

Cleaning and Conditioning of Biomass Gasification Gas to Produce Biomethane

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Nowadays, it is urgent to develop new energy production and utilisation routes to achieve sustainable development with low environmental impact. Gasification of biomass wastes followed by biomethane production may contribute to achieve these goals. The objective of this paper is to study hot cleaning and upgrading processes of gasification gas to allow it to be suitable for biomethane production. Gas produced by gasification of eucalyptus wastes at 750 °C and 850 °C was used to study the hot gas conditioning process. For this, two sequential fixed bed steps with different catalysts or sorbents and at different temperatures were tested. In Pathway A, a low cost natural mineral, limestone, was used in both steps at temperatures from 500 ° to 700 °C. In Pathway B, limestone was used in the first step and in the second one, a nickel-based catalyst was tested. The effect of temperature was also studied by using temperatures between 500 °C and 700 °C. Pathway B showed to be the best option, especially at the highest temperature tested, producing a syngas richer in H₂ and CO₂, with very low contents of tar and heavier gaseous hydrocarbons. Pathway B was also effective for great NH₃ and H₂S reductions, around 90 %, leading to final NH₃ and H₂S concentrations of around 158 and 21 mg/m³, respectively. Further reductions will be studied by testing new multi-functional and more specific catalysts in the next studies, accordingly with new biomethanation catalysts requirements.

1. Introduction

Nowadays, climate change is one of the most challenges of humankind and it is urgent to reduce drastically GHG (greenhouse gases) emissions. Therefore, in the near future, it is essential to diversify energy carriers and to decrease environmental impact of energy production and utilisation routes. The use of biomass will help to decrease fossil fuels utilisation and the accumulation of wastes produced by different activities like agriculture, food production and forestry management. Europeans goal is to increase the share of bioenergy to renewable energy supply to more than two thirds (Ahmadvand et al., 2023).

Biomethane is a favourable renewable fuel for the decarbonisation of energy and transport systems, but it is fundamental to improve the viability of sustainable processes to produce this renewable gas. It is important to enlarge the existing technologies for biomethane production, developing alternative processes to anaerobic digestion. One of those processes is gasification of biomass wastes followed by catalytic methanation of syngas (gasification gas) (Striūgas et al., 2023).

There is great information about biomass gasification using different types of gasification technologies, the most used are fixed bed, fluidised bed and entrained flow. Fluidised bed is a suitable technology to process biomass wastes with high heterogeneous composition. Advanced processes like Dual Fluidised Bed (DFB) gasification and Sorption-Enhanced Reforming (SER) have shown to be suitable technologies for bio-hydrogen production (Pinto et al., 2023). However, there are still some drawbacks and technical challenges that need to be solved to increase economic and environmental feasibility of gasification fuel production routes.

Syngas produced by biomass gasification contains hydrogen (H₂), carbon dioxide (CO₂), carbon monoxide (CO), gaseous hydrocarbons, mostly methane (CH₄), other higher gaseous hydrocarbons (C_nH_m) and minor undesirable components, like tar, ammonia (NH₃), hydrogen sulphide (H₂S), hydrogen chloride (HCl), etc. These contaminants have to be removed before syngas could be used in further applications, like high efficient electric energy generation, fuels production and building block chemicals synthesis (Boccia et al., 2021). The contents

accepted for each contaminant depend on syngas utilisation, being the first utilisation the least demanding. In this context, Rubinsin et al. (2024) reviewed biomass gasification processes, mainly gasification parameters optimisation and the performance of different catalyst types used during gasification, with the aim of improving gas composition and yield, to facilitate syngas cleaning and upgrading processes before methanation to convert CO and CO₂ into biomethane.

Syngas composition depends on gasification conditions, technology and mostly on biomass wastes type and composition. Currently, there is a huge interest in using poor quality wastes with high amounts of undesirable components. These wastes originate syngas with high needs of cleaning and conditioning before methanation, as the performance of the catalysts used are affected by syngas undesirable components. Thus, syngas cleaning and conditioning procedures are of main importance to biomethane production route from biomass wastes gasification, as the removal of harmful compounds is a key issue of the overall process for biomethane production and affects its economic viability. Ren et al. (2020) stated that the removal of HCl and H₂S is important to avoid the deactivation of methanation catalysts, but tar removal before methanation is not crucial when methanation temperature is higher than tar condensation temperature and syngas is kept at high temperature between gasification and methanation.

