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Production of Syngas Suitable to be Used in Fermentation to Obtain Biochemical Added-Value Compounds

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Lignin-rich residues are a side stream in advanced ethanol biorefineries and they are usually used for heat and power production. However, an alternative is the lignin valorisation by thermochemical and biochemical processes that might be economically more suitable. In this work lignin-rich residues were firstly thermochemical converted to syngas in a fluidised bed gasifier, using steam and oxygen as gasifying agents. The obtained results so far showed that the rise of steam/lignin-rich residues ratio favoured the release of H_2 and CO_2 and led to a decrease in CO and hydrocarbons content, as steam reforming reactions were favoured. On the other hand, the rise of the equivalent ratio clearly favoured partial oxidation reactions and thus the release of CO and CO_2, while H_2 and hydrocarbons contents were reduced, due to their partial combustion. The increase of temperature favoured the formation of H_2, at the expenses of hydrocarbons and tar release, as both decreased. However, it is fundamental to control gasification temperature to prevent ash melting and consequent bed agglomeration, due to the high ash content in lignin-rich residues, generally with high content of silica and alkali metals. The results led to the selection of gasification conditions (800 °C, equivalent ratio of about 0.13 and steam/lignin ratio of around 0.4) that headed to the following gas ratio $CO/CO_2/H_2$=1:0.7:0.7, which was tested for further bacterial fermentation. Fermentation tests with *Butyribacterium methylotrophicum* showed that the above syngas composition strongly influenced the production levels of acetic and butyric acids. Marked differences in the CO, H_2 and CO_2 consumption rates were also observed and were correlated with cell growth and metabolites production.

1. Introduction

The production of bioethanol in lignocellulosic feedstock-based biorefineries originates high volumes of lignin-rich residues that contain lignin, other unconverted fibres, feedstock minerals, and process chemicals. These lignin-rich residues are commonly used for heat and power production. However, gasification could be another valorisation process. Gasification of lignin rich feedstocks may bring same technical challenges due to the high ash content of lignin-rich residues, usually with high silica and alkali metals content, which may originate bed agglomeration, gasifier erosion and serious damage (Pinto et al., 2015).

Syngas produced by lignin-rich residues gasification may have several end-uses depending on its composition and properties. Most applications are very demanding towards syngas quality and impurities contents, which oblige to a strict optimisation of the gasification process and to a more or less complex syngas cleaning and upgrading processes, increasing the processing costs. Pinto et al. (2015) studies on lignin oxy-gasification have showed that the increase of temperature and steam flow rate favoured the destruction of gaseous hydrocarbons (C_nH_m) and tar, leading to the decrease of their contents and to the formation of H_2. The rise of oxygen flow rate also decreased hydrocarbons and tar contents, due to partial oxidation reactions, but syngas higher heating value (HHV) was reduced. Cerone et al., 2016 stated that the presence of steam in eucalyptus wood chips gasification helped to stabilise the process and to promote the formation of H_2 in the syngas and to reach H_2/CO ratios around 1.17. The H_2/CO ratio in the syngas can be increased up to 2.08 by injecting steam as co-gasifying agent (Cerone et al., 2017). Widjaya et al. (2018) stated that non-woody biomass gasification can achieve higher conversion efficiencies and lower pollution than conventional combustion, however, the gasification of these

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feedstocks are usually difficult due to the heterogeneous nature, low density and high silicates contents. Lignin may present different mineral compositions, depending on the process to obtain lignin (values from 0.1 to 14 % were observed), thus syngas composition may be affected. Hence, the first step needs to be the optimisation of gasification, as there are some technical bottlenecks that need to be overcome and further studies of gasification of lignin-rich feedstocks are still needed.

Another challenge in lignin-rich residues gasification is the definition of the right application for syngas produced. Most published information about lignin gasification focus the use of syngas, with very small amounts of impurities, for energy production, while the novelty of the present is the production syngas to be used in fermentation. The use of syngas for bacterial fermentation to produce added-value compounds is quite a new application. The presented work aims to obtain syngas with right $CO/CO_2/H_2$ ratio for fermentation. Thus, the main innovation of the work is the integration of gasification with syngas fermentation.

