to coal, the availability of experimental studies on the influence of the application of CO₂ on gasification of biomass is even more limited than the researches on the impact of pressure. In the available literature, it was shown that CO₂ can take part in gasification systems similar to steam and thus act as both fluidizing and active gasification agent [13–15]. Usage of CO₂ shifts equilibrium of both Boudouard reaction and water–gas shift reaction in favour of production of CO. It also has higher specific heat capacity and hence presents the tendency to lower the temperature of gasification, which implies higher heat demand and keeping higher air–fuel equivalence ratios (λ). In the general scheme of gasification process conditions, the introduction of CO₂, in the place of steam, raises drastic changes not only to the gasification reactor but also to every downstream unit operation, which the product gas needs to undergo. This is particularly important as similarly to steam only a part of the fed CO₂ reacts with fuel and yields product gas, while the rest leaves the reactor as a dilution gas. However contrary to steam, CO₂ cannot be separated from product gas by simple cooling/condensation or drying. Thus, the unreacted CO₂ together with CO₂ produced, i.e. in carbon oxidation reactions, remains in the product gas and can only be extracted through the use of additional, dedicated separation processes (amine washing, membranes, adsorption). Contribution of the CO₂ in product gas can reach 50–60 vol%, which diminishes the usefulness of the application of the dry state of reference, which is commonly used to report composition of product gas produced in conventional gasification processes. The concept of using CO₂ for increasing C conversion and lowering C footprint is known and has been extensively subjected to research in coal gasification and oxy-combustion studies. For biomass, the use of CO₂ can make an installation additionally C-

negative, which is very promising for the future perspective of active reduction of the amount of CO₂ in the atmosphere [13–16].

The article presents experimental results on pressurized gasification of waste biomass performed in an FB reactor. Two feedstocks (wood bark and lignin residue from the production of bio-ethanol) were compared with a reference fuel (softwood pellet, SWP) regarding their gasification efficiency. The tests were performed in autothermal mode with use of O₂/CO₂/H₂O mixture as a gasifying agent. The registered process data on FB gasification and product gas quality were confirmed through performing mass and energy balances.

To be able to monitor the FB gasification experiments and thus obtain results comparable with the ones obtained previously or reported in the literature, it is essential to establish a precise range of control variables which often are based on commonly applied process indices. However, for O₂/CO₂/H₂O gasification process, the opposing influence of CO₂ and H₂O on process gas composition causes the application of conventional indices to give results which cannot be compared with the ones obtained through air/oxygen/steam gasification. Thus, a group of verified process and efficiency indices, which more precisely describe the CO₂ gasification runs, are presented here. Here, analysis of presented results provides answers in the field of production of FT fuels from CO₂ gasification of waste biomasses.

Finally, the research allowed also screening process conditions which lead towards low efficiency of the system or unstable behaviour of FB. Presented results were obtained during stable operation of the reactor, while process conditions that lead to instability of the FB system at increased pressures are discussed. Agglomeration of the bed was the main technological issue encountered during the tests. Aspects of the process that promote the probability of agglomeration are discussed herein. The article debates also the relevance of laboratory ash tests and slagging indices with regard to the operational experience.

2 Materials and methods

2.1 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 (6 mm outer diameter) to improve their density and homogeneity; however, due to the small size of screw feeders used in this lab-scale unit, the fuel pellets additionally needed to be crushed and sieved before use. Average particle size distribution and bulk density of the feedstocks after size reduction were measured. Preparation and characterization of the

feedstocks were performed in the Institute for Chemical Processing of Coal and the measured physicochemical properties of the gasified biomasses are shown in Table 1.

Ashes from the feedstocks were analysed with a visual method to assess their thermal behaviour in the half-reducing atmosphere. The procedure followed the CEN/TS 15370-1 standard.

Primary bed material used in the research was olivine, obtained from Magnolit GmbH (Austria). Table 2 presents the most important information regarding the bed material applied in this research in comparison with the standard silica sand.

For all tested feedstocks, IDT was measured to be lower than 850 °C, which is the set benchmark temperature of this FB reactor. Moreover, also the ST of softwood pellets and lignin was measured to be low in comparison with conventional clean woody biomass, what in the case of lignin, and its high ash content, may indicate potential problems with defluidization of the bed. When comparing the data with reference available e.g. in Phyllis2 database, the measured IDT and ST of the feedstocks are low. Reports for SWP, bark and lignin samples can be found stating the two temperatures to reach a 1000–1100 °C range [18–20]. However, concerning waste feedstocks previously analysed by IChPW, such values are not surprising. Physicochemical parameters of fuels applied in this research are comparable with parameters of feedstocks of similar kind but procured from a different source.

2.2 Research installation

The experiments were carried out on a lab-scale installation presented in Fig. 1. The main part of the unit is a fluidized-bed gasifier with an in-bed feeding system. The reactor is electrically heated during start-ups. 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 an internal diameter of 105 mm and height of 1500 mm. The bottom part of the reactor is 300 mm long and has a conical shape, which tapers to the diameter of 75 mm at the distributor level. Fluidization medium is distributed within the reactor with the use of a perforated plate of ca. 4% open area. Temperature measurements inside the reactor and the freeboard are carried out with the use of five vertically mounted K-type thermocouples. Three bottom thermocouples are placed within the bed while the remaining two indicate a temperature profile of the freeboard. A more in-depth description of the details of the installation can be found in the literature [21, 22].

