



Full Length Article

Gasification of lignin-rich residues for the production of biofuels via syngas fermentation: Comparison of gasification technologies

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ABSTRACT

This paper reports the use of lignin-rich residues from second generation bioethanol production, to produce syngas that can be applied in the gas fermentation process. Three gasification technologies at a different scale were considered in this study. Fixed bed updraft gasification of about 30 kg/h solid feed, bubbling fluidized bed gasification of about 0.3 kg/h solid feed and indirect gasification of about 3 kg/h solid feed. Two lignin-rich residues with different properties were tested and the results were evaluated in terms of feedstock pretreatment (grinding, drying and pelleting) and syngas quality requirements for the fermentation process. The molar H₂/CO ratio (ranging from 0.6 to 1.0) and the tar yield (18–108 g/Nm³) obtained from the three gasification technologies was quite different. For the syngas fermentation process, low H₂ to CO ratio is preferred, as most of the organisms grow better on CO than H₂. Furthermore, different contents of impurities that can reduce the fermentability of the gas (such as hydrocarbons, HCN, HCl, NH₃, COS and other organic S- compounds) were detected in the product gas. The concentration of these compounds in the syngas is related to the content of the corresponding compounds in the original feedstock. The different characteristics of the lignin-rich feedstocks are related to the specific pre-treatment technologies for the (hemi)cellulose extraction. By tuning the pre-treatment technology, the properties of the feedstock can be improved, making it a suitable for gasification. Tar and unsaturated hydrocarbon compounds need to be removed to very low levels prior to the fermentation process. As a next step, the combination of the gasification and the appropriate product gas cleaning, with the syngas fermentation process for the production of bio-alcohols will be evaluated and the overall efficiency of the gasification-fermentation process will be assessed.

1. Introduction

In many biorefinery concepts, valorization of the lignin-rich residues is still a major issue. Second generation biorefineries for the production of bioethanol use pre-treatment technologies to make the polycarbohydrates accessible for enzymatic hydrolysis [1]. Unfortunately, in most pre-treatment processes, lignin ends up in a residue together with unconverted fibers, feedstock minerals, and process chemicals like sulphates, enzymes and flocculants. This type of residue is usually burned for production of heat or electricity on site, which is a rather low-added-value application. Having in mind that lignocellulosic biomass generally contains 30–40% lignin, the optimal valorization of this residue is a key factor for the economic and environmental sustainability of a biorefinery [2]. The syngas obtained from gasification of

lignin-rich biorefinery residues offers the potential to produce higher-added-value products, such as liquid fuels and chemicals [3], but this has been assessed only to a limited extent on bench and pilot scale [4–6]. Gasification of lignin differs significantly from gasification of lignocellulosic biomass, mainly because lignin has different physico-chemical characteristics. The structure and chemical composition of lignin, that is an aromatic polymer with higher C/O ratio than lignocellulosic biomass, favours tar formation (defined as all the condensable organic hydrocarbons of molecular weight higher than benzene [7]). Tar content varies depending on gasifier type, bed geometry and gasification conditions (temperature, residence time, gasifying agent). The condensed tar compounds may lead to problems such as clogging and fouling of pipes and equipment [8], therefore the appropriate gasification conditions to minimize tar production should be

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applied.

The pretreatment of the feedstock prior to gasification is a crucial parameter for the process. The objective of the pretreatment is to make biomass suitable for a specific gasification system. Lignin-rich feedstocks have also different physical properties compared to woody biomass; they do not consist of fibers and depending on the original feedstock might have a powder-like consistency or comprise of big, dense particles. Therefore, the pretreatment system can become a critical aspect of minimizing failure in the process (e.g. stickiness and blocking problems during feeding) and usually includes size reduction, drying and densification. Lignin-rich feedstocks usually have irregular shape and size, with varying composition. Size reduction (usually grinding and sieving) is required to obtain the desired particle size and to provide a uniform size for gasification or for the next pretreatment step. In general, smaller particles have larger surface areas, allowing better heat transfer and higher reaction rates but the desired size also depends on the type of the gasifier used. For example, too large or dense particles are not problematic for fixed bed gasifiers but may result in low conversion or cause difficulties in the feeding process in bubbling fluidized bed gasifiers. Fine particles (< 0.5 mm), on the other hand, are not desired because they also cause difficulties in feeding, low conversion, pressure drop in fixed bed or entrainment in fluidized bed reactors and therefore should be sieved out. Furthermore, lignin-rich residues have high moisture content and therefore drying is typically required for reducing the moisture content to 10–15%. If the lignin-rich residues have a low bulk density, densification (e.g. torrefaction and pelleting or briquetting) can be applied as a pre-treatment for use as a solid fuel [9].

In the frame of the EU-funded project Ambition [10], different gasification technologies were tested for the valorization of lignin-rich residues, obtained from the production of second generation bioethanol. A key target of the project is to convert the solid residues into a syngas which can be used in a biological process to produce bio-alcohols. Some anaerobic microorganisms, known as acetogens, can be used as biocatalysts for the microbial conversion of syngas into short-chain organic acids and alcohols, from C₂-compounds, acetate and ethanol, to butanol, butan-2,3-diol and butyric acid [11]. The ability of these microorganisms to withstand some of the impurities contained in the syngas and their flexibility to use different mixtures of CO and/or CO₂ and H₂ makes them an attractive alternative to the chemical catalytic processes. However, the integration of gasification with syngas fermentation is still in an early stage of development, where many questions exist concerning the syngas quality needed in the fermentation process. Current syngas fermentation efforts are predominantly focused on ethanol production.

Syngas fermentation has been chosen as an attractive conversion route by several companies for pilot-, demo- and near commercial-scale cellulosic ethanol production [12]. LanzaTech is deploying two commercial ethanol-producing facilities and has three commercial-scale projects under development, using off-gases and syngas from orchard wood and nutshells [13]. LanzaTech has also demonstrated the production of acetone and isopropanol [14]. Coskata was addressing ethanol production in a demo- unit, first using syngas from biomass gasification and later from methane reforming, but went out of business in 2015 [14]. INEOS New Planet BioEnergy, developed a syngas-to-ethanol process, but stopped the operations by 2016 due to the high levels of hydrogen cyanide in syngas [15].

While these developments are promising, challenges associated with the scale-up and operation of this novel process, such as low mass transfer efficiency and the presence of inhibitory compounds in syngas still remain. According to the literature [16–19], the main requirement for syngas for fermentation is low contents of contaminants like tar, ethylene and benzene, as they inhibit fermentation and adversely affect cell growth. Most of the organisms grow better on CO than H₂. As a result, the H₂ to CO ratio can be low, i.e. a water-gas shift reaction after gasification is not needed. However, many of these requirements, such

as the tolerance to sulphur, will depend on the particular type of microorganisms used. The challenge is to define the gasification conditions that lead to lower tar production while keeping the H₂/CO ratio at values suitable for syngas fermentation.

In this work we compare the performance of three gasification technologies: updraft fixed bed, bubbling-fluidized bed (BFB) and indirect gasification, for valorization of two kinds of lignin-rich residues from second generation bioethanol production. The three technologies chosen for gasification are very different and each one has unique features, which allows its integration with the syngas fermentation process.

Updraft fixed bed gasification, is typically operated at medium and small scale (10–15 MW), therefore is a good match with the fermentation technology and has several advantages such as high overall energy efficiency and fuel conversion, simple structure, low investment cost and easy maintenance. However, the tar compounds and other pyrolysis products are not cracked in the combustion zone, since they are carried by the gas flow to the gasifier top [20]. Thus, a very crude gas is produced with significant amounts of tar compounds, so the challenge would be to reduce the tar content to the suitable levels for the fermentation process.

Bubbling fluidized bed (BFB) direct gasification is suitable for medium to large scale applications. BFB gasifiers are able to produce a synthesis gas with relatively high heating value and can be operated at constant temperature. Silica sand or a catalytic bed material (like lime, dolomite and olivine) can be used as fluidization medium to improve the gasification process. This process is flexible in feedstock and can be considered a mature technology.