Although there is little knowledge about the right syngas composition to be used for bacterial fermentation to produce biochemical compounds, current information indicates that the $CO/CO_2/H_2$ ratio, the carbon conversion efficiency, the effect of inhibitory gaseous compounds and the microbial preference of carbon substrate need to be carefully addressed (Karthikeyan et al., 2016).Thus, the first stage of this study was the study of the effect of gasification experimental conditions on syngas yield and quality, namely gasifying agent, temperature and equivalent ratio (ER) to select the conditions to produce syngas suitable for fermentation.

2. Experimental part

A bubbling-fluidised-bed (BFB) gasification reactor with an inside diameter of 80 mm and a height of 1500 mm was used for lignin tests. The feeding system was cooled by water to avoid clogging, caused by eventual pyrolysis of lignin, prior to the entry into the gasifier. To help the feedstock feeding and to avoid a gas back flow, a nitrogen flow was also used. The gasifying/fluidising agent was a mixture of steam and oxygen, introduced through a gas distributor located at the base of the reactor.

The gasification gas (syngas) went through a cyclone to remove particulates. Gasification gas was sampled for tar determination. Isopropanol (2-propanol or isopropyl alcohol) was used for tar collection, using the CEN/TS 15439:2006 procedure. The homogeneous liquid sample was evaporated under well-defined conditions, the evaporation residue was weighed to calculate the amount of tar in g per Nm^3. Tar and condensable liquids were removed from syngas in a quenching system. Afterwards, the gas was filtered, before it was injected into CO and CO_2 on-line analysers. Syngas was sampled and collected in bags to determine its composition by GC (gas chromatography). The concentration of CO, CO_2, H_2, O_2, CH_4 and other higher gaseous hydrocarbons, mentioned as C_nH_m, were determined. After each experiment, solid bed residue, containing silica sand, ashes and unconverted carbon was collected.

Gas was also sampled for H_2S and NH_3 determination. Most of sulphur released into syngas is in the form of H_2S, usually 90 to 97 % mole of the gaseous sulphur compounds. Other sulphur compounds may also be identified, such as: COS (1 – 7 %) and in much smaller amounts of sulphur organic forms, like: thiophene (C_4H_4S), aryl and alkyl-sulphides, benzo-thiophene (C_8H_6S), very small amount of dibenzo-thiophene ($C_{12}H_8S$) and thiols. Thus, only the H_2S contents were determined in syngas produced. NH_3 is the main nitrogen compound formed during gasification, though other nitrogen compounds might be present in syngas in much smaller concentrations. Nitrogen oxides are not usually found, due to gasification reduction conditions and HCN is generally detected in very low concentration. Hence, only NH_3 composition was analysed in syngas.

Lignin flow rate was around 5g daf (dry and ash free)/min. Lignin-rich residue contained about 14.0 % (dry basis) of ashes and 64.6 % (dry basis) of volatiles, C/H was 8.45 (daf basis) and nitrogen and sulphur contents were 1.51 % daf and 0.20 % daf, respectively.

Several experiments were done to study the effect of experimental conditions, namely: temperature, oxygen and steam flow rate, on lignin gasification performance and on gas yield and quality. Temperatures in the range of 750 ° to 900 °C were tested, together with steam/lignin ratios (wt.) between 0 and 0.8. Oxygen was introduced inside the reactor and equivalent ratio (ER) values from 0 to 0.23 were used to study the effect of this parameter. ER is defined as the ratio between the amount of oxygen added and the stoichiometric oxygen needed for complete combustion of the feedstock. Each experiment lasted between 90 and 120 min, depending on the time necessary to collect all the samples at stable conditions. Experiments were repeated more than 2 times when experimental results deviations were higher than 5 %.

Syngas composition is affected by lignin mineral composition, thus the first step was the optimisation of gasification process and only after that the use of syngas in fermentation process should be studied. Hence, fermentation studies began by using two synthetic syngas compositions analogous to the obtained syngas from lignin-rich solids. These syngas were anaerobically fermented by *Butyribacterium methylotrophicum*: Syngas I ($CO+CO_2+H_2+N_2$, 30/20/30/20 % vol.) and Syngas II ($CO+CO_2+H_2+N_2$, 26/19/18/37 % vol.) with a CO/H_2 ratio of 1.0 and 1.4, respectively.