The fuel feeding system consists of three storage tanks. Two of them are equipped with knife gate valves, which enable fuel loading while the experiments are conducted in overpressure. The biomass flow is regulated by changing the rotational speed of the upper screw feeders. From the fuel dosing

Table 1 Physicochemical characteristic of gasified feedstocks—crushed pellets (d – dry state, ar – as received or working state)

		SWP	Bark	Lignin
Moisture (ar)	wt%	5.28	3.51	10.80
Ash (d)	wt%	0.22	9.87	4.37
Volatile matter (d)	wt%	84.8	71.7	66.7
C (d)	wt%	52.1	49.2	57.6
H (d)	wt%	5.38	4.45	4.86
N (d)	wt%	0.06	0.48	1.41
S (d)	wt%	0.02	0.03	0.21
HHV (d)	J/g	20,799	17,986	22,428
Characteristic ash melting temp.	IDT/ST/HT/FT, °C	660/900/1420/1560	760/1500/1530/1540	600/690/1310/1540
Bulk density (ar)	kg/m ³	502.8	797.9	777.6
Particle size distribution, wt%				
> 3.15 mm	wt%	31.41	11.65	4.49
3.15–2 mm	wt%	35.13	35.97	25.29
2–1.4 mm	wt%	25.57	19.49	31.15
1.4–1 mm	wt%	5.84	9.54	15.31
1–0.8 mm	wt%	1.14	4.10	6.17

tanks, the fuel is fed into a drop tube. The drop tube ends with a high capacity in-bed screw feeder which is additionally cooled via a water jacket. This technical solution prevents heating-up of the stored fuel and its uncontrolled pyrolysis during transitional and intermittent phases of experiments. For safety reasons, the feeding system is continuously purged with small quantities of nitrogen.

Downstream of the reactor, product gas reaches a cyclone where particles of the entrained char, ash and bed material are recovered. Product gas after dedusting is directed through a

pressure relief valve towards a flare. After the reduction of pressure, the product gas is sampled for analyses.

Gasification agent mixture is prepared from gas cylinders (arranged into bundles with separate pressure regulators) containing technical grade O₂, N₂ and CO₂. The flow rate of each agent is measured independently using Bronkhorst EL–FLOW SELECT mass flow controllers. The gas mixture flow lines are electrically heated at 320 °C. The steam flow rate is regulated by FWT di Tommaso Commonara water dosing pump (max. flow 4 dm³/h) positioned upstream of the steam generator and steam preheater.

Table 2 Physicochemical characteristic of fluidized bed materials. Comparison of the olivine applied in this research with the standard silica sand

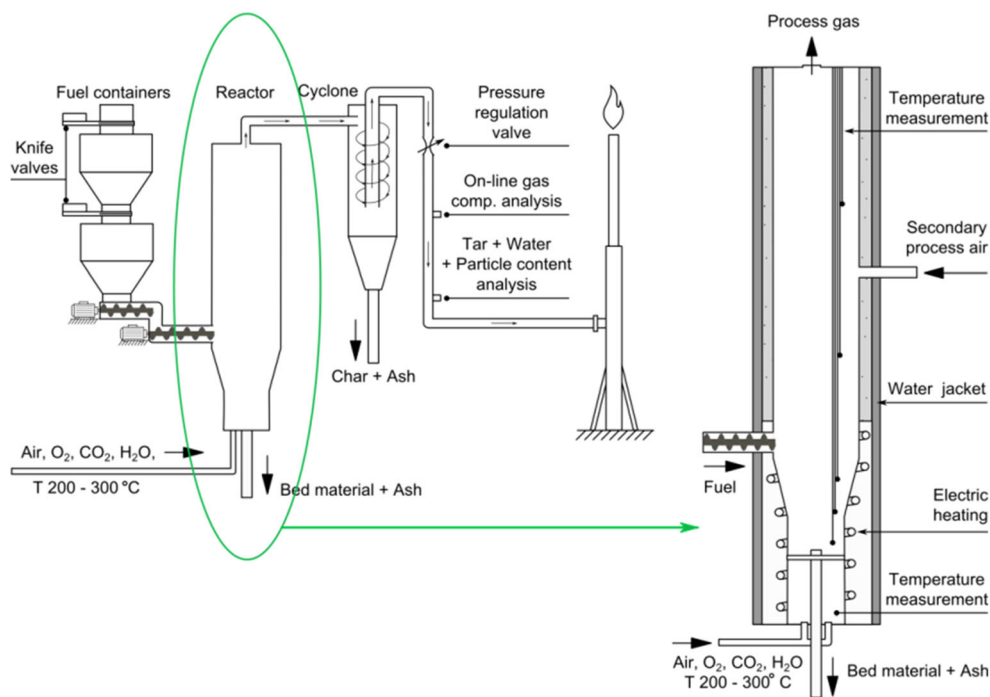
		Silica sand	Olivine
Bulk density (d)	kg/m ³	1468	1504
Particle density (d)	kg/m ³	2366	2722
Real density (d)	kg/m ³	2654	3248
Grain porosity	–	0.11	0.16
Fixed bed porosity	–	0.38	0.45
Particle size distribution, wt%			
> 315	µm	0.54	0.09
250–315	µm	37.40	31.17
200–250	µm	50.33	60.32
160–200	µm	9.58	8.19
100–160	µm	2.06	0.23
< 100	µm	0.09	0.00
Mean particle diameter	µm	235.22	234.91
U _{mf} [17]	m/s	0.0422	0.0484

2.3 Method and operating conditions of the reactor

Start-up of the reactor was initiated by electrical preheating of the unit at 700 °C. Afterwards, a small stream of the fuel was fed into the bed to start a controlled combustion process with air and a small amount of steam. For this research, when the temperature in the bed reached 750 °C, the air was replaced by carbon dioxide and oxygen mixture. Flow rates of gas and fuel were further adjusted to obtain steady combustion parameters and good control over heating-up of the bed to starting temperature of the process (840 °C). Usually, the longitudinal profile of temperatures in the freeboard zone stabilized between 600 and 750 °C. If the conditions in the reactor/installation (i.e. temperature and pressures) were sufficient, the fuel stream was further increased to initiate the gasification process. The 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 flow rate of oxygen, fuel and water fed into the

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



reactor jacket. During the balancing points, the reactor pressure was set at 0, 1 and 2 bar_g.