Indirect gasification allows high fuel conversion and better control and process optimization. The combustion products (flue gas) and gasification products (product gas or synthesis gas) are not mixed. This means that the product gas is not diluted with N₂ coming from the air used for combustion, and thus, is suitable for synthesis or fermentation applications after proper cleaning and upgrading without the need for an expensive air separation unit. N₂ dilution of the product gas intended for fermentation would result in lower mass transfer efficiency, as well as higher energy demand to compress an inert gas and bigger reactors and equipment downstream resulting in higher OPEX and CAPEX costs. Furthermore, indirect gasification produces a high value gas which contains compounds such as CH₄, C₂-C₄ gases (including ethylene and acetylene), benzene, toluene and xylene (BTX), and tar. The separation of the most valuable components of the product gas is a good way to maximize the value from the feedstock via co-production schemes [21].

Besides syngas productivity and energy balance, the important focus points are the pre-treatment of the lignin feedstocks and the gas quality, since the requirements for syngas fermentation are very different compared to a chemical catalytic processes. The product gas from the lignin-rich feedstock gasification, will be utilized in the fermentation process for the production of bio-alcohols, after appropriate cleaning and conditioning to remove impurities that can reduce the fermentability of the gas (such as tar compounds, BTX, unsaturated hydrocarbons, HCN, HCl, COS and other organic S-compounds).

The use of biomass derived syngas for fermentation is quite a new subject, so limited information about the requirements of the syngas is available. The required syngas composition also depends on the type of microorganism used in the fermentation process. It is difficult to select which gasification technology is most suitable to produce syngas to be used in fermentation, because the required syngas composition depends on the final fermentation product and hence the type of microorganism. The main objective of the work presented is to provide information about the different syngas composition obtained from different gasification technologies. After knowing the requirements of a certain fermentation process, the gasification technology will be chosen to ensure the desired gas composition. As a result of this work, the total efficiency of the process, from the lignin residue until the final biofuel



Fig. 1. Lignin A (a) as received, as used in the updraft gasification test (b), as used in the BFB gasification test (c) and as used in the indirect gasification test (d).

synthesis, will be assessed and the results will be reported in the near future.

2. Experimental

2.1. Feedstock properties and pretreatment

Two technical lignins derived from steam explosion and enzymatic hydrolysis were received from two biorefineries and will be referred throughout the manuscript as lignin A and lignin B. Lignin A is originating from wheat straw and was further filter pressed, therefore consists of big dense particles, while lignin B originates from softwood and consists partly of large spherical particles and partly of small, brittle particles and a lot of powder. The as received materials can be seen in Figs. 1(a) and 2(a), respectively.

Table 1 summarises the main thermochemical properties of the fuels. The detailed ash composition, determined by ICP-AES, can be found in the Appendix. As can be seen, the amount of volatile matter is lower for both tested materials compared to beech wood which is around 81 wt% [22], especially for lignin A. What stands out is the high ash content of lignin A (14 wt%) that mainly consists of silica (5.4 wt% of the feedstock), with minor amounts of calcium (0.5 wt%) and potassium (0.3 wt%). This could lead to agglomeration and corrosion issues at high temperatures (above 900 °C) especially to the BFB and indirect gasifier, due to alkali-silicate melt phase formation on the bed material [9,23]. Furthermore, the sulphur and nitrogen content of both lignin-rich feedstocks is relatively high compared to woody biomass, which can lead to high S- and N- compounds in the product gas (such as H₂S, COS, NH₃, etc.). The higher ash, lower volatile, lower carbon and the higher potassium and calcium content of lignin A compared to lignin B are attributed to the original feedstocks [22].

The materials were received with high moisture contents, 36 wt% for lignin A and 52 wt% for lignin B, as shown in Table 1 and with evident mold on the surface, probably because of the sugar content and

the mild environmental temperature. For this reason, drying of the materials was required prior to the gasification tests.

For the updraft gasification, the larger pieces were broken down to suitable size (20–50 mm) and were dried indoors on canvas. The final moisture content of the feedstock as gasified is shown in Table 2. The two feedstocks, as used in the updraft gasification tests, are shown in Figs. 1(b) and 2(b). The bulk density was 427 kg/m³ for lignin A and 335 kg/m³ for lignin B.

For the BFB gasification, the feedstocks were roughly ground and dried at 60 °C for 72 h. After drying to the final moisture content (see Table 2), the samples were further milled and sieved to obtain the desired size (2–10 mm) for the gasification tests. The feeding point was inside the bed and the aforementioned particle size range was selected to ensure stable feeding and avoid entrainment of the particles out of the reactor, which is usually the case with very small particles. Lignin A and lignin B are shown as used in the gasification tests in Figs. 1(c) and 2(c), respectively.

For the indirect gasification, the feedstocks were dried at 90 °C for 48 h at a final moisture content of 2 wt%. Lignin A was ground using a Retsch SM300 cutter mill at 750 rpm and sieved using a 6 mm round screen to obtain the suitable size (0.5 – 6 mm). Lignin A, as used in the indirect gasification test, is shown in Fig. 1(d). Lignin B, after drying, had a powder-like consistency which proved difficult to feed due to the high amount of small particles (< 0.5 mm). In order to increase the density of lignin B, it was pelletized with the addition of steam, and the pellets were ground using a 10 mm screen. The sample obtained after milling consisted of denser particles below 10 mm size but still a considerable amount of fines was present, as shown in Fig. 2(d). The final moisture content of the feedstocks is shown in Table 2.

2.2. Description of the experimental set-ups and product analysis

2.2.1. Updraft gasifier

The updraft gasification tests were carried out using the pilot plant



Fig. 2. Lignin B (a) as received, as used in the updraft gasification test (b), as used in the BFB gasification test (c) and as used in the indirect gasification test (d).

Table 1
Thermochemical properties of lignin-rich feedstocks.

	Lignin A	Lignin B
Moisture content 105 °C (wt.%, as received)	36	52
Ultimate analysis (wt.%, dry basis)		
C	47.2	57.7
H	5.6	6.2
O	33.0	33.8
N	1.3	0.8
S	0.18	0.13
Cl	0.020	0.002
Proximate analysis (wt.%, dry basis)		
Ash 550 °C	14.0	0.1
Volatile matter	64.6	72.1
Lower heating value (MJ/kg)	18.4	22.9
ICP-AES analysis (mg/kg, dry basis)		
Al	380	17
Ca	4750	380
Fe	290	48
K	3250	210
Mg	385	68
Na	906	390
P	930	160
S	1750	1300
Si	54,000	< 30

PRAGA (uP drAft GASification) at ENEA Research Center of Trisaia. The rig and the main components are shown in Fig. 3. The core of the plant is the fixed bed updraft gasifier which is operated slightly above atmospheric pressure. The plant is equipped with a real time measurement of non-condensable gases (N_2 , H_2 , CO , CO_2 , CH_4 , O_2) by online GC analysis. Moreover, the syngas is sampled at the exit of the gasifier for offline analysis of water and organic volatiles, following the CEN/TS 15439:2006 procedure. The feedstock was fed into the gasifier by screws in a semi continuous mode, in batches of 4.2–4.5 kg, under N_2

atmosphere at intervals of about 12 min and completed in few seconds. More details about the updraft gasifier and the chemical analysis are provided elsewhere [5,24]. Lignin A and lignin B were introduced in the reactor at the ambient humidity contents of 7.8 wt% and 8.3 wt%, respectively. The gasification conditions used can be seen in Table 2. The biomass was fed into the gasifier by screws in a semi continuous mode, in batches of 4.2–4.5 kg, under N_2 atmosphere at intervals of about 12 min, and completed in few seconds. The gaseous streams, serving as gasification media, were injected at the bottom with constant rate.

