

Biomass as a Renewable Source to Produce Synthesis Gas by Catalytic Gasification Process

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Technical feasibility to reduce tar concentration in the gas obtained by steam gasification of biomass by using a continuous biomass gasification plant, mainly composed of a fluidized bed gasifier with an internal diameter of 0.1 m containing in its freeboard a ceramic candles filled with commercial catalyst pellets used for the steam reforming of naphtha was verified. The tests have shown that it is possible to obtain a tar reduction in the producer gas comparable to that obtained by using a vegetable oil absorption plant. This process configuration allows you to reach greater energy efficiency of the entire gasification process as the transformation of tar compounds into light gases such as H₂ and CO. The catalyst strongly reduces the concentration of NH₃ to levels of about 30 ppm and methane to concentrations below 1% by volume.

1. Introduction

In recent years, public opinion has grown concerned about all the consequences of climate change. The increase of CO₂ in the atmosphere, due to the use of fossil fuels to produce energy, is leading to an increase in the average temperature of the earth. This increase in temperature, favors greater evaporation of water with consequent greater precipitation, overflow of rivers and flooding. In the last years, the use of renewable energy sources than fossil fuels has not produced significant effects on the environment because the use of coal is still predominant in many countries. Furthermore, in the last decade, oil consumption has risen steadily for the increased use of cars and the doubling of world air traffic. In the year 2020, the total world consumption of electricity has been 26823 TWh of which 708 TWh were from photovoltaic panels, 1420 TWh from wind turbines and 9421 TWh from coal (BP, 2021). In the near future, the electricity productions from photovoltaic and wind will increase significantly and hopefully integrated with electricity produced by using nuclear fusion plants.

However, for the movement of airplanes, ships, trucks and even cars, liquid and/or gaseous renewable fuel will always be required. Using renewable electricity to produce hydrogen and then using this energy vector to reproduce electricity by means fuel cell, it is energetically very dispersive. It would be more suitable to produce synthetic fuels from renewable sources such as biomass. All agricultural by-products and organic waste can integrate the local biomass production that often if not collected, are the main cause of fires.

There are two ways to transform biomass into a liquid and/or gaseous energy carrier: biological and thermochemical conversions. The biological conversion, unlike the thermochemical one, leads to the formation of only two compounds, ethyl alcohol and methane. In the USA, fermentation of corn seeds produce ethyl alcohol meanwhile in Brazil the raw material for fermentation is sugarcane. In the latter case, more than 10 million hectares of land cultivated at sugarcane have produced in the year 2019, 37.38 billion liters of ethanol (Barros and Woody, 2020). These large territorial extensions used for the production of sugarcane are not possible in densely populated countries such as those in Europe.

The use of cereals for the production of bio-alcohol even in the past it was not the main reason for the increases food and animal feed prices, this does not mean that in the future this cannot represent a reason for competition between energy and food needs (Sims et al. 2010).

From the other side, the biological production of bio-alcohol starting from lignocellulosic materials has not proved industrially feasible. The first plant in the world for the production of bioethanol from non-food biomass, owned by Beta Renewables, opened in Italy in 2013, with an annual potential of 75 million liters of ethanol, fed with residual agricultural products, has closed its activity in 2018. Gasification processes, unlike biological processes, can use all types of biomasses, cultivable, crop residues and the organic fraction of municipal solid waste.

Unlike combustion, where the heat must be used on site to produce steam and then electricity, the gasification process produces a combustible gas that can be used both on site and transported remotely.

Since gasification is a process lacking in oxygen and therefore in a reducing environment, the nitrogen compounds sulfur and chlorine, if are present, are transformed into NH_3 , H_2S , COS and HCl . Removing these polluting gases from the producer gas, prevent the formation of NO_x , SO_x and dioxins in the exhaust gases, during the combustion process. However, the gas produced by gasification can be efficiently converted into electricity by using molten carbonate and solid oxide fuel cells, or it can be used for the production of methanol (Iaquaniello et al. 2017), synthetic gasolines by Fisher Tropsch synthesis (Korberg et al. 2021), synthetic natural gas, (SNG) or used as a source of hydrogen. While it is possible to estimate the production costs of synthetic fuels starting from coal and natural gas, this forecast is not possible when we start from biomass. A correct forecast of the costs associated with the transformation of biomass into liquid fuel requires the construction of demonstration plants and the definition of the biomass supply chain (Haarlemmer et al. 2014).