The influence of total water present in the process was determined in the range of 0.55–1.2 H₂O/C. The index was calculated with the following formula:

$$\frac{H_2O}{C} = \frac{\dot{m}_{Steam,ga} + \dot{m}_{H_2O,fuel}}{\dot{m}_{C,fuel}} \quad (1)$$

In terms of fluidization number, the tests were conducted at the level of $U/U_{mf} = 8.5 \pm 1.5$, except for lignin which demanded the reactor to be operated at higher in-bed velocities.

2.4 FB gasification efficiency indices

In conventional gasification systems where air/H₂O or O₂/H₂O mixtures are used as gasifying agent, the conversion efficiency indices are well-established and successfully allow comparing different reactors and process conditions. To the list of indices of primary importance belong cold gas efficiency (CGE), carbon conversion efficiency (CCE) and H₂O/C.

CGE gives direct information about the amount of useful chemical energy of fuel converted into product gas. It can be calculated based on either higher or lower heating values and importantly this index is not sensitive for the composition of a gasifying agent. Here, Eq. 2 was used to calculate the reactor’s CGE.

$$CGE = \frac{(HHV_{pg}) \times \dot{m}_{pg} \times 100\%}{(HHV_{fuel}) \times \dot{m}_{fuel}} \quad (2)$$

In gasification systems, CCE is an index that gives information regarding the efficiency of conversion of carbon contained in a feedstock towards product gas rather than to co-products such as tars or chars. It is based on the C balance of the system and can be calculated by the following equation:

$$\varphi_{C,fuel \rightarrow C,pg} = \frac{X_{C,pg} \times \dot{m}_{pg} \times 100\%}{X_{C,fuel} \times \dot{m}_{fuel}} \quad (3)$$

Noteworthy is the fact that Eq. 3 does not take into account any additional sources of C fed into the reactor. Hence in this research, with the use of the conventional form of CCE index, one could calculate process efficiencies exceeding 100%. To counteract this, the CCE needs to be modified with an additional term related to the CO₂ fed into the reactor as a gasification agent. For this reason, Eq. 4 was proposed as the best simple approximation of the logic standing behind the conventional CCE index. It is a direct C balance equation which takes into account the additional substrate fed into the process.

$$\varphi_{C,in \rightarrow C,pg} = \frac{X_{C,pg} \times \dot{m}_{pg} \times 100\%}{X_{C,fuel} \times \dot{m}_{fuel} + \dot{m}_{C,CO_2,ga}} \quad (4)$$

The same reasoning was applied towards determination of a correct way to define an index based on H₂O/C, which

Table 3 Collation of the most important gasification reactions impacted by the partial pressure of H₂O and CO₂

Irreversible reactions	
$C + O_2 \rightarrow CO_2$	$Q = -405 \frac{kJ}{mol}$
Complete oxidation of C	
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$Q = -242 \frac{kJ}{mol}$
Oxidation of H ₂	
Reversible reactions	
$C + H_2O \rightleftharpoons CO + H_2$	$Q = 131 \frac{kJ}{mol}$
Water–gas reaction	
$CO + H_2O \rightleftharpoons CO_2 + H_2$	$Q = -41 \frac{kJ}{mol}$
Water–gas shift reaction	
$C_x H_y + xH_2O \rightleftharpoons xCO + \frac{(y+2x)}{2}H_2$	$Q = +(endo.)$
The general steam reforming reaction	
$C + CO_2 \rightleftharpoons 2CO$	$Q = 172 \frac{kJ}{mol}$
Boudouard's reaction	
$C_x H_y + xCO_2 \rightleftharpoons 2xCO + \frac{y}{2}H_2$	
or	
$C_x H_y + \frac{y}{4}CO_2 \rightleftharpoons (x + \frac{y}{4})C + \frac{y}{2}H_2O$	$Q = +(endo.)$
The general CO ₂ reforming reaction	

would serve the purpose of relating the amount of steam used as a gasifying agent, to the amount of carbon fed to the reactor with fuel and CO₂. 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 are shown in Table 3. Boudouard and reverse water–gas shift reactions are the main pathways through which CO₂ influences gasification systems. Both are endothermic and yield CO while consuming H₂.

To follow the combined influence of the applied ratio of CO₂ and H₂O, several indices have been formulated and analysed. The most reliable results were found when the index H₂O/(C+CO₂) was calculated. These results were also the most coherent and clear in evaluation:

$$\frac{H_2O}{(C + CO_2)} = \frac{\dot{m}_{Steam,ga} + \dot{m}_{H_2O,fuel}}{\dot{m}_{C,fuel} + \dot{m}_{CO_2,ga}} \quad (5)$$

This expression can be calculated with both mass and molar values. However, the usefulness of the obtained results differs; hence, this research utilized Eq. 5 based on molar values.