2.2.2. Bubbling fluidized bed gasifier

The BFB gasification tests were carried out in the bench scale installation at LNEG research center, in Portugal. A scheme of the BFB gasifier is shown in Fig. 4 and a detailed description can be found elsewhere [6]. The BFB reactor is operated at atmospheric pressure and is placed inside a furnace which is electrical heated. Steam and oxygen were used as gasification agents, they were mixed in the windbox located below a gas distributor at the base of the reactor. Equivalent ratio (ER) values from 0 to 0.23 (0.3 g of oxygen/g daf feedstock) were used to study the effect of this parameter. ER is the ratio between the oxygen used and the stoichiometric amount required for complete combustion. The effect of temperature was studied at a range of 750–900 °C and the effect of the steam flow rate was studied at a range of 0–0.9 (g of steam/g daf of feedstock). The feedstocks were continuously fed into the gasifier through a screw feeder. To help the feeding and to avoid gas back flow, a small nitrogen flow was used in the feeding system, which was also water cooled to avoid clogging. Silica sand was used as the fluidization bed. Each experiment lasted between 90 and 120 min, depending on the time necessary to collect all the samples at stable conditions. Isopropanol was used for tar sampling, using the CEN/TS 15439:2006 procedure.

Table 2
Optimum gasification conditions used by the different gasification technologies.

Gasification agent	Updraft gasification		BFB gasification		Indirect gasification	
	Air		Oxygen/Steam		Steam	
	Lignin A	Lignin B	Lignin A	Lignin B	Lignin A	Lignin B
T gasification (°C)	776	687	800	800	780	870
T combustion reactor (°C)	–	–	–	–	805	905
Fuel, dry (kg/h)	28.8	27.9	0.35	0.30	2.9	1.8
Fuel moisture content (wt.%)	7.8	8.3	10.5	7.8	2.0	17.0
Steam (kg/h)	3.0	2.6	0.1	0.1	1.3	1.0
Carrier gas CO ₂ (NL/min)	–	–	–	–	4	4
Fluidization N ₂ (NL/min)	–	–	–	–	20.0	17.3
Air in gasifier (kg/h)	31.4	36.2	–	–	–	–
O ₂ in gasifier (NL/min)	–	–	0.82	0.88	–	–
ER (O ₂)	0.17	0.18	0.13	0.13	–	–
ER (H ₂ O)	0.10	0.07	–	–	–	–
Tracer gas Ne (NL/min)	–	–	–	–	0.02	0.02
Tracer gas Ar (NL/min)	–	–	–	–	1	1
Combustion air (NL/min)	–	–	–	–	100	100
Afterburner air (NL/min)	–	–	–	–	400	400

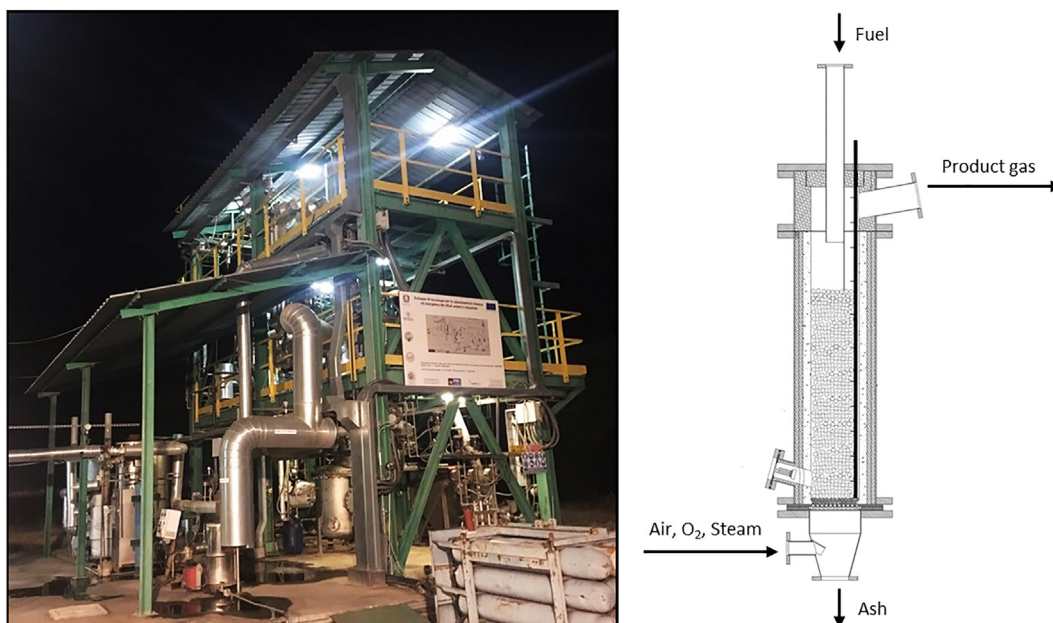


Fig. 3. PRAGA updraft gasifier.

2.2.3. Indirect gasifier

The indirect gasification tests were carried out in the lab scale 30 kW MILENA indirect gasifier at ECN part of TNO research center, in the Netherlands. MILENA is an indirect gasification technology developed by ECN which consists of a riser where gasification takes place and a bubbling fluidized bed combustor in an integrated design [25]. A picture and a scheme of the installation is shown in Fig. 5, including the two sampling points that were used to analyse the product gas (S1) and the flue gas (S2). The gasification conditions used can be seen in Table 2. Lignin A and lignin B were introduced in the reactor at a rate of 2.9 kg/h and 1.8 kg/h, on a dry basis, respectively and at the environmental humidity contents of 2 wt% and 17 wt%. Fresh Austrian olivine, a mineral based on an iron-magnesium orthosilicate structure (FeMgSiO₄), was employed as the bed material. The gasification temperature was approximately 780 °C and 870 °C, for Lignin A and Lignin B, and steam fluidization was conducted at 1.3 kg/h and 1 kg/h, respectively. Additional nitrogen (20 NL/min for lignin A and 17 NL/min for lignin B gasification) was used in this lab scale test, to compensate for reduced gas velocity in the riser, due to the low amount of volatile

matter of lignin A. The riser reactor of the lab scale installation is designed for wood chips, therefore, in order to achieve the required velocity for sufficient circulation, higher lignin feeding rates would be required but it is not possible due to the limited capacity of the afterburner. Furthermore, neon and argon gases were injected at 0.02 NL/min and 1 NL/min as tracer gases. The product gas flow after the gasifier was calculated from the tracer gases molar balance. The gasification system was operated at atmospheric pressure.

After the gasifier, a slip stream of the product gas for analysis was cooled down to 5 °C in order to remove the condensate (water and tars) from the dry gas, thus protecting the gas analysis set. Online monitoring of product gas (H₂, CO, CO₂, CH₄) and flue gas (O₂, CO₂, CO, C_xH_y, N₂O, NO, NO₂) was carried out. ABB CALDOS 17 Thermal Conductivity Detector was used for H₂, ABB URAS 14 Non Dispersive Infra-Red Analyser (NDIR) for CO, CO₂, CH₄, N₂O, SO₂, ABB MAGNOS 16 Paramagnetic O₂ sensor for O₂, Ratfish RS55 Flame Ionisation detector was used for the trace hydrocarbons in the flue gas and ABB LIMAS 11 UV detectors for NO and NO₂. Complementary, the product gas composition was measured online using a micro-GC (Varian Micro-GC CP

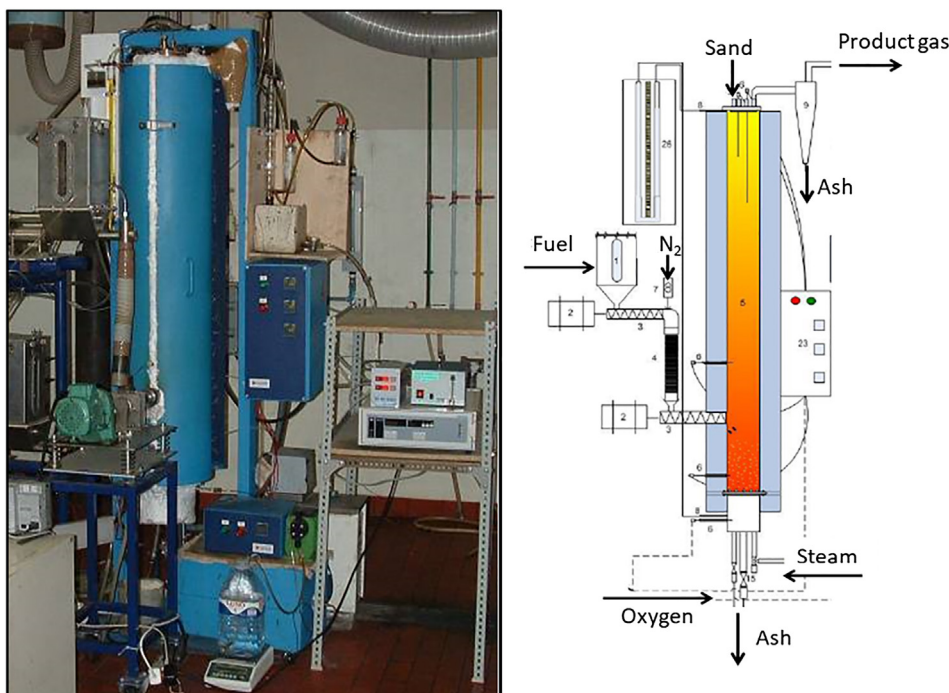


Fig. 4. Bubbling fluidized bed gasifier.