Concerning biomethane production, the syngas has to contain H₂, CO₂ or/and CO, with the right ratios, which should be 4 and 3, respectively, to guarantee high conversion rates. Nevertheless, H₂:CO and H₂:CO₂ ratios in the syngas from biomass gasification are usually lower, and depend on gasifier type, gasification conditions, and feedstock. To increase these ratios, H₂ obtained by electrolysis could be added to syngas and/or syngas has to be conditioned using suitable catalysts to improve syngas composition.

Two options may be used for syngas cleaning and conditioning: hot gas cleaning and cold gas cleaning. The latter operates at atmospheric pressure and near ambient temperature, while in the former syngas is kept at high temperature and different sorbents and catalysts may be used for thermal catalytic cracking processes. When after cleaning and upgrading, syngas is used at high temperature processes like methanation, hot gas cleaning is the best option to reach lower operating costs and better energy management. Catalytic thermochemical processes have proven to be one of the best options for tar abatement, using mineral based catalysts like olivine, dolomite or zeolites and an organic catalyst such as biochar (Singh et al., 2023). More expensive and specific metal-based catalysts like nickel-based catalysts have shown to be more efficient in tar removal. Singh et al. (2023) studied a new process, where after reforming, light tar is further removed by biochar obtained by wood chips. These authors reported overall tar removal of about 80 %, being reforming responsible for 40 %, while adsorption by biochar led to tar reduction of around 60 % of the residual tar. Boccia et al. (2021) studied the effect of temperature (750 °C – 850 °C) and of steam content (0 % – 10 %) on reforming and on water-gas shift reactions, using Naphthalene (C₁₀H₈) as a tar model compound and commercial activated carbon catalyst and found that at 800 °C and with a steam content of 7.5 %, conversion over 90 % were obtained. The challenge is the use of low-cost catalysts with high activity and big resistance to contaminants to ensure catalysts long life. Thus, more research and development are still needed for catalyst progress.

Regarding catalyst use to promote biomethane production from syngas, nickel catalysts have been used for biomass gasification and biomethane production, but carbon deposition on catalyst surface has lowered syngas conversion (Striūgas et al., 2023). These authors developed and tested two catalysts, magnesium nickel and magnesium nickel hydride for biomethane production from syngas and found that the latter showed good activity for CO and CO₂ conversion into methane. Ren et al. (2020) reviewed several catalysts for CO₂ methanation and stated that Ni-based and noble metal-based catalysts (Ru, Rh, Pt, etc.) within common supports were suitable. The main objective of this paper is to study thermochemical cleaning and upgrading processes of syngas produced by gasification of lignocellulosic-based materials like forestry biomass. A two-stage process for syngas cleaning and upgrading was tested, using different operation conditions and catalysts types to select the best operation routes, depending on syngas initial composition and on desired final composition for conditioned syngas, considering also overall complexity, catalysts cost and degradation.

2. Material and Methods

Forestry biomass was gasified in a bubbling-fluidised-bed (BFB) gasification reactor with an inside diameter of 80 mm and a height of 1500 mm. The reactor operated at atmospheric pressure. To prevent biomass clogging, caused by eventual pyrolysis, the feeding system was cooled by water and a nitrogen flow was also used to help biomass feeding and to avoid a gas back flow. The gasifying and fluidising agent was a mixture of steam and oxygen, introduced through a gas distributor located at reactor bottom.

Eucalyptus was the biomass used. It presented 2.0 % (dry basis) of ashes and 89.9 % (dry basis) of volatiles, C/H was 8.6 daf (dry and ash free basis) and sulphur and nitrogen contents were 0.03 % daf and 0.20 % daf, respectively. Eucalyptus was gasified at 750 °C and 850 °C with a flow rate around 5 g daf/min. Biomass/steam ratio (wt.) was around 1 and equivalent ratio (ER) was about 0.2.