Air–fuel equivalence ratio was calculated here with the use of a standard formula (Eq. 6) relating the amount of oxidant (air/oxygen) and fuel fed to the reactor (named air-to-fuel ratio) to the stoichiometric amount of oxidant that is needed for complete combustion of a unit of fuel.

$$\lambda = \frac{(\dot{m}_{O_2,ga}/\dot{m}_{fuel})}{(\dot{m}_{O_2,ga}/\dot{m}_{fuel})_{stoich.}} = \frac{(\dot{n}_{O_2,ga}/\dot{n}_{fuel})}{(\dot{n}_{O_2,ga}/\dot{n}_{fuel})_{stoich.}} \quad (6)$$

2.5 Design of experiment

When conducting gasification experiments in FB reactors, it is vitally important to keep similarity of process conditions alike between each test run, hence, the usefulness of the abovementioned indices (U/U_{mf}, λ, CO₂/C, H₂O/C, \dot{m}_{fuel} , etc.). Importantly though, in a situation when reactor pressures are varied or a ternary mixture of a gasifying agent is used (O₂/CO₂/H₂O), this goal becomes difficult to reach. To simplify the number of strategies which can be used to design FB experiments, two most commonly applied are described hereafter. For any FB test run, the fundamental condition is to keep hydrodynamic parameters of the bed constant. A subsequent variable is the stream of fuel which can either be kept constant (constant heat input) or be raised with increasing pressure (varying heat input). The way in which the amount of fuel fed is increased can also be varied, and this function can have a linear or exponential character, depending on the feedstock and gasifier. For biomasses, the rise in the reactor output power can be approximated to change linearly with increasing pressure (up to 8 bar) [9, 23, 24]. In the constant heat input case, it is impossible to keep the relations between the amount of H₂O/CO₂ fed into a reactor with a gasifying agent and the feedstock (carbon in fuel) constant. Either H₂O or CO₂ needs to be used as the excess to keep the hydrodynamic conditions of the bed stable between different pressures. On the other hand, when variable heat input strategy is applied, the relations between fluidizing gas composition and the feedstocks can be kept constant, but in this case, the problem of the increasing amount of ash material present in the system needs to be addressed. On the one hand, the increase of ash concentration in bed material can have a positive influence on the kinetics of the gasification process, while on the other, it can also lead to severe problems with the agglomeration of the bed material. In this research, the variable heat input strategy was applied.

2.6 Determination of product gas composition and content of contaminants

Samples of the product gas, after primary dedusting in a cyclone and lowering of pressure, were collected in Tedlar bags and analysed with gas chromatography (GC). The GC analyses were done using a Varian CP3800 GC, coupled with a flame ionization detector, a thermal conductivity detector and a pulse flame photometric detector. The qualitative and quantitative analyses were performed using the external gas standard method.

Moreover, product gas was also sampled to determine its water, tar and solid particle content. The sampling system consisted of a probe, two impinger bottles and a tube filled with cotton wool. The probe was introduced axially into the product gas line, after the sampling port used for

determination of product gas composition. 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 were collected. The glass tube filled with cotton wool, fitted at the end of the probing set, acted as a droplet collector. The product gas was sucked by a pump coupled with a flow regulator. The sampling line was presented on Fig. 2.

For the determination of water content in the product gas, the Karl Fischer method was applied. Dust particles collected in the isopropanol solution were filtered off, washed with an additional portion of isopropanol, dried and weighed after a constant mass was reached. Mass of gravimetric tars was measured after evaporation of the solvent under reduced pressure (0.1 bar, 80 °C) and final drying until a constant mass was reached. Conditions of the abovementioned procedure stand for definition of tars adopted in this research.

The total amount of solid particles contained in raw process gas after the FB reactor was calculated as a sum of the weight of solids recovered from the primary cyclone and the remaining amount of solids measured through the above-described sampling of the process gas. Results of proximate and ultimate analysis of the cyclonic particles were used for calculation of mass and energy balances as well as the calculation of process efficiency parameters.

This product gas sampling method is derived from the Tar protocol guidelines; however, since no qualitative and quantitative analysis of lightweight organic fraction was performed here, there also was no need to comply with the complete setup proposed by the guidelines for absorption in isopropanol. The setup applied in the research was compared against the complete probing set proposed in the Tar protocol and the same results of gravimetric tars (molecular mass too high for GC) were obtained with both methods. This comes from the fact that heavy tars tend to set/condense directly on the first elements of the probing set, being quartz filter or in

the first impinger bottle, while the following impinger bottles tend to recover mostly the solvent evaporated from the upstream impinger bottles as well as lightweight organic compounds.

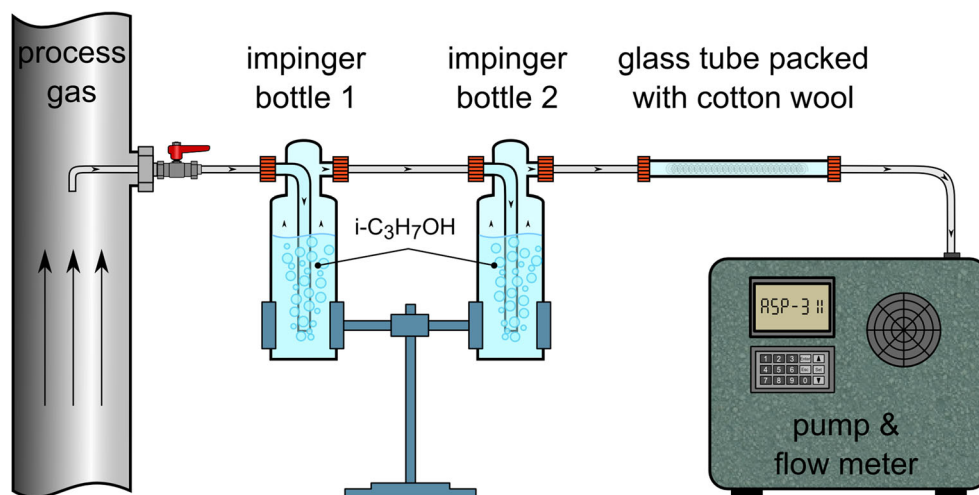
3 Results and discussion

3.1 Gasification study

The goal of this research was to perform screening tests that will determine optimal gasification conditions for the feedstocks and give grounds for the design of gasification experiments that will be performed at higher pressures. The obtained results will thus be optimized at later stages of the project through gasification experiments, conducted in a larger scale CFB reactor (40–120 kg/h). Gasification temperature of 850 °C, measured as the highest recorded in bed, was set as common for all the tested biomasses. For all feedstocks, a set of stable gasification parameters were achieved except for gasification of lignin at 2 bar_g. Furthermore, for gasification of lignin at 2 bar_g, also temperatures of 830 °C and 800 °C were tested; however, these experiments still always needed to be terminated prematurely, due to defluidization of the bed. Importantly though, with lower gasification temperatures of lignin, the time until defluidization occurred rose. Results of the stable gasification runs were presented in Table 4.