4900). The product gas was also sampled at the exit of the gasifier for offline analysis of the trace hydrocarbons (GC-FID) and sulphur compounds (GC-FPD). The determination of HCl, NH₃, HCN in the product gas was carried out by wet chemical analysis. Additionally, the tar guideline method was used for the determination of the content and composition of the tar compounds in the product gas, following the CEN/TS 15439:2006 procedure, as well as the water content using Karl Fischer titration.

3. Results and discussion

3.1. Updraft gasification

3.1.1. Lignin A

Fig. 6 reports the temperature profile at steady operating conditions

recorded along the vertical axis by the set of 11 thermocouples during the updraft gasification test of lignin A. This thermal profile inside the gasifier bed appears complex because it depends on the equilibrium between several exothermic and endothermic chemical reactions at the solid-gas interface and in the gas phase as well as on heat and mass transfer. Steady conditions were assumed when the thermal profile inside the gasifier was stable, except for the fluctuations in the freeboard where the biomass was loaded. In the freeboard, at steady state, the temperature was 280 °C, while in the bed it was 776 °C with a maximum of 1040 °C at 0.728 m bed height, which is almost at the middle of the reactive bed. The use of steam had positive effects on the stabilization of the gasifier, because the highest temperatures were found in the middle of the gasifier and not at the bottom where ashes are at the pure state and could agglomerate at melted state [4]. The heating rate of the particles moving downward from the top of the

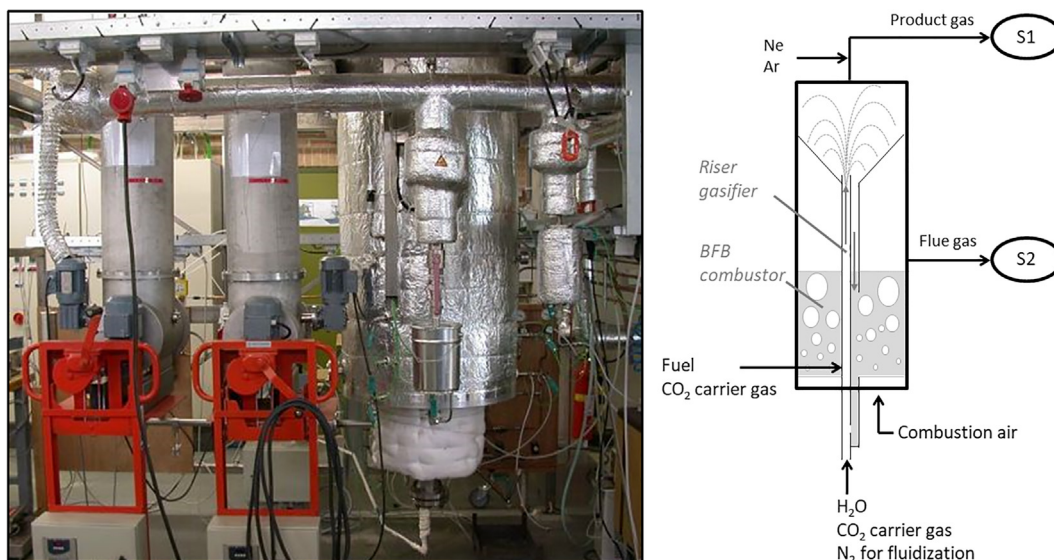


Fig. 5. MILENA indirect gasifier.

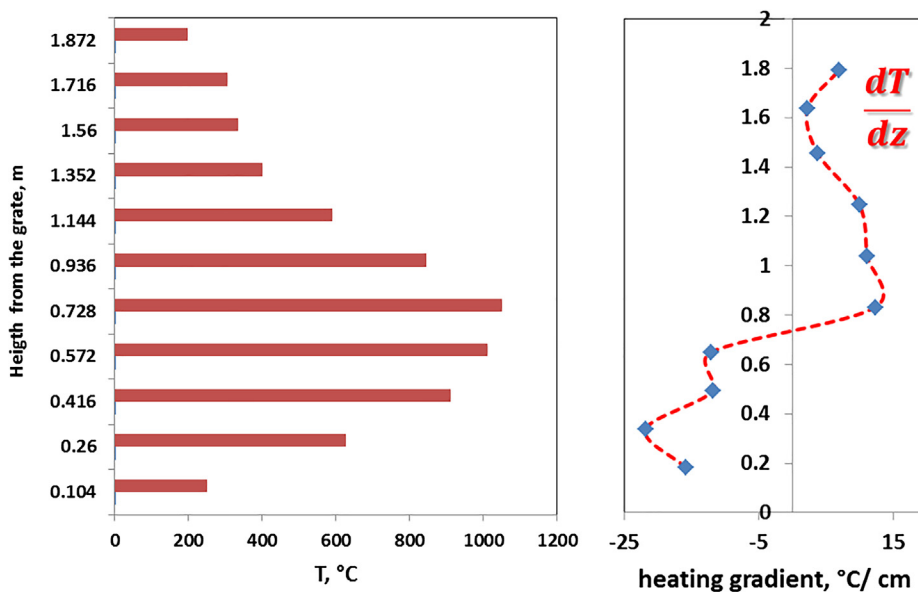


Fig. 6. Temperature inside the updraft reactor along the vertical axis (z) and the derivative (right) during the gasification of lignin A.

reactor is also shown in Fig. 6. Starting from the top of the gasifier, there are two zones where endothermic reactions prevailed and the thermal gradient approached its minimum: at 1.6 m it can be ascribed to the primary pyrolysis of the feedstock and at 1.0 m can be associated with gasification and cracking reactions. The exothermic reactions prevailed in correspondence of the maxima peaks: at 1.2 m due to the contribute of WGS reaction and at 0.8 m associated with the combustion of lignin that provided most of enthalpy for the endothermic reactions.

In Fig. 7, the concentration of the main product gas components during the updraft gasification of lignin A, as measured by the online GC, is presented. After the start up period, there was a period of steady operation of the plant between 60 and 200 min. The fluctuations of the gas composition is attributed to the biomass feeding steps that was of semi-batch type.

The data were averaged from 60 to 200 min and with other chemical analysis (tar content, water content) are reported in Table 3. At steady conditions, the average composition of the gas – on dry basis – was 26.0 vol% H_2 , 24.8 vol% CO , 9.5 vol% CO_2 , 3 vol% CH_4 , 36.4 vol% N_2 and 0.2 vol% O_2 . The H_2/CO ratio was slightly above 1. The total content of condensable organics was found $80 \text{ g}/\text{Nm}^3$, of which $67 \text{ g}/\text{Nm}^3$ classified as tar after the CEN 15439; the main compounds that

were identified by the HPLC were Acetic acid, 5-HMF, single ring aromatic molecules (Benzene, Toluene, substituted Phenols) and traces of Naphthalene. HCl and NH_3 were measured in the syngas equal to 37 and 7900 ppmV, respectively, equivalent to 55 wt% and 70 wt% of the Cl and N in the original feedstock. The lower heating value of the product gas was $7.3 \text{ MJ}/\text{Nm}^3$.