The main problem that has hitherto blocked the construction of industrial plants based on the thermochemical gasification of biomass is the presence in the producer gas contaminants such as a mixture of high molecular weight hydrocarbons, which make its use problematic. The sum of all the hydrocarbon compounds present in the gas with a molecular weight greater than benzene represents the concentration of tar in the gas.

The maximum values of the concentrations of pollutants that may be present in the gas obtained from the gasification of biomass for the various applications are widely reported in the literature (Shahabuddin et al. 2020, Marcantonio et al. 2020). Solid particles present in the gas, can be efficiently eliminated by using ceramic or metal filters able to operate at high temperatures and capable of removing 99.999% of the solids having a diameter less than 100 μm (Sharma et al., 2008). The concentration of solid dust in the gas can be reduced down to 1 mg/Nm^3 (Heidenreich, 2013). Tar deposition on the equipment, on the valves and on the measurement systems occur during the cooling of the raw gas, limiting and / or blocking their operations. Physical and/or chemical methods to reduce as much as possible the concentration of tar in the producer gas are widely used (Valderrama Rios et al. 2018). The first action is to reduce the quantity of tar produced during the gasification process.

2. Methods to reduce tar in the producer gas

The introduction of the biomass into the fluidized bed has a positive effect to decrease the quantity of tar in the producer gas (Rapagnà and Latif, 1997, Pio et al., 2021) especially when catalytic materials are present in the bed inventory. The use of materials with catalytic properties in transforming tar into light products is a widespread way in the management of industrial plants and methane concentration in the producer gas gives an indication of the catalytic activity of the particles making up the fluidized bed. The addition of Ca and K-based additives is common practice to avoid tar condensation when the producer gas is cooled-down to temperatures below 200 °C, taking care to avoid the formation of $\text{K}_2\text{O}\cdot 4\text{SiO}_2$ compound, which has melting temperature below 800 °C. However, biomass gasification temperature must remain in the range 800 - 870 °C to avoid agglomeration of the particles making up the fluidized bed. Most of the primary catalyst that have been used in a laboratory scale, are granular dolomite, olivine, alumina, Fe/olivine, Ni/Olivine, Rh/CeO₂/SiO₂, Rh/La₂O₃-Al₂O₃, Ni/Alumina, Ni/dolomite and Co/MgO (Rapagnà et al. 2018). However, the industrial application of catalysts containing metals into the fluidised bed is almost impossible because fines and ashes would contain heavy metals that are dangerous for the environment, and expensive to dispose. However even active materials are utilized into the fluidised bed, the amount of tar in the producer gas is too high and further gas treatments are necessary to decrease it. Phuphuakrat et al. 2011, used different types of organic solvents to verify their aptitude to absorb tar, and noted that the absorption efficiency can be ranked in the following order; diesel fuel > vegetable oil > biodiesel fuel > engine oil > water. Their recommendation was to use vegetable oil (60% Soybean oil, 40% Canola oil) in the scrubber to avoid a high loss of diesel and biodiesel fuels due to their easy evaporation. Bhoi et al., 2015, used Soyben oil due to its low cost and its high availability, to evaluate its efficiency in removing model producer gas tar compounds in a wet packed bed scrubbing system. Oil-gas scrubber (OLGA) is a process that use oil to clean the gas. However, available information on the operating conditions and the liquid used in the columns is rare (Harb et al., 2020). Considering naphthalene as a representative component of the tar, by using diesel fuel as adsorbent, the maximum removal efficiency would be 97.4%. This means that if the quantity of tar contained in the gas coming from biomass gasification is in the range of 3-20 g/Nm^3 (Marcantonio et al., 2020)