From all the feedstocks, lignin turned out to be the most difficult to gasify. During its gasification, at atmospheric process conditions, a high amount of char and ash remained in the bed, which had a negative impact on the quality of fluidization (high temperature difference in FB). Here also, the freeboard temperatures were lower than for other feedstocks. On the other hand, when fluidization number was slightly reduced (test performed at 1 bar_g), lignin exhibited a high tendency for fragmentation, and a large portion of the fuel was elutriated

Fig. 2 Schematic diagram of the gas sampling line



from the bed. Hence, during this test, higher freeboard temperatures were noticed. To assess if this property is characteristic for lignin, the bark was also gasified at higher fluidization velocities. However, in this case, no signs of feedstock fragmentation, heterogeneous bed behaviour (segregation of the bed) or any other symptoms pointing towards the tendencies of the bed to defluidize were noticed (e.g. through rising temperature or pressure difference in the bed). For bark and SWP, the variable heat input design of experiment needs to be rated as a success, as it gave results that can be compared. Also for these two feedstocks, no conditions were observed when the FB would defluidize.

Concerning gas yield, lignin produced much higher amounts of gas species, primarily CO, when compared with other feedstocks. Figure 3, presented below, shows the product gas composition after recalculation to CO₂-free basis. This action brings the product gas composition closer to 'dry-state conditions', which is the reference state often used to report product gas composition from conventional air/O₂/steam gasification runs. Furthermore, a general trend was noticed here, where for all tested feedstocks, increase in pressure always led to an increase in yield of CH₄. For higher hydrocarbons (C_xH_y), the trend remained unclear.

To perform a synthesis of chemicals from product gas, firstly it needs to be upgraded to syngas and depending on the application, a certain ratio of H₂/CO needs to be assured. For FT, it is preferable for the ratio to slightly exceed 2. With conventional O₂/H₂O gasification and with use of mildly catalytic bed material such as olivine or CaO, this goal is often attainable without the use of additional water–gas shift reactors. However, in the performed experiments, it was shown that the addition of even small amounts of CO₂ has a substantial effect on the yield of H₂. The highest ratio of H₂/CO = 0.78 was obtained for gasification of bark when the H₂O/(C+CO₂) was equal to 0.51 (H₂O/C = 1.03). For lignin, the same trend was noticed. However, the ratio of H₂O/C = 1.2 yielded only H₂/CO = 0.69 (at H₂O/(C+CO₂) = 0.57).

When process efficiency is concerned, the highest CGE of over 79% was reached for bark. Consecutively, lignin and SWP gave lower CGE, yet still, for both feedstocks, CGE > 70% was calculated. A recurrent picture can be seen, where gasification of lignin occurred at lower CGE and higher CCE when compared with bark. Noteworthy, the presented CGE was calculated for balancing points where the reactor was operated without electrical heating and had reached steady conditions (min-max registered temperature spread at all available reactor thermocouples < 30 °C). The values are in line with previous gasification experiments performed with the use of this reactor. No clear information could be determined though, as to the impact of total gasification pressure on CCE. Uniquely for bark, a stable rise in CGE can be noticed.

The effect of H₂O/(C+CO₂) on the ratio of H₂/CO produced was summarized in Fig. 4. The amount of data available to this point on gasification of biomasses with the ternary gasification mixture composed of O₂/CO₂/H₂O is limited; however, projection of the values available shows that at a constant feed of C into a reactor (with fuel and CO₂), the H₂/CO ratio of 2 could be reached at H₂O/(C+CO₂) ratios of 2.2, 2.9 and 3.5 respectively for lignin, bark and SWP. For O₂/H₂O gasification of biomass, the H₂/CO ratio of 2 is reachable often at ca 1–1.2 H₂O/C ratios. This discrepancy shows clearly how much addition of even small amounts of CO₂ hinders the production of H₂ and promotes the production of CO. The issue of the influence of gasification with the use of pure CO₂ was recently, extensively discussed and validated by Mauerhofer et al. [11, 25]. The reactor system used there was a dual-fluidized bed (DFB) which enables the production of the product gas in allothermal mode, thus separating the influence of combustion reactions. The authors indicate that at the DFB gasification conditions (760–840 °C), the reverse water–gas shift reaction is the predominant route for CO₂ conversion, which supports the discussion and projection described herein.