3.1.2. Lignin B

During lignin B gasification, the temperature profile of the updraft gasifier was monitored and the average values, are reported in Fig. 8. As can be observed, the thermal profile of lignin B updraft gasification was significantly different than lignin A (shown in Fig. 6). Indeed, the average temperature in the bed was 687°C and the peak temperature was 948°C , which is 89°C and 102°C lower than for lignin A, respectively. The enthalpy for lignin A was $H_{in} = 530 \text{ MJ}/\text{h}$, while for lignin B $H_{in} = 630 \text{ MJ}/\text{h}$, calculated from the lower heating value of the lignin (shown in Table 1) and the fuel rate (shown in Table 2). From this data we expected higher temperature during the gasification of lignin B but the opposite was detected. The lower temperature of the gasifier could be explained by a higher shift of potential enthalpy from the solid to the gas. The heating value of the product gas was $7.8 \text{ MJ}/\text{Nm}^3$ (shown in Table 4), which is higher than lignin A and is a consequence of such

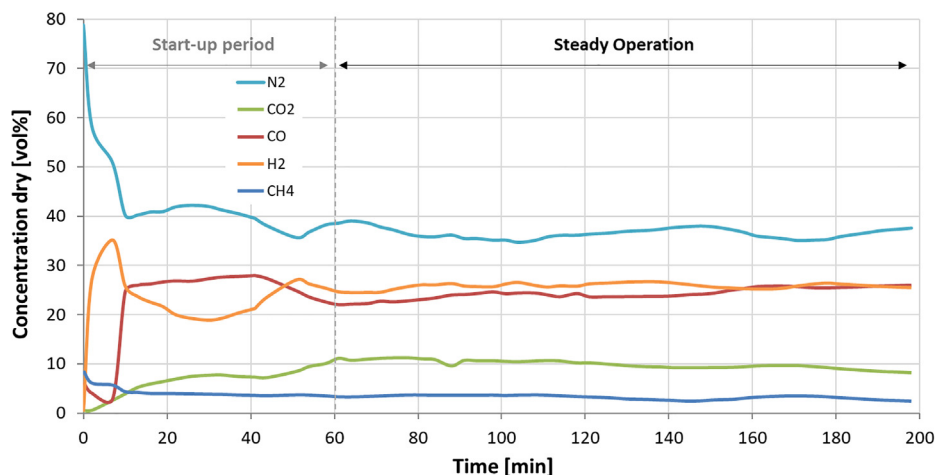


Fig. 7. Syngas composition from Lignin A obtained in air-steam gasification test with the ENEA updraft gasifier PRAGA. Steady operation: 60–200 min.

Table 3

Product gas composition for lignin A gasification. Experimental conditions as given in Table 2.

Gasification agent	Updraft gasifier Air	BFB gasifier Oxygen/ Steam	Indirect gasifier Steam	Units
CO	24.8	28.0	13.9	Vol%
H ₂	26.0	22.0	8.6	Vol%
CO ₂	9.5	21.0	17.9	Vol%
CH ₄	3.0	14.0	5.9	Vol%
N ₂	36.4	10.0	45.1	Vol%
O ₂	0.17	nd	–	
C ₂ H ₂	nd	nd	0.1	Vol%
C ₂ H ₄	nd	4.5	2.8	Vol%
C ₂ H ₆	0.05	0.3	0.3	Vol%
Benzene	0.10	nd	0.5	Vol%
Toluene	0.01	nd	0.1	Vol%
Ar tracer gas	–	–	2.1	Vol%
Sum C ₃	921	950	3115	ppmV
Sum C ₄ -C ₆	nd	800	921	ppmV
H ₂ S	nd	781	1099	ppmV
COS	nd	nd	29	ppmV
Thiophene	nd	nd	34	ppmV
Methylmercaptane	nd	nd	32	ppmV
Other S-organics	nd	nd	9	ppmV
NH ₃	7900	7466	8765	ppmV
HCN	nd	nd	1290	ppmV
HCl	37	nd	8	ppmV
Ne tracer gas	–	–	409	ppmV
Tar content [*]	80	18	34	g/Nm ³
Water content	22	40	43	Vol%
Product gas flow (dry, tar free)	1.7	0.9	1.0	Nm ³ / kg _{dry feedstock}
Product gas LHV (tar free)	7.3	12.2	9.8	MJ/Nm ³

Values are at Normal conditions at temperature of 0 °C (273.15 K) and absolute pressure of 1 atm (1.01325 × 105 Pa).

nd: not determined.

^{*}Higher than toluene, on dry basis.

lower heat release in the bed.

The syngas composition in the two cases suggested that lignin A is more reactive towards the water gas shift (WGS) reaction than lignin B. Indeed, careful calculations considering the exothermicity of the WGS (-41.7 kJ/mol) and the difference in H₂/CO led to a difference of 104 °C in two adiabatic systems (in the Appendix more details are provided

Table 4

Product gas composition for lignin B gasification. Experimental conditions as given in Table 2.

Gasification agent	Updraft gasifier Air	BFB gasifier Oxygen/ Steam	Indirect gasifier Steam	Units
CO	28.0	28.0	15.6	Vol%
H ₂	20.1	20.0	14.1	Vol%
CO ₂	7.7	15.0	18.0	Vol%
CH ₄	5.1	15.0	6.9	Vol%
N ₂	38.7	19.0	39.2	Vol%
O ₂	0.17	nd	–	
C ₂ H ₂	nd	nd	0.3	Vol%
C ₂ H ₄	nd	2.7	2.0	Vol%
C ₂ H ₆	0.11	0.2	0.1	Vol%
Benzene	0.2	nd	0.7	Vol%
Toluene	0.02	nd	0.1	Vol%
Ar tracer gas	–	–	3.6	Vol%
Sum C ₃	800	840	355	ppmV
Sum C ₄ -C ₆	nd	270	583	ppmV
H ₂ S	nd	654	644	ppmV
COS	nd	nd	20	ppmV
Thiophene	nd	nd	18	ppmV
Methylmercaptane	nd	nd	2	ppmV
Other S-organics	nd	nd	3	ppmV
NH ₃	6930	834	4164	ppmV
HCN	nd	nd	114	ppmV
HCl	nd	nd	12	ppmV
Ne tracer gas	–	–	404	ppmV
Tar content [*]	100	108	30	g/Nm ³
Water content	22	34	42	Vol%
Product gas flow (dry, tar free)	2.1	1.0	1.6	Nm ³ / kg _{dry feedstock}
Product gas LHV (tar free)	7.8	13.0	8.6	MJ/Nm ³

Values are at Normal conditions at temperature of 0 °C (273.15 K) and absolute pressure of 1 atm (1.01325 × 105 Pa).

nd: not determined.

^{*}Higher than toluene, on dry basis.

regarding the thermal calculation). In turn, the different degree of WGS could be attributed to the higher potassium and calcium content in the ash of lignin A, that catalyses the reaction [26].

In Fig. 9 the concentration of the main product gas components during the updraft gasification of lignin B - as measured by the online GC - is presented. After the start up period, there was a period of steady

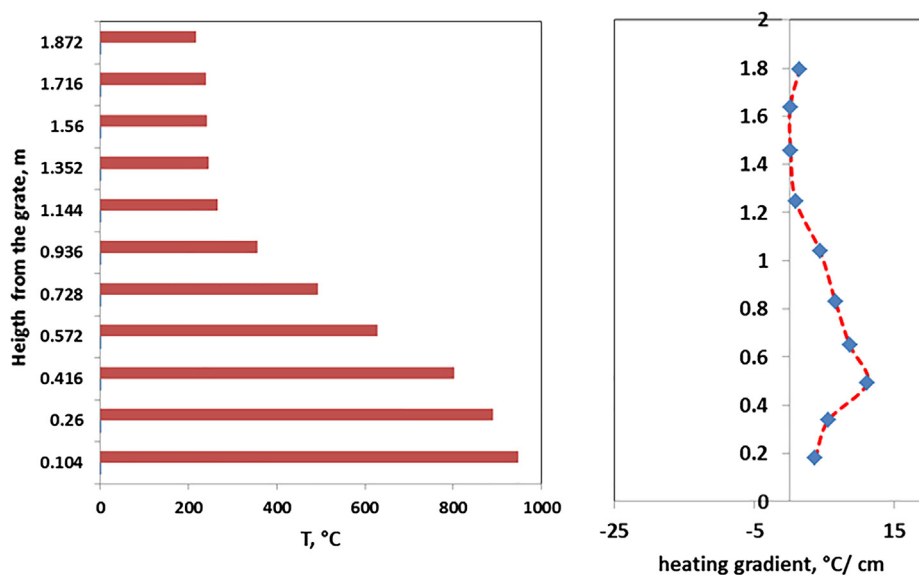


Fig. 8. Temperature inside the updraft reactor along the vertical axis (z) and the derivative (right) during the gasification of lignin B.