The gasification gas produced went through a cyclone to remove particulates. Afterwards it went through a reactor for cleaning and upgrading by catalytic and thermal processes. This reactor contained two sequential fixed bed steps. Different types of sorbents or catalysts may be used in each step to achieve tar cracking and reforming reactions and also to retain some sulphur and halogens compounds that might be present in syngas. The abatement of these compounds is fundamental, as they may poison expensive catalysts used in some syngas uses like methanation. Limestone, a low-cost natural material, was used in the first reactor step. In the second step, limestone was also tested, but in other experiments, a nickel-based catalyst was used, as it is a more specific catalyst to promote additional tar destruction and sulphur and halogens compounds abatement. Each gasification followed by syngas conditioning experiment lasted between 90 and 120 minutes, depending on the time necessary to collect all the samples at stable conditions. In Figure 1 are presented a schematic diagram of syngas cleaning and upgrading system.

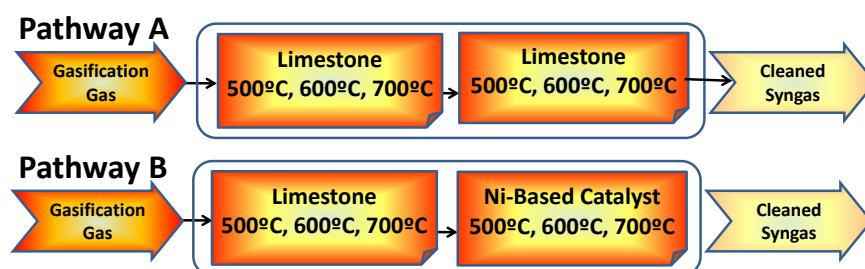


Figure 1: Schematic diagram of syngas cleaning and upgrading pathways.

The nickel-based catalyst used, G-90 B 5, was supplied by C&CS (Catalysts & Chemical Specialities) in cylindrical pieces with 16 x 8 mm and 5 holes. It contained 11% of Ni, 6-9% of CaO and 76-82% of Al₂O₃. Both fixed bed steps worked at temperature from 500°C to 700°C. As syngas transported an excess of steam introduced into the gasifier, no extra steam was added to the fixed bed steps.

Syngas and conditioned gas were sampled in three points: after gasification, first step cleaning and second step conditioning. In each of these sampling points syngas was collected to determine the composition of CO, CO₂, H₂, CH₄, and other higher gaseous hydrocarbons, mentioned as C_nH_m by GC (gas chromatography). Syngas was also sampled for tar quantification, using the CEN/TS 15439:2006 procedure. H₂S and NH₃ contents in syngas were also measured, as these are the main compounds containing sulphur and nitrogen, respectively, usually 90 to 97 % mol. Besides H₂S, COS (1–7%) may also be found and in much smaller amounts. Sulphur organic compounds, like: thiophene (C₄H₄S), aryl and alkyl-sulphides, benzo-thiophene (C₈H₆S) and even smaller amounts of dibenzo-thiophene (C₁₂H₈S) and thiols may be detected. Other nitrogen compounds might be found in syngas, but in much smaller concentrations than NH₃. Due to gasification reduction conditions, nitrogen oxides are not usually found, and HCN is generally detected in very low concentrations. Thus, only H₂S and NH₃ contents were measured.

3. Results Discussion

3.1 Effect of syngas cleaning and conditioning process on syngas gaseous compounds

Eucalyptus gasification gas was produced at the gasification conditions mentioned before. Syngas produced was cleaned and upgraded using the two pathways presented in Figure 1. The composition of the main gaseous compounds of syngas obtained after each catalyst treatment and temperature for both pathways are presented in Figure 2. Not all the results are presented, but only those more representative of the effect of syngas treatment on gas composition.

When the gasification obtained at 750 °C gas was first treated with limestone at 500 °C, there was some increase in H₂ content and some decrease in gaseous hydrocarbons concentration. These concentration changes were higher with the rise of temperature during limestone treatment, probably because reforming reactions were favoured. The same effect was observed for the syngas produced by gasification at 850 °C. These results are in agreement with tar contents reduction observed in Figure 3. For syngas produced at 750 °C, no great changes were observed in CO and CO₂ concentration, though a decreasing tendency was detected in CO, followed by some increase in CO₂ content. For syngas produced at 850 °C, these changes were even milder. The greatest variations were observed when syngas was treated with limestone at 700 °C.