still remain in the producer gas, after the scrubber, 78 - 520 mg/Nm³ of tar. The situation would be worsen when soyben oil is used, as suggested by the authors, because the removal efficiency would drop to 93.5% with a consequent naphthalene content in the gas equal to 195-1300 mg/Nm³. These quantities are larger higher than that allowed for many applications. Moreover, scrubbing with an organic compound performed at temperatures higher than the water condensing temperatures, does not reduce the quantities of sulfur, nitrogen and chlorine compounds such as H₂S e COS, NH₃ and HCl from the producer gas. After the scrubber with oil, a scrubber with water is needed in order to eliminate NH₃ and HCl, followed by an absorption of the light tar with activated carbon and the transformation of organic compounds containing S and Cl by hydrodesulfurization process (HDS) in H₂S and HCl (Haro et al., 2016). HCl could be removed by Na₂CO₃·NaHCO₃·2H₂O at around 526-650°C and H₂S removal could occur at 400 °C with a ZnO-fixed bed (Marcantonio et al., 2020).

Biomasses are a low energy density resource, so transport has a decisive impact on the final cost of energy obtained with these plants. However very often, to make up for the scarce availability of biomass, they are imported from abroad, eliminating the benefits of local biomass production, resulting in irritation of the populations living around the gasification plant itself, i.e. gasification plants should be small in order to be powered with the biomass found around them. In order to limit both investment and operating costs, it is required that the small-sized plants are necessarily simple, i.e. consisting of few equipment and low operating costs.

In order to have few equipment, it is necessary to intensify the process as much as possible by performing the reduction of tar contained into the gas produced by biomass gasification, inside the gasification reactor itself.

All the works reported in the literature consider different catalysts such as Ni/alumina, dolomite, Ni/monolith, Ni-Perovskites, etc., many of which containing active Ni, positioned in fixed bed reactors outside the gasifier. Since the steam reforming process of tar is an endothermic process, it is necessary to bring heat to the reforming reactor via an external heat source, in order to avoid a lowering of temperature with consequent carbon formation on the catalyst. In order to assure a catalyst temperature > 800 °C the wall temperature of the tubes should be in the range 900 °C -1050 °C and the exit temperature of the firing gas about 950-1000 °C. These reformers are expensive and rather complex to operate, unskilful operation may lead to tubes plugging and breaking.

To overcome these operating problems, filter candle filled with catalyst pellets, placed in the freeboard of the gasifier, can be utilised. This technological solution allows the complete elimination of dust and to drastically lowering the tar content in the producer gas, using a single reactor (Rapagnà et al., 2009).

3. Experimental apparatus

Figure 1, shows the scheme of the bench scale gasification plant, extensively described elsewhere (Rapagnà et al., 2010), that was used to test ceramic filter filled with catalyst powders obtained by impregnation of MgO-Al₂O₃ support with a nickel nitrate hexahydrate solution to assure a NiO concentration of 47 % by weight, related to the catalyst support amount. Furthermore, the wall of the ceramic filter having a thickness of 10 mm, was first impregnated with a fine wet-milled alcoholic suspension of MgO-Al₂O₃ with a mass ratio of MgO/Al₂O₃ of 70/30, and in a second impregnation step with nickel nitrate hexahydrate to assure a NiO loading of 70% related to catalyst support (Rapagnà et al., 2012). By carrying out biomass gasification test with this catalytic candle placed in the freeboard of the fluidised bed made up of olivine particles, at temperature of 809 °C and gas filtration rate of 84 m/h, the concentration of tar in the producer gas at the exit of the fluidised bed gasifier was about 150 mg/Nm³. This tar concentration value is lower or in any case comparable to the concentration of the tar obtainable by using a tar absorption plant downstream the gasifier, like the OLGA process. However, it is impossible to use a laboratory-made catalyst on an industrial scale.