3. Results and discussion

3.1 Effect of gasification experimental conditions

The effect of steam/lignin ratio on gas composition, obtained by gasification of lignin-rich residue, with oxygen and steam was studied. The obtained results are shown in Figure 1(a), which shows that the presence of steam favoured steam reforming reactions and thus the release of hydrogen and the conversion of hydrocarbons, whose composition decreased significantly. This behaviour may be explained by assuming that hydrocarbons conversion by steam reforming reactions leads to the release of CO, CO_2 and H_2. However, CO content also decreased, probably due to its conversion into CO_2, by water gas shift reaction (CO reaction with H_2O to form CO_2 and H_2). Consequently, CO/H_2 ratio decreased with the rise of steam/lignin ratio, but CO/H_2 ratio was higher than 1 for most tests. The highest value (1.9) was obtained for the lowest steam/lignin ratio (in absence of steam). On the other hand, the presence of steam also promoted tar destruction by steam reforming reactions. Therefore, tar content decreased with the increase of steam/biomass ratio, as shown in Figure 1(b). As expected, tar content was quite high for the lowest steam/lignin ratio, around 90 g/Nm^3. Thus, the conditions that favoured the highest CO/H_2 ratio were not suitable for assuring adequate tar contents.

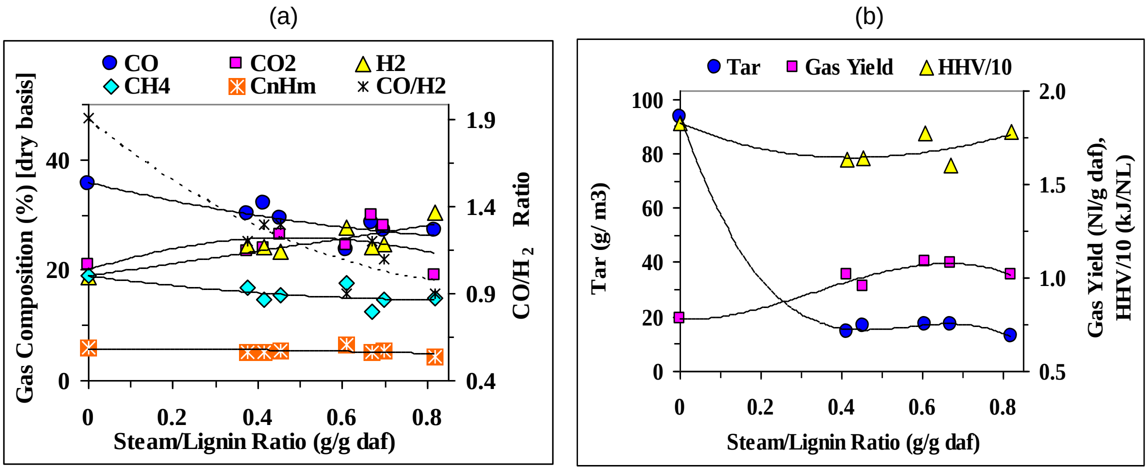

Figure 1: Effect of steam/lignin ratio on gas composition (a) and on tar content, gas yield and HHV (b), obtained by gasification of lignin-rich residues with oxygen and steam (conditions: 800°C, ER = 0.13).

Figure 1(b) also presents the gas yield and syngas higher heating value (HHV). There was an increase in gas yield with the rise of steam/lignin ratio, which agrees with the destruction of tar and its conversion into gases. On the other hand, syngas HHV decreased first with the rise of steam/lignin ratio, probably due to the reduction of hydrocarbons and CO contents, but it increased slightly for the highest steam/lignin ratio possibly as a result of the high hydrogen contents.

The results are in agreement with literature information (Pinto et al., 2015). Cerone et al. (2017) also reported that the increase of steam flow rate promoted the formation of H_2 in the syngas and the decrease of CO/H_2 ratio. The obtained results led to the selection of the steam/lignin ratio of 0.4 for further studies, as the CO/H_2 ratio was around 1.3 and tar contents were considered acceptable.

The effect of gasification temperature on syngas yield and composition was also studied. As presented in Figure 2(a), the rise of temperature clearly favoured the formation of H_2, probably at the expense of hydrocarbons (C_nH_m) and tar release, as both contents decreased, Figure 2(b). No significant changes were observed in CO_2 concentration, but there was a clear decrease in CO content. The highest H_2, contents and the lowest CH_4 and C_nH_m concentrations were observed at 900 °C. As the increase of temperature allowed increasing H_2 syngas content and at the same time led to a decreased in CO concentration, CO/H_2 ratio was observed to decrease. Only for temperatures below 850°C, it was possible to obtain CO/H_2 ratios higher than 1. Furthermore, the rise of temperature promoted steam reforming and cracking reactions, thus allowed significant tar destruction, and at the same led to some increase in syngas yield, Figure 2(b). The increase of temperature from 750 to 900 °C, with a constant ER and steam/lignin ratio, allowed increasing gas yield of about 20 %, due to tar conversion into gases. On the other hand, a decrease in gas HHV of around 16 % was obtained, mainly due to the destruction of gaseous hydrocarbons, favoured by the rise of temperature. This decrease was not higher because of H_2 contribution to HHV value.