When syngas obtained after limestone treatment was further treated with the nickel-based catalyst (Pathway B) great decreases in gaseous hydrocarbons, especially those referred as C_nH_m, were observed for all syngas

concentrations tested. C_nH_m reductions varied between 40 and 62% and were in agreement with the high increases observed in H_2 concentrations. Water gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) might also have been promoted, which would explain the increase in H_2 and CO_2 contents and the reduction in CO , as shown in Figure 2. After the nickel-based catalyst, final gas was richer in H_2 and CO_2 and poorer in hydrocarbons. CH_4 was the only hydrocarbon detected in substantial amounts. These trends were observed for all temperatures studied (500 °C, 600 °C and 700 °C).

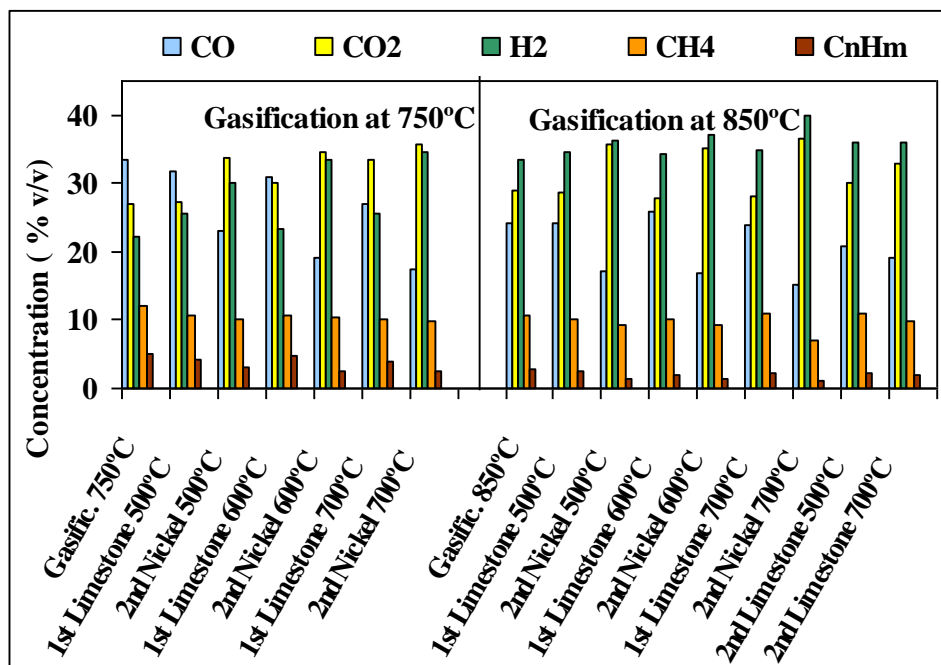


Figure 2: Effect of syngas cleaning and upgrading pathways with different catalysts and temperatures on syngas gaseous compounds.

When limestone was used in the second step (Pathway A), final gas composition had lower H_2 and CO_2 , and higher CH_4 , hydrocarbons and CO , in relation to the use of Ni-based catalyst (Pathway B). As expected, this last catalyst showed to be more efficient in promoting hydrocarbons destruction and water gas shift reaction than limestone (Pinto et al., 2019). The results presented in Figure 2 show that Pathway B is a better option for upgrading gasification gas than Pathway A.