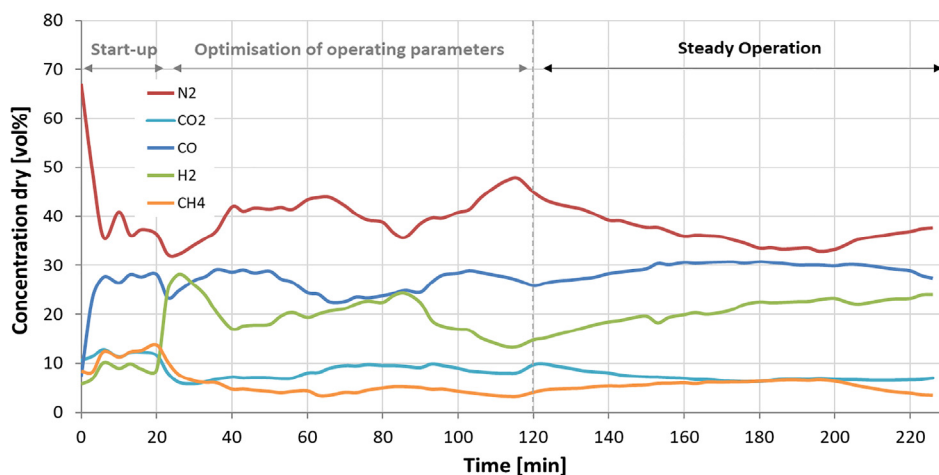


Fig. 9. Product gas composition from Lignin B obtained in air-steam gasification test with the ENEA updraft gasifier PRAGA. Steady operation: 120–230 min.

operation of the plant between 120 and 230 min, during which the conditions were kept stable. The average composition of the gas – on dry basis – was 20.1 vol% H₂, 28.0 vol% CO, 7.7 vol% CO₂, 5.1 vol% CH₄, 38.7 vol% N₂ and 0.2 vol% O₂ (Table 4). The use of steam as a gasification agent increases the partial pressure of H₂O inside the reactor, promoting the endothermic water gas reactions in the regions with high temperatures. The lower steam addition during lignin B gasification compared to lignin led to a lower hydrogen content: 26.0 vol% for lignin A and 20.1 vol% for lignin B, for 3.0 kg/h and 2.6 kg/h of steam, respectively. The H₂/CO ratio resulted from gasification of lignin B was lower than that for lignin A, 0.7 versus 1.0, even at similar operating conditions (feeding rate, ER(O₂)), as shown in Table 2. The product gas composition appears less regular than lignin A throughout the test, due to the irregular shape and size of lignin B that consisted of small particles with the aptitude to produce powder (shown in Fig. 2(b)). In this sense, lignin B was not an optimal feedstock for updraft gasification and a few pre-treatment steps (like compression, drying and palletisation) would be required in the Biorefinery to obtain pellets with good properties.

The GC data were averaged from 120 to 230 min and together with the other chemical analysis (tar content, water content) are reported in Table 4. The total organic condensable content was 100 g/Nm³ for lignin B, of which 89 g/Nm³ classified as tar after the CEN 15439, which is higher than lignin A. This is ascribed to the higher bed temperature during gasification of lignin A (776 °C versus 687 °C for lignin B) that favors the tar cracking reactions. Moreover, the tar production can be correlated with the fluid dynamic of the system and more specifically with the residence time of the syngas in the bed: long residence time led to low tar content according to a zero order kinetics of tar decomposition in the bed producing incondensable hydrocarbons [4,24]. The use of a higher air quantity as gasification agent during the tests of lignin B (36.2 kg/h versus 31.4 for lignin A) resulted in higher total syngas flow with a corresponding decrease in the residence time, leading to larger tar content in the gas.

3.2. Bubbling fluidized bed gasification

Based on a previous study about the effect of the experimental conditions on the syngas production from lignin by oxy-gasification [6], the effect of the steam/lignin ratio, gasification temperature and oxygen flow rate, was studied in the present work. Steam/lignin weight ratios between 0 and 0.8, as well as temperatures in the range of 750–900 °C were tested. The effect of the equivalent ratio (ER) was studied in the range of 0–0.23, by varying the oxygen flow inside the reactor. When ER was 0, only steam was introduced inside the reactor. Each experiment lasted between 90 and 120 min, depending on the

time necessary to collect all the samples at stable conditions. The optimum experimental conditions that were used for the BFB gasification of the two lignins can be found in Table 2.

During the BFB gasification of lignins, the presence of steam favoured the steam reforming reactions, thus the conversion of tar and hydrocarbons to CO, CO₂ and H₂. H₂ concentration increased with increasing steam/lignin ratio, however, CO content decreased due to its conversion into CO₂ via the WGS reaction. The steam/lignin ratio of 0.35 was chosen as the optimum, in terms of tar content, product gas yield and LHV and low H₂/CO ratio.

The increase of temperature clearly favoured the formation of H₂, at the expense of CO, CH₄, higher hydrocarbons and tar compounds concentration. This is attributed to steam reforming and cracking reactions that led to an increase in syngas yield, accompanied by a decrease in the gas LHV. The use of lower gasification temperature prevents problems associated with bed agglomeration and leads to H₂/CO ratio lower than 1, which is required for the syngas fermentation process, but has the disadvantage of producing syngas with higher tar contents, which is not favourable for further fermentation tests. For the aforementioned reasons, the temperature of 800 °C was selected as the optimum.

The increase of ER clearly favoured partial oxidation reactions and the release of CO and CO₂, at the expense of CH₄, other gaseous hydrocarbons and tar compounds. Oxidation reactions also favoured the formation of H₂O. The conversion of tar into gases, led to an increase in the gas yield but with a corresponding decrease in the LHV, as expected. The optimum ER value was found to be 0.13 to ensure the H₂/CO ratio required for fermentation.

In Table 3 and Table 4, the average product gas composition for the optimum conditions tested, during lignin A and lignin B gasification, respectively, is presented. As it may be observed, similar values were obtained for both lignins in relation to the main gaseous components (CO, CO₂, H₂ and hydrocarbons). The H₂/CO ratio was 0.8 for lignin A and 0.7 for lignin B. The heating value of the product gas was 12.2 MJ/Nm³ for lignin A and 13.0 MJ/Nm³ for lignin B.

The tar content of the gas from the two lignin-rich feedstocks BFB gasification was quite different and could be related to the different composition of the feedstocks. The total tar content in the raw syngas was found 18 g/Nm³ for lignin A and 108 g/Nm³ for lignin B. Quantitative determination of the individual tar components was not carried out. NH₃ and H₂S concentrations for lignin A were 780 and 7470 ppmV, respectively. For lignin B the concentrations were quite lower, 650 and 835 ppmV, respectively, which agrees with the lower N and S contents in the original lignin (see Table 1).

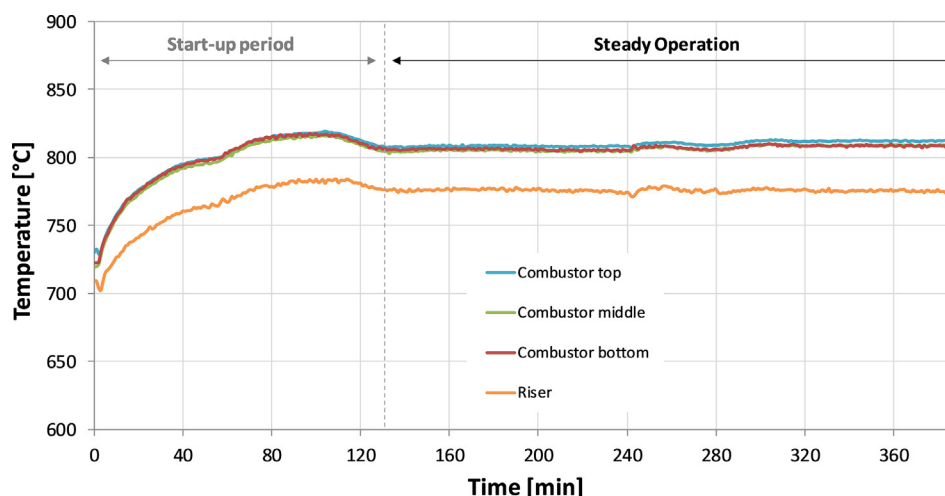


Fig. 10. Temperature in the riser and combustor bed zones of MILENA during lignin A indirect gasification. Steady operation: 130–390 min.