The use of lower gasification temperatures prevents problems associated with bed agglomeration (Widjaya et al., 2018) and leads to CO/H_2 ratio higher than 1, but has the disadvantage of producing syngas with higher tar contents. The analysis of all the obtained results led to the selection of the temperature of 800 °C for next gasification tests, as CO/H_2 ratio were higher than 1 and tar content were acceptable. The obtained results clearly agree with others found in literature (Pinto et al., 2015). Widjaya et al. (2018) also reported that the rise of gasification temperature increased gas production, while lowering tar release.

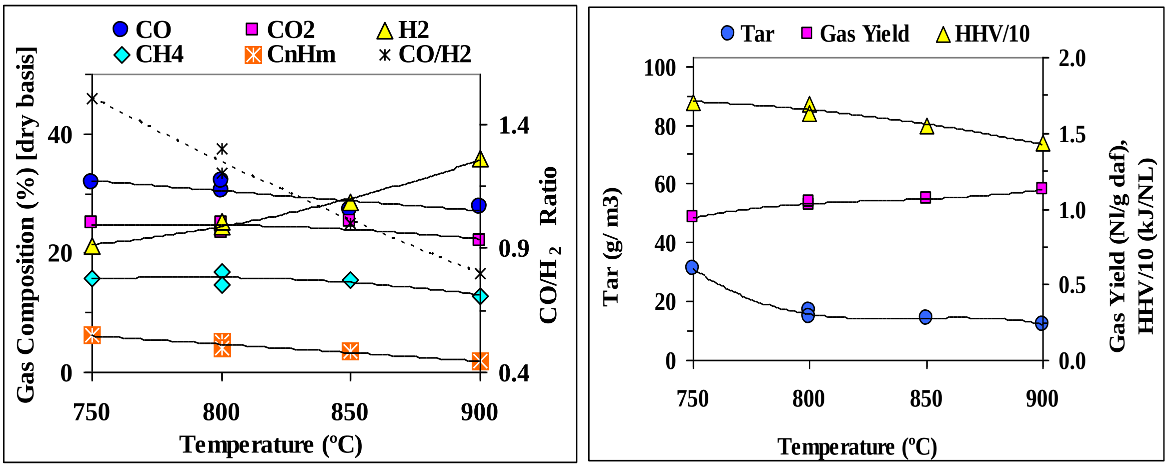
(a) (b)

Figure 2: Effect of temperature on gas composition (a) and on tar content, gas yield and HHV (b), as obtained by lignin-rich residues gasification with oxygen and steam (conditions: ER = 0.13, steam/lignin = 0.4 g/g daf).

The effect of ER (or oxygen flow rate) on syngas composition was also studied. The rise of ER clearly favoured partial oxidation reactions and thus the release of CO and CO_2. Both CH_4 and other gaseous hydrocarbons relative concentration were reduced by the rise of this parameter, Figure 3(a), due to their partial combustion. Oxidation reactions favoured the formation of H_2O and CO_2, being the latter observed in Figure 3(a). Further increase of ER would lead to further enrichment of syngas with CO_2 and to a reduction in H_2 and hydrocarbons relative contents, as the experimental conditions will approach those of combustion. As the rise of ER led to an increase in CO and to a small decrease in H_2, there was an increase of CO/H_2 ratio.