3.2 Effect of syngas cleaning and conditioning process on tar destruction

In Figure 3 is shown the effect of syngas cleaning and upgrading pathways on gas yield and tar content, using different catalysts and temperatures. The first treatment with limestone led to the decrease in tar content for both syngas obtained at 750 °C and 850 °C. The rise of temperature on limestone stage favoured the reduction of tar content. Tar content reduction was in accordance with the rise of gas yield, because tar destruction by cracking and reforming reactions led to the formation of gas. The further treatment of syngas with the nickel-based catalyst allowed even higher tar reductions, as shown in Figure 3. This trend was observed for all temperatures studied (500 °C, 600 °C and 700 °C). As expected tar destruction during nickel-based catalyst was favoured by the increase of temperature (Rubinsin et al., 2024). The lowest tar contents and the highest gas yields were obtained with nickel-based catalyst treatment at the highest temperature, 700 °C (Pathway B). When limestone was used for the second syngas upgrading stage, there was also some decrease in tar content followed by the consequent gas yield increase. These changes were higher when the temperature changed from 500 °C to 700 °C. However, final tar contents were much higher than those obtained when the nickel-based catalyst was used in the second stage, as this catalyst is more specific for tar destruction than limestone. Therefore, lower gas yields were also obtained when the nickel-based catalyst was used in the second stage upgrading instead of limestone for all the temperatures tested. Figure 3 results also show that Pathway B was more effective for tar reduction than Pathway A, which is in accordance with Figure 2 results.

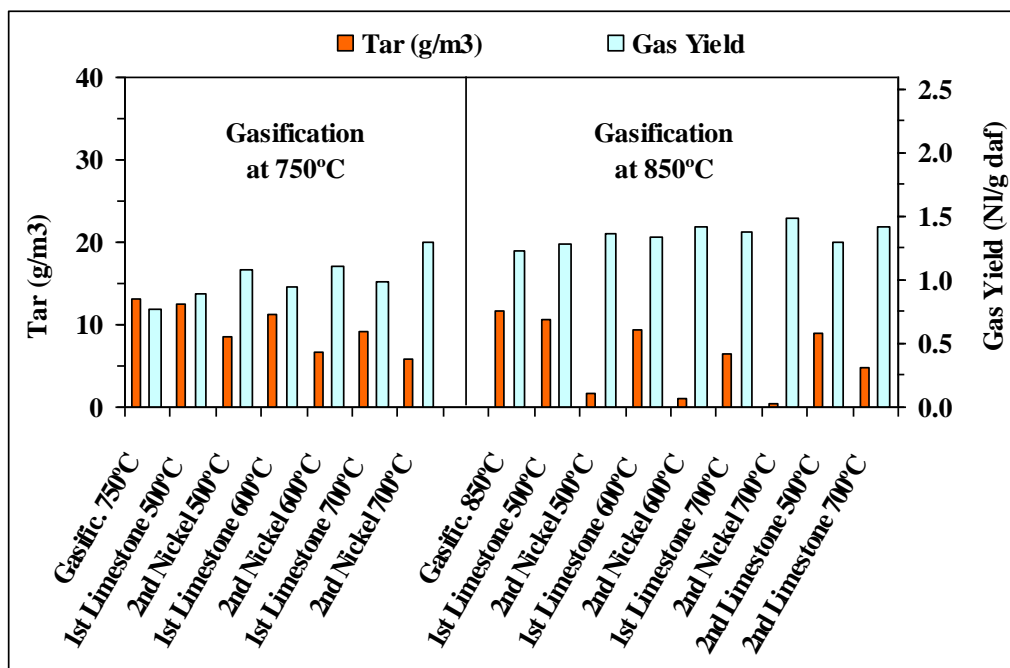


Figure 3: Effect of syngas cleaning and upgrading pathways with different catalysts and temperatures on gas yield and on tar content.

3.3 Effect of syngas cleaning and conditioning process on H₂S and NH₃ concentrations

Besides tar, contaminants like H₂S and NH₃ are disadvantageous for many syngas utilisations. The presence of these compounds in syngas depends on several parameters that affect NH₃ and H₂S formation and destruction during gasification. Nitrogen and sulphur contents in the feedstock to be gasified are of most importance, but also gasification experimental conditions, including the catalyst used have great effect. NH₃ and H₂S may be initially formed from nitrogen and sulphur in the feedstock, but these compounds may be decomposed or retained inside the gasification bed. The increase of gasification temperature and of ER usually lead to NH₃ and H₂S reductions, while the increase of steam flow rate normally leads to higher NH₃ and H₂S concentrations (Pinto et al., 2019).