3.2 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 the formation of only a small amount of very fine agglomerates in the bed (sieve analysis of particles > 1 mm). However, for none of the process conditions did the agglomeration of bark ash lead 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 an FB is increased, situations, where the bed does not fluidize stably, are encountered often. Origins of this behaviour may lie simultaneously in maldistribution of the fluidizing gas, due to the increasing amount of char material present in FB, as well as in reaching the critical concentration of ash present in the bed material. In industrial process conditions, it is the know-how and experience of the operator that dictates the rate at which the bed material needs to be regenerated or renewed. However, the concept of physicochemical determination of the critical concentration of ash in bed material is

Table 4 Results of experimental test runs, process efficiency parameters and indices

Fuel	Softwood pellet			Oak bark			Lignin		
	1	2	3	4	5	6	7	8	9
Run number	1	2	3	4	5	6	7	8	9
In bed temp. (°C)	852.8	843.6	853.6	853.3	853.7	854.9	852.0	853.9	–
Reactor pressure (bar _g)	0.0	1.0	1.9	0.0	1.0	2.0	0.0	1.0	2.0
Fuel ar. (kg/h; kW)	2.52; 13.9	5.64; 30.9	7.35; 39.9	2.95; 14.0	5.73; 27.6	8.51; 41.0	2.62; 14.6	5.37; 29.6	–
Composition of the gasifying agent (kg/h)									
O ₂	1.02	1.81	2.77	1.08	2.14	3.04	1.28	2.58	–
CO ₂	2.90	2.74	6.62	3.18	4.95	4.95	4.36	5.33	–
H ₂ O	0.73	2.48	3.70	0.60	2.49	3.86	0.70	2.70	–
Product gas composition (vol% dry)									
H ₂	11.88	15.16	13.21	14.21	15.60	19.66	12.13	18.00	–
CO	21.62	24.00	23.56	24.18	27.01	25.10	24.91	26.04	–
CO ₂	53.41	42.44	48.84	49.71	44.39	43.12	52.00	44.45	–
CH ₄	4.67	8.76	8.70	4.21	4.77	6.05	3.18	4.21	–
C ₂ H ₄	2.46	3.32	2.60	1.59	1.41	1.52	1.01	1.00	–
C ₂ H ₆	0.26	0.37	0.27	0.14	0.16	0.31	0.18	0.09	–
HHV (MJ/Nm ³)*	8.42	11.41	10.27	8.15	8.78	9.72	7.08	8.38	–
Product gas yield (Nm ³ /kg _{daf})	1.61	1.31	1.57	1.74	1.63	1.55	2.26	1.94	–
H ₂ O (g/Nm ³)	228.1	364.0	383.0	161.0	306.0	309.0	172.8	312.0	–
Tar (g/Nm ³)**	5.50	5.29	4.34	0.64	5.20	5.60	1.62	4.95	–
Solids (g/Nm ³)	4.54	3.30	2.60	68.76	54.77	52.52	10.51	7.87	–
FB gasification parameters									
U/U _{mfr} (–)	8.93	7.99	7.31	8.87	9.84	8.79	11.57	11.39	–
λ (–)	0.30	0.24	0.30	0.29	0.29	0.28	0.34	0.33	–
H ₂ O/C (g/g)	0.67	1.00	1.15	0.55	0.99	1.03	0.73	1.21	–
H ₂ O/(C+CO ₂) (mol/mol)	0.27	0.53	0.51	0.22	0.44	0.51	0.26	0.57	–
H ₂ /CO (vol%/vol%)	0.55	0.63	0.56	0.59	0.58	0.78	0.49	0.69	–
Gasification efficiency parameters (%)									
CGE – Eq. 2	70.9	77.4	73.1	76.8	78.3	79.2	76.2	75.1	–
CCE – Eq. 3	160.5	125.2	148.6	158.4	145.5	129.5	185.8	150.9	–
CCE – Eq. 4	98.4	98.7	99.0	97.2	97.3	97.1	98.7	98.6	–

* Product gas in the dry state with CO₂

** Tar measurement and definition described above

being studied extensively since it is particularly promising for increasing the reliability of FB reactors and extension of the range of feedstocks that can be applied to FB processes (particularly for waste feedstocks). The critical ash concentration concept stipulates that there exists a limit below which, the concentration of ash in bed material will not lead to its defluidization, as the amount of liquid phase present in the system is insufficient to cause agglomeration of the particles. The issue was studied in both simulated and real process conditions and first approximate equations determining the ‘time before defluidization’ were developed [25, 26]. Because at lab-scale gasification installations it is very difficult to perform a constant renewal of bed material (to withdraw the excess ash agglomerated in the bed),

for future research, it is proposed to seek a solution to this problem in either lowering the gasification temperature, increasing height of the bed (larger bed inventory) or lowering the heat input into the reactor.

In search of the differentiating factor between ash agglomeration characteristic of the tested fuels, their lab analysis was investigated as first. Interestingly, IDT for all 3 tested feedstocks is well below the temperature of performed gasification runs. Thus, the IDT does not give direct information regarding maximal temperature in which gasification of a feedstock can be done. The first parameter differentiating the feedstocks was their ST. SWP and bark had ash ST higher than the FB temperatures and respectively 210 °C and 810 °C higher than ST of lignin. Moreover, the ash content of the fuels differed greatly. SWP contrasted with bark and lignin by having a much