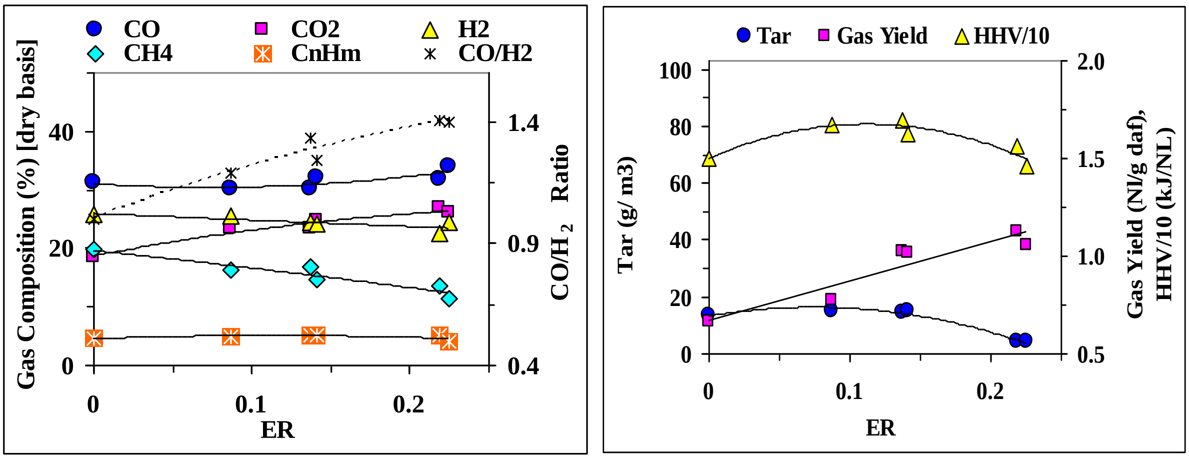
(a) (b)

Figure 3: Effect of ER on gas composition (a) and on tar content, gas yield and HHV (b), as obtained by gasification of lignin-rich residues with oxygen and steam (conditions: 800 °C, steam/lignin = 0.4 g/g daf).

As shown in Figure 3(b) the rise of ER led to tar destruction, as partial oxidation reactions were promoted. For the highest ER value, the tar content was surprisingly low. Gas yield was also observed to increase with the rise of ER, to which tar conversion into gases contributed. The increase of ER values, keeping temperature and steam lignin ratio constant, led to a 37 % increase in gas yield. Otherwise, as the gas was poorer in hydrocarbons and richer in CO, as presented in Figure 3(b), the gas HHV only decreased around 12 %. Further increase of ER would lead to more decreases in syngas HHV.

The obtained results showed that the ER value of 0.13 was a good option to study the effect of temperature and of steam/lignin ratio on lignin-rich residues gasification. The obtained results also agree with others reported in literature. Pinto et al. (2016) also reported that the use of oxygen and steam was a good option to obtain high energy conversion and good gas composition.

3.2 Effect of experimental conditions on H_2S and NH_3 concentrations in syngas

Besides tar, syngas may also contain other contaminants like H_2S and NH_3. Thus, the effect of experimental conditions on NH_3 and H_2S content, obtained by gasification of lignin-rich residues is presented in Figure 4. H_2S and NH_3 formation is a very complex issue, as it depends on several parameters, such as: gasification experimental conditions, nitrogen and sulphur content of the feedstock and also the presence of different mineral matter elements in the feedstock or even in reactor building metals. All these parameters may affect NH_3 and H_2S formation and destruction reactions. These compounds may be formed from nitrogen and sulphur in char (char-N and char-S), but afterwards the initially formed compounds may be decomposed or retained inside the gasification bed. For instance the presence of Ca, Zn, Fe, Mn, etc. favours the formation of the respective sulphides and, hence, sulphur retention. Due to the huge amount of reactions that may occur in gasification medium the effect of the experimental conditions on NH_3 and H_2S release is not easy to predict. Figure 4 shows the decrease of NH_3 and H_2S release with the rise of temperature, which agrees with reported information found in literature. Several authors have reported decreases in NH_3 contents with the rise of temperature, because the thermodynamic decomposition of NH_3 is favoured by temperature increase, as it is an endothermic reaction (Pinto et al., 2016).

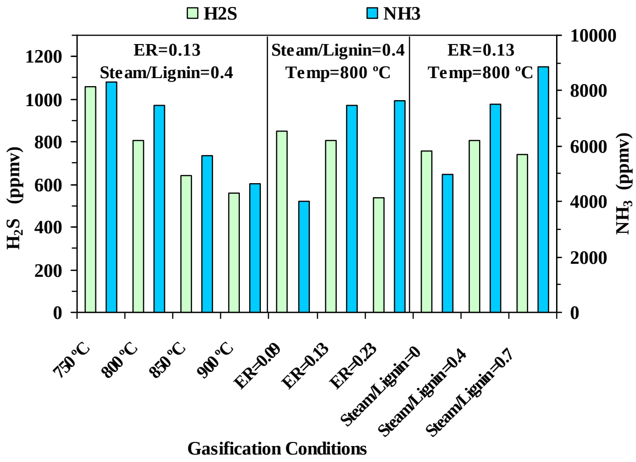

Figure 4: Effect of experimental conditions on NH_3 and H_2S obtained by gasification of lignin-rich residues.