It is possible to decrease NH₃ and H₂S release into syngas by adjusting gasification conditions, and by the use of sorbents or catalysts. However, most syngas utilisations require very low contents of these contaminants, thus, syngas cleaning and upgrading is needed. Pathways A and B were tested to analyse their effect on syngas NH₃ and H₂S contents. The use of limestone in the first stage of syngas treatment led to average H₂S reductions between 50 to 60 %, the highest decreases were obtained at the highest temperatures tested. The use of limestone in a second stage (Pathways A) led to further decrease of H₂S, being the maximum reductions about 75 %. The highest reductions in H₂S contents were obtained when the nickel-based catalyst was used (Pathways B), due to the presence of CaO in this catalyst that reacted with H₂S and formed CaS. Pathways B led to the highest H₂S reductions of about 90 % in average.

NH₃ reductions of about 40 to 50 % were obtained when syngas was first treated with limestone. The use of limestone for the second stage treatment also led to some decrease in NH₃ concentrations, but the highest NH₃ reductions were observed in syngas after the use of the nickel-based catalyst, being about 90 % in average, being this catalyst very effective in NH₃ destruction. Therefore, Pathways B was the most effective for the decrease in H₂S and NH₃ contents, as the nickel-based catalyst promoted NH₃ destruction and sulphur retention. It was possible to obtain final NH₃ and H₂S concentrations of around 158 and 21 mg/m³, respectively. A procedure using in a first step a low-cost catalyst and in the second one a more specific and expensive catalyst, like a nickel-based one (Pathway B) showed to be a good option, as it also led to great tar and heavier gaseous hydrocarbons reductions. However, depending on methanation catalyst requirements, further syngas treatments may be needed or the use of more specific catalysts. In the first step, other materials may be used instead of natural minerals, like limestone. Other sorbents like ZnO have shown to be more efficient for retaining sulphur. The vaporisation of elemental zinc may be solved by the addition of Fe or Ti to ZnO, though some other problems may appear like spalling and cracking. Besides these problems, the cost of the materials used has also to be considered, as it will increase operational costs. Depending on syngas composition and syngas use,

choosing a low-cost catalysts or sorbent for the first stage seems to be a suitable option to first deal with a syngas with higher contents of tar and other disadvantageous compounds. Thus, a cleaned syngas will contact with a more specific and also more expensive catalyst.

It is planned to carry on these studies by testing different catalysts, more specific and multi-functional, especially in the second stage upgrading treatment, as the use of natural minerals in the first stage is a good option. However, other minerals like dolomite or olivine may perform accordingly. Depending on the requirements for final syngas composition, a third upgrading stage may also be considered, using catalysts that are even more expensive. Nevertheless, the increase in complexity and in operational costs will have to be well justified.

4. Conclusions

It is possible to control the release into syngas of tar, H₂S and NH₃ by the right selection of gasification experimental conditions. However, syngas utilisations like catalytic methanation require very low contents of these contaminants. Thus, syngas cleaning and upgrading is needed.

A hot gas conditioning process, using two sequential fixed bed steps led to positive results. Pathway A, that used limestone in both stages led to significant contaminants reduction in syngas, but the best configuration was obtained with Pathway B that used first a low-cost natural mineral, limestone, and in a second stage a nickel-based catalyst, G-90 B 5, supplied by C&CS.

Pathway B showed to be a good option, as tar and heavier gaseous hydrocarbons cracking and reforming reactions were promoted and thus their conversion into CO₂ and H₂. Water gas shift reaction was also favoured in this pathway, hence CO was converted into H₂ and CO₂. The use of higher temperatures promoted the reactions occurring in the hot cleaning process, thus favouring final gas composition. Thus, final gas obtained at 700 °C was richer in H₂ and CO₂ and poorer in hydrocarbons. CH₄ was the only hydrocarbon detected in significant amounts. Only small amounts of tar were detected in final syngas composition.

Pathway B also showed to be a good configuration for NH₃ and H₂S reductions, as limestone promoted H₂S destruction and CaO present in G-90 B 5 further reduced H₂S. This catalyst was also effective for NH₃ and further tar reduction.

Besides the good results of Pathway B, more demanding syngas utilisations and specific biomethanation catalysts are expected to require even lower contents of tar, NH₃ and H₂S. Thus, this study will carry on by testing new and more specific catalysts, especially for the second stage conditioning treatment.

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