3.3. Indirect gasification

3.3.1. Lignin A

In Fig. 10, the temperature monitored by four thermocouples placed within MILENA indirect gasifier, during gasification of lignin A, is shown. After the initial start-up, stable conditions were achieved for 260 minutes, as indicated in the graph. The average temperature in the gasification reactor - above the riser - during the steady operation, stabilizes at around 780 °C. The average temperature in the combustor, given by 3 thermocouples located at the bottom, middle and top part of the combustor, was stable at 805 °C, indicating good bed material circulation. The small deviations in temperature between the 240 and 280 min of the test are caused by a system disorder (instant pressure increase due to hampered hydrodynamics of the bed material).

In Fig. 11, the concentration of the main product gas components during the indirect gasification of lignin A, as measured by the gas analyser, is presented. During the stable conditions the average composition of the gas – on dry basis – was 8.6 vol% H₂, 13.9 vol% CO, 17.9 vol% CO₂ and 5.9 vol% CH₄. However, 7.2 vol% of the CO₂ is due to the CO₂ used as a carrier gas in the feeding screw and steam generator, as shown in Fig. 5. The H₂/CO ratio was 0.6, which is on the low side compared to a woody biomass gasification test [25], due to the use of relatively inactive olivine. Over prolonged run times, the Fe component in olivine is activated [25,27] and the K and Ca ash components are incorporated into the bed material, forming a uniform Ca-layer and

K enrichments on the surface of the olivine [28]. It has been reported that activated olivine enhances H₂ production and decreases CO and CH₄ content compared to silica sand, due to its catalytic effect on the reforming of hydrocarbons and tar and the promotion of the water–gas shift (WGS) reaction [28–31]. Due to the presence of iron at the surface of the material, olivine has the ability to transfer oxygen between the combustion side and the gasification side of the indirect gasification system [31,32]. The high CO and CO₂ content is attributed to this ability and has a beneficial effect in the application of the gas to the fermentation process, since high CO and CO₂ concentrations are required.

In Table 3 the average gas composition of the product gas, during indirect gasification of lignin A, is shown. What stands out in the overall gas composition is the high concentration of S-species (in the form of H₂S, COS and other S-organic components, 1200 ppmV in total), NH₃ (8765 ppmV) and HCN (1290 ppmV) concentration. These high concentrations can naturally be explained by the high content of the corresponding compounds, shown in Table 1.

The high concentration of HCN, benzene and sulphur compounds (especially thiophene) of the product gas might cause problems in the gas application to the fermentation process [33]. Therefore, the cleaning of product gas is essential before being utilized downstream.

The total tar (higher than toluene) concentration – on dry basis – in the product gas is 34 g/Nm³. The main tar components formed from lignin A gasification are aromatic (1-ring) components, such as xylene,

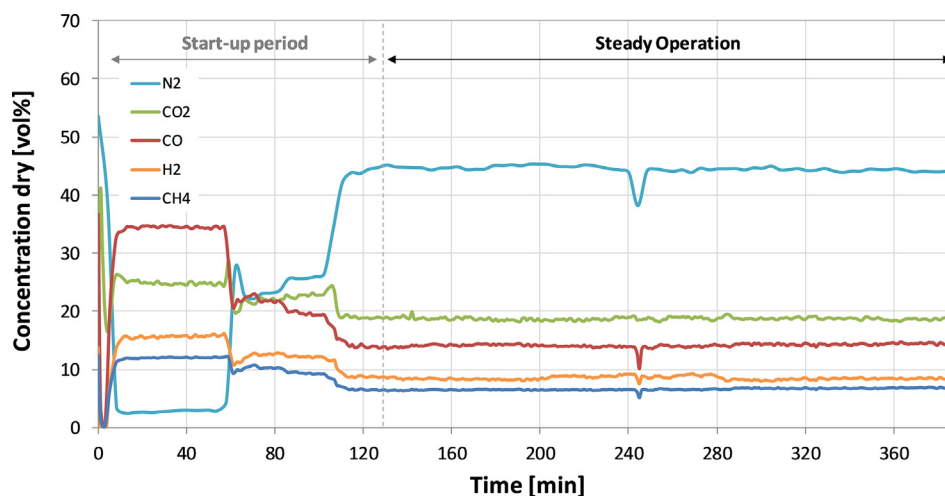


Fig. 11. Product gas composition during lignin A indirect gasification (as measured by the online gas analyser). Steady operation: 130–390 min.

Table 5
Flue gas composition for lignin A and B during indirect gasification.

Component	Concentration		Units
	Lignin A	Lignin B	
O ₂	2.3	2.2	Vol%
CO ₂	14.8	13.9	Vol%
CxHy	3.2	1.5	ppmV
CO	20.4	0	ppmV
NO	556	364	ppmV
NO ₂	11	5	ppmV
N ₂ O	7	< 1	ppmV

styrene and toluene, together with heterocyclic aromatic compounds, like phenol and cresol. Naphthalene was detected in considerable amounts, along with small concentrations of other light and heavy polyaromatic hydrocarbons (e.g. acenaphthylene, phenanthrene).

The total tar concentration of the lignin A indirect gasification was higher than of lignocellulosic biomass [25] and is attributed to the multi ring nature of the lignin molecule which favours tar formation, as well as to the inactive olivine – due to the small duration of the test – that is not able to crack the heavy tars effectively. In order to use the product gas for fermentation, all the tar components must be removed downstream, possibly using the OLGA unit [34]. The lower heating value of the product gas was 9.8 MJ/Nm³.

The average composition of the flue gas at the exit of the combustor reactor, during the steady operation of lignin A gasification, is shown in Table 5. The small amounts of CO and hydrocarbons show that complete combustion was achieved. However, the total NO_x emissions are quite high (574 ppmV, most of it being NO), compared to a woody biomass gasification test [25], due to the high concentration of nitrogen in the original feedstock.

3.3.2. Lignin B

In Fig. 12, the temperature in MILENA indirect gasifier, during gasification of lignin B, is shown. After the initial start-up, stable conditions were achieved for 155 minutes, as indicated in the graph. The average temperature in the gasification reactor – above the riser – during the steady operation, stabilizes at around 870 °C. The average temperature in the combustor, given by 3 thermocouples located at the bottom, middle and top part of the combustor, was stable at 905 °C, indicating good bed material circulation.

In Fig. 13, the concentration of the main product gas components during the indirect gasification of lignin A, as measured by the gas analyser, is shown. During the stable conditions the average

composition of the gas – on dry basis – was 14.1 vol% H₂, 15.6 vol% CO, 18.0 vol% CO₂ and 6.9 vol% CH₄. Again, 7.2 vol% of the CO₂ is due to the CO₂ used as a carrier gas in the feeding screw and steam generator. The H₂/CO ratio was 0.9, which is higher than lignin A. The higher H₂ concentration is probably attributed to the water gas shift reaction that is favoured by the higher gasification temperature and the higher steam to carbon rate that is applied to lignin B gasification, compared to lignin A (shown in Table 2).