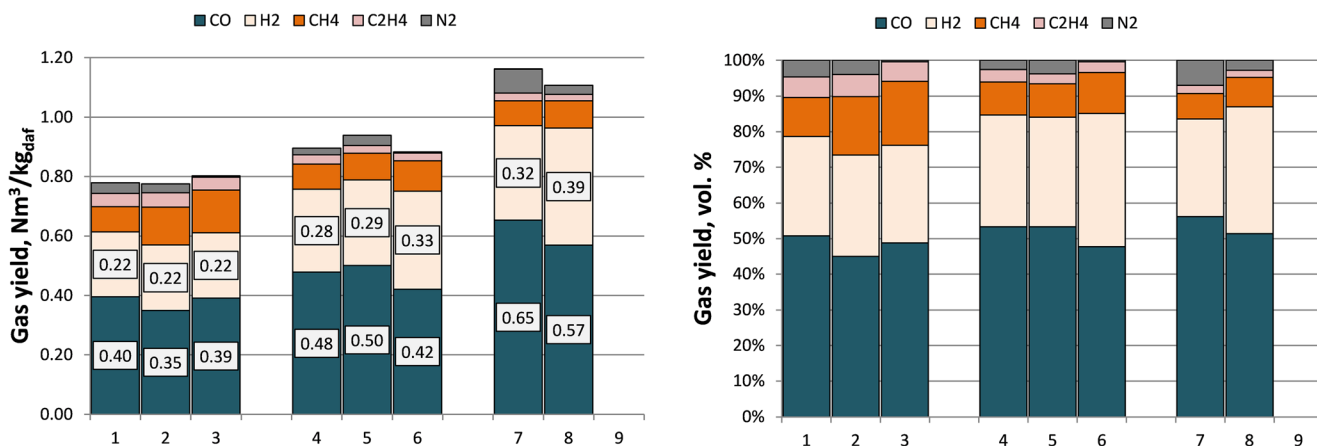


Fig. 3 Yield of main product gas constituents presented on CO₂-free basis

lower concentration of ash, which corresponds well with the slightly lower efficiencies of the gasification process that can be related to the lower ash concentration in the bed material. On the other hand, gasified bark was characterized by almost two times higher than the concentration of ash in comparison with lignin. This information strengthens the assumption that it is the combined influence of ash content in the bed material and its thermal characteristic that is responsible for sintering and defluidization of an FB.

3.3 Ash agglomeration indices

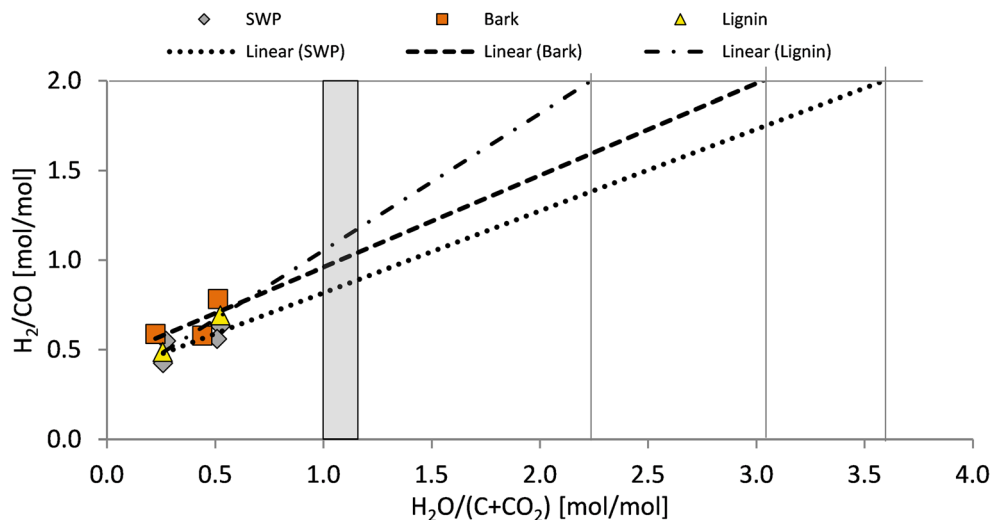
In industrial practice, the use of slagging indices has found a niche in giving the first approximation regarding the agglomeration behaviour of feedstocks. During the years, more than 20 indices have been published in the literature for a range of feedstocks. The most important ones from gasification perspective were collated in [25, 27–31]. Generally, the ash slagging indices are based on the chemical composition of ash.

Evaluation of the indices needs to be done for feedstocks of similar origin to adequately describe their thermal behaviour. Since many slagging indices were developed for coal applications, they often do not take into account ash constituents which are characteristic for biomasses. Thus, it is essential to use indices that incorporate all important constituents of biomass ash, such as K, Na, Si, P, Ca, Mg and Al. From the family acid-to-base ratio indices, Eq. 7 does incorporate all the abovementioned biomass ash forming species:

$$R_{B+\frac{P}{A}} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + P_2O_5}{SiO_2 + TiO_2 + Al_2O_3} \quad (7)$$

However, for the infinitely diverse family of biomasses, it is very demanding to give a useful, general interpretation of $R_{B+\frac{P}{A}}$ values. Another approach to the solution should be sought through analysis of the lab-determined, standardized procedure that indicates characteristic ash melting temperatures. A very

Fig. 4 Impact of H₂O and CO₂ present in the reactor feed on the ratio of H₂/CO obtained in the product gas



useful approximation can be found through the calculation of the Ash Fusion Index, which takes the form of Eq. 8:

$$AFI = \frac{4 \times IDT + HT}{5} \text{ [}^\circ\text{C]} \quad (8)$$

where the characteristic temperatures are measured for half-reducing atmosphere.

For coals, values of AFI were interpreted in the following order of ash slagging intensity: low > 1340 °C; medium 1340–1230 °C; high 1230–1150 °C; sever < 1150 °C. From practice in gasification of biomasses, where the process is commonly operated at 800–900 °C, the following interpretation can be proposed: low > 900 °C, medium 900–800 °C, high 800–700 °C, sever < 700 °C.

Also, another good and simple rule of thumb can be based only on the information given by ST of ash. Firstly, when the gasification process is operated at temperatures below 900 °C and simultaneously below the feedstock ST, the process rarely leads to bed agglomeration. Secondly, when measured ST of a feedstock is lower than 800 °C, the probability of bed agglomeration is generally high.

The two abovementioned indices are solely based on visual lab analysis of ash deformation characteristics. This analysis is done on ash samples pressed into pellets where a chemical reaction between each ash particle is prone to occur. In FB reactors though, majority of the reacting atmosphere is an emulsified phase composed mostly of bed material, gasifying agent and product gas. Here, contact between ash particles is less likely, while bed material—ash—interactions dominate. For these reasons, it is important to take into account also the concentration of ash in bed material when designing and analysing FB experiments.