Figure 4 also shows that the increase of steam/lignin ratio clearly favoured the release of NH_3, while no great changes were observed for the release of H_2S. The increase of steam flow rate is expected to lead to higher NH_3 and H_2S formation, through hydrolysis reactions. However, the formation and destruction of these compounds and S and N partitioning in different phases may be a very complicated issue, as mentioned before. The rise of ER is usually expected to decrease NH_3 and H_2S contents, due to their destruction by partial oxidation reactions (Pinto et al., 2016), which allows explaining the decrease observed in H_2S (Choi et al. 2017). On the other hand, a small increase in ER may favour gasification general reactions and thus the release of char-N, this may help to understand the increase of NH_3 observed at the ER value of 0.13. Further increase of ER to values higher than 0.3, is expected to lead to significant decreases in NH_3 concentration. This will be investigated in future gasification tests.

3.3. Syngas fermentation

Two syngas compositions – Syngas I and II - were used for the production of acetic and butyric acids by *B. methylotrophicum*. Whereas Syngas I levelled the CO/H_2 ratio to 1.0, Syngas II composition mimicked the lignin syngas obtained by application of gasification conditions, which maximised the CO concentration in the gas ($CO/CO_2/H_2$=1:0.7:0.7). The concentration of acetic (19.9 and 11.9 mM) and butyric acid (5.3 and 3.0 mM) produced by *B. methylotrophicum* from Syngas I and Syngas II, respectively, varied directly with the carbon amount of each syngas composition and the conversion efficiency. The CO, H_2 and CO_2 were simultaneously metabolised by *B. methylotrophicum*, but CO was first depleted in all cases. The H_2 consumption accelerated when CO reached ≤ 6 mM in Syngas I, which is in agreement with the inhibition of the hydrogenase activity by CO (Heiskanen et al., 2007). The major H_2 concentration decrease, of 12.1 and 7.1 mM between 0 and 72 h in Syngas I and Syngas II fermentation respectively, was time coincident with the highest CO_2 negative balance (5.2 and 2.5 mM, respectively). As the CO_2 concentration results from a metabolic consumption/production balance, it decreased slowly with either one of the tested syngas compositions but only until H_2 depletion. After 72 h, H_2 was depleted in Syngas I fermentation or residual in Syngas II fermentation, and the CO_2 concentration was maintained, respectively, at 2.7±0.2 and 5.3±0.2 mM until 120 h of incubation. As such, the extent of the CO_2 carbon conversion in batch fermentations for the production of acetic and butyric acid is ultimately determined by the presence of H_2 in the syngas.

4. Conclusions

No major changes were needed in existing gasification installation, as lignin-rich residues gasification did not give rise to any operational problems, regarding both the feeding system and the gasification process.

The rise of steam/lignin favoured the release of NH_3, while no great changes were observed for H_2S. The rise of steam/lignin ratio promoted steam reforming reactions, thus the release of tar and gaseous hydrocarbons decreased, but also CO/H_2 ratio. As this ratio should be equal or higher than one, the steam/lignin ratio should be around 0.4. Temperature promoted cracking and reforming reactions and thus tar and hydrocarbons destruction, favouring H_2 release. NH_3 and H_2S decrease was also observed. The temperature of 800 °C is a good option, as the CO/H_2 ratio of about 1.3 and acceptable tar contents were obtained. This temperature also allows a better control of the problems associated with bed agglomeration. The rise of equivalent ratio favoured partial oxidation reactions and thus the release of CO and CO_2, while gaseous hydrocarbons, H_2, tar and H_2S decreased. Equivalent ratio of about 0.13 is a good option, as CO/H_2 was around 1.2.

The amount of carbon in syngas was determinant to increase the concentrations of acetic and butyric acids produced. However, to improve the carbon conversion efficiency, it can be advantageous to adjust the CO/CO_2/H_2 ratio stepwise to favour the initial *B. methylotrophicum* growth with CO and, in a second stage, of product formation, increase the concentration of H_2, so as not to limit CO_2 consumption.

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