In Table 4 the average gas composition of the product gas, during indirect gasification of lignin B, is shown. The tar (higher than toluene) content – on dry basis – was 30 g/Nm³, which is lower than lignin A and is ascribed to the higher gasification temperature that favours the tar cracking reactions. Unlike lignin A, lignin B produced primarily light polyaromatic (2, 3-ring) compounds, like naphthalene, together with acenaphthylene and phenanthrene. In smaller concentrations aromatic and heavy polyaromatic compounds were also formed. The concentration of the total S-species was 690 ppmV, much lower than lignin A and can be attributed to the lower S-content in lignin B. NH₃ and HCN concentration in the product gas was 4160 ppmV and 115 ppmV, respectively. Again, much lower than lignin A due to the lower N-content in lignin B.

Regarding the concentration of lower hydrocarbons, CH₄ concentration is higher compared to lignin A as expected due to the higher gasification temperature. Ethane, ethylene and C₃+ hydrocarbons concentration decreases compared to lignin A and this can also be attributed to the increased gasification temperature which promotes cracking reactions into methane and hydrogen (whose concentrations are higher compared to lignin A). The high concentration of HCN, benzene and sulphur compounds (especially thiophene) in the gas might cause problems in the gas application to the fermentation process. Therefore, cleaning of producer gas is essential before the downstream fermentation process. The lower heating value of the product gas was 8.6 MJ/Nm³.

The average composition of the flue gas after the combustor, during the steady operation of lignin A gasification, is shown in Table 5. The small amounts of CO and hydrocarbons show that complete combustion was achieved. The total NO_x emissions was 370 ppmV (most of it being NO), are lower than lignin A, due to the lower concentration of nitrogen in the feedstock.

4. Conclusions

The gasification of lignin-rich feedstocks is technically feasible with the three different gasification technologies considered in this study, proving that it is possible to convert this kind of residue into a valuable

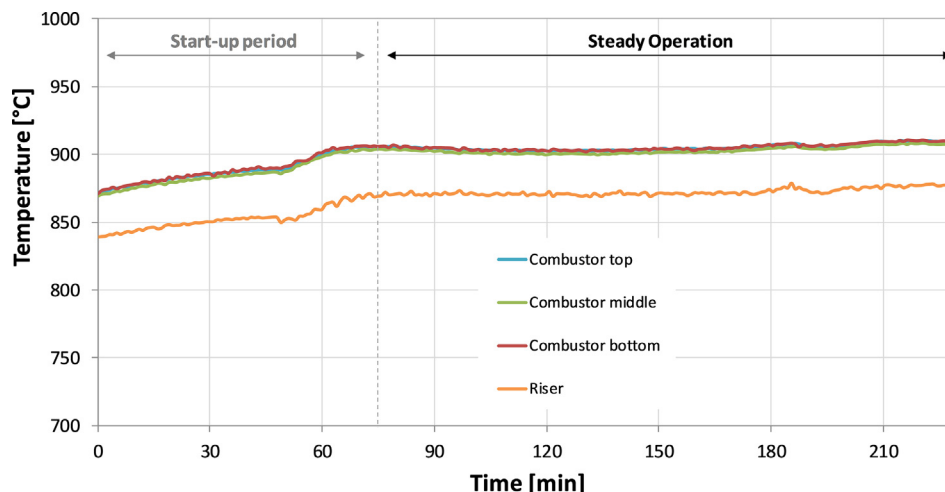


Fig. 12. Temperature in the riser and combustor bed zones of MILENA during lignin B indirect gasification. Steady operation: 75–230 min.

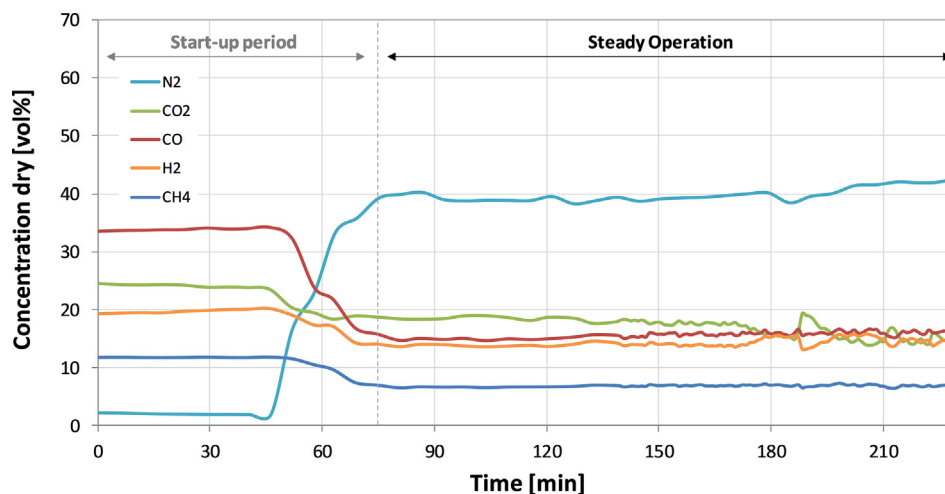


Fig. 13. Product gas composition during lignin B indirect gasification (as measured by the online gas analyser). Steady operation: 75–230 min.

synthesis gas which can be used for the production of biofuels.

Lignin A was identified as an interesting candidate for syngas fermentation, since it is not an easy feedstock for other applications. Lignin B, on the other hand, is a more demanding feedstock in terms of feeding, due to the irregular shape and size with the high amount of fines and requires more pretreatment steps than lignin A. However it is a feedstock with high purity (low sulphur and ash content) that could be valorized via alternative pathways into high value products like resins and phenol(ics).

The H_2/CO ratio obtained from the three gasification technologies was quite different and varied from 0.6 to 1.0. The optimal H_2/CO ratio required depends on the application of the product gas. For the syngas fermentation process, low H_2 to CO ratio is preferred, as most of the organisms grow better on CO than H_2 [12]. The tar content was also very different between the three gasification technologies, as expected, varying from 18 to 80 g/Nm^3 for lignin A and from 19 to 108 g/Nm^3 for lignin B.

In the fixed bed, the higher tar content produced from lignin B gasification (100 compared to 80 g/Nm^3 for lignin A) is mainly attributed to the lower gasification temperature and the lower residence time due to higher air quantity used as gasification agent. Fluidized bed gasification led to the lowest tar content for lignin A (20 g/Nm^3), which was expected as this technology favours mass and energy transfer and thus tar destruction. Lignin A led to lower tar than lignin B (108 g/Nm^3), because of the higher mineral matter content. In the fluidized bed, the lower tar content obtained from lignin B gasification (30 compared to 34 g/Nm^3 for lignin A) is an effect of the higher gasification temperature that favours tar cracking reactions, resulting in improved gas yield and quality.

Furthermore, different contents of impurities that can reduce the fermentability of the gas (such as hydrocarbons, HCN, HCl, NH_3 , COS and other organic S- compounds) were detected in the product gas. The gasification results show that the concentration of these compounds is related to the content of the corresponding compounds in the original feedstock.

For updraft fixed bed gasification, lignin A – consisting of bid dense particles – is a better match than lignin B – consisting of brittle particles with powder-like consistency – since a more stable thermal profile and operating conditions were achieved. For BFB gasification, both lignins seem to gasify without problems. However, it should be noted that the big dense particles of lignin A might cause char build-up in the bed or the very brittle particles of lignin B might lead to carbon loss due to entrainment. For indirect gasification, lignin B showed more promising results, despite the difficulties in feeding. The lower ash content than lignin A, allowed for higher gasification temperature, resulting in

higher gas yields that is beneficial for the fermentation process.

The difference in the lignin-rich residues characteristics is attributed to the specific pre-treatment technologies for the (hemi)cellulose extraction. By steering the pretreatment technology, the properties of the feedstock can be improved, making it a suitable for gasification.

The main impurities in the synthesis gas from the lignin-rich feedstocks gasification, that need to be removed to very low levels are unsaturated hydrocarbons and tar compounds. The effect of contaminants such as CH_4 , C2-C5 hydrocarbons, HCN, HCl, NH_3 and sulphur compounds on alcohol production and cell growth is not clear as it has not been thoroughly studied.

The next step is going to be the combination of the gasification process and the appropriate product gas cleaning, with the syngas fermentation process for the production of bio-alcohols. There is a limited number of studies focusing on the integration of the two technologies, so this study will contribute to the design and commercialization of the gasification-fermentation process and add to the economic and environmental sustainability of a biorefinery.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2019.04.081>.

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