Therefore, following the experimental data obtained in the research, a new index combining the characteristics of the ash, its concentration in the feedstock and fluidized bed temperature was sought. This approach is aimed to free the ash agglomeration index interpretation from changing gasification process conditions. Thus, Eq. 9 was formulated to describe the Ash Agglomeration Propensity Index:

$$AAPI = 100 + AFI (1 - X_{Ad}) - T_{FB} \text{ [}^\circ\text{C]} \quad (9)$$

A general interpretation of the index is proposed to be the following: ≤ 100 °C – severe; $-100 \div 0$ °C – high; $0 \div 75$ °C – medium; $75 \div 150$ °C – low; > 150 °C – none.

The index has been checked against results from gasification of hard coals, lignites, solid recovered fuels and different kinds of biomasses. For a very broad spectrum of feedstocks, AAPI gives a good approximation of the feedstock agglomeration behaviour directly in regard to the process temperatures in which it is treated.

4 Conclusion and outlook

The presented experimental research was conducted for three kinds of feedstocks, varied pressures and changing stream of fuel (variable heat input). For all experimental runs, similar fluidization conditions were sought. This mode of design of FB experiments has given good comparability of results obtained from tests conducted at a very broad spectrum of gasifying agent compositions. Hence, this method is especially proposed for future research on pressure gasification with the use of CO₂.

For the tested waste biomasses, the bark was determined to give the best overall gasification behaviour, with good yield and quality of product gas. For bark, max. CGE and CCE were calculated for the process conducted at 2 bar_g and respectively were equal to 79.2% and 97.1%. Connecting these efficiency figures, with the fact that gasification runs performed on bark were very stable, makes this feedstock very promising for future research. SWP used here as reference material produced product gas of worse characteristics and at lower CGE concerning both bark and lignin. However, at the same time, it was also the only feedstock which showed no signs of ash agglomeration. Noteworthy, the gasification experiments for all feedstocks were conducted at similar 850 °C gasification temperature. Due to favourable ash chemistry of SWP, the gasification temperature can easily be increased to 900–920 °C, thus improving its CCE and CGE. For bark and lignin, the tested gasification temperature was already high, which was stated because respectively small and large amounts of agglomerates were observed in bed materials recovered from the reactor after gasification of these two waste biomasses. Obtained data indicate the importance of maintaining control over the concentration of ash present in bed material to reach high gasification efficiency while simultaneously avoiding defluidization of the bed.

Furthermore, it was found that gasification of lignin had frequently led to defluidization of the bed as the stream of fuel fed and system pressure increased. It can be hypothesised here that the bed defluidization observed for lignin occurred through a mechanism which involves a combined influence of the chemical characteristic of ash as well as reaching a certain limiting concentration of the ash in the fluidized bed. Due to the experimental findings, the Ash Agglomeration Propensity Index was formulated (Eq. 9) to indicate more precisely ash behaviour of feedstocks at different process conditions and regardless of the origin of the fuel.

Experience gained during the conducted trials indicates that lignin is a difficult, but not impossible feedstock for gasification. Due to the abundance of lignin, its waste character and stable annual availability, it should be considered a viable option for diversification of the group of waste feedstocks that are applicable for thermochemical conversion in gasification systems.

The conducted experiments show that the concept of chemical sequestration of CO₂ is technically feasible through the gasification of biomass. However, the influence of the applied CO₂ on the composition of the yielded product gas is very high and thus may cause that its utilization for chemical synthesis to be difficult without the availability of hydrogen from an external source (e.g. electrolysis of water or aqueous phase reforming) or extensive upgrading of the product gas.

Since the addition of CO₂ into a gasification system changes the applicability of common 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 H₂O/(C+CO₂) (Eq. 5) indices were proposed.

Code availability Not applicable.

Authors' contributions Authors MATEUSZ SZUL and KRZYSZTOF GŁÓD performed the experiments, MATEUSZ SZUL and TOMASZ ILUK were involved in planning and supervised the work, and MATEUSZ SZUL processed the experimental data, performed the analysis, drafted the manuscript, designed the figures and performed the calculations. TOMASZ ILUK and KRZYSZTOF GŁÓD aided in interpreting the results and worked on the manuscript. All authors discussed the results and commented on the manuscript.

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Data availability Full.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Abbreviations λ, air-fuel equivalence ratio (AFER); AFI, Ash Fusion Index (°C); AAPI, Ash Agglomeration Propensity Index (°C); bio-SNG, bio-synthetic natural gas; CCE, carbon conversion efficiency (%); CGE, cold gas efficiency (%); CAST, characteristic ash sintering temperatures (°C); IDT, initial deformation temperature; ST, softening temperature; HT, hemisphere temperature; FT, flow temperature; DME, dimethyl ether; DFB, dual-fluidized bed; FB, fluidized bed; GC, gas chromatography; H₂O/C, water/carbon ratio; HHV, higher heating value (J g⁻¹) or (MJ·(Nm³)⁻¹); SWP, softwood pellet; U/U_{mf}, fluidization number, the ratio of actual fluidization velocity to min. fluidization velocity (m s⁻¹/(m s⁻¹))**Symbols** φ, conversion (kg h⁻¹/(kg h⁻¹)); *m*, mass stream (kg h⁻¹); *n*, mole stream (mol h⁻¹); *R*, ash agglomeration index (-); *Q*, heat (kJ mol⁻¹); *U*, fluidization velocity (m s⁻¹); *X*, mass fraction (-)**Indices** ar, as received; *B* + $\frac{P}{A}$, acid-to-base ratio with phosphorus and aluminium; d, dry state; g, gauge; in, inlet; ga, gasifying agent; mf, minimum fluidization; pg, product gas

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