After having demonstrated the technical feasibility of being able to reduce drastically the tar in the producer gas by using a single reactor, to render this process feasible on an industrial scale, it is necessary to use filters and catalysts already available on the market, to verify their effectiveness to reduce tar.

A commercial non-catalytic ceramic candle and a commercial catalyst used for the steam reforming of naphtha, were chosen. The commercial catalyst pellets with 3 mm diameter and height were placed in the ring formed by the internal of the ceramic candle, having diameter of 40 mm and the outside of a porous tube positioned in the center of the candle itself having an external diameter of 21 mm (see Figure 1).

Since it is common in industrial gasification plants to add compounds containing Ca into the fluidized bed, we carried out the tests with a bed inventory composed of 2800 g of olivine and 700 g of dolomite.

The biomass consists of almond shell having an average particle size of 1090 µm. To facilitate the biomass particles to flow down into the probe well inside the hot fluidized bed, a small nitrogen flow is utilised.

The gas stream coming from the gasifier goes through two couples of condensers: the former is made of stainless steel and cooled with tap water; the latter is made of glass and cooled with diethylene glycol solution as refrigerant. The produced gas feeds online gas analyzers (IR and TCD) for the detection H₂, CO, CO₂, CH₄ and NH₃.

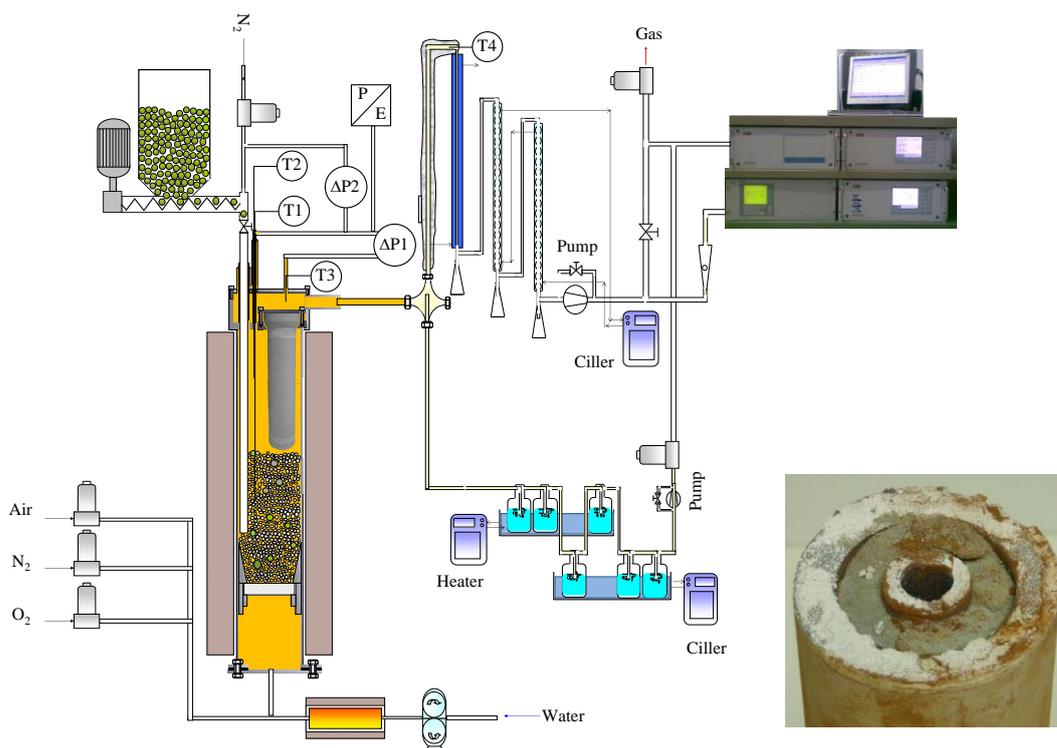


Figure 1. Scheme of continuous biomass gasification plant and picture of ceramic catalytic candle containing catalyst powder.

All the instruments utilised to measure the producer gas composition as well as the thermocouples and the flowmeters used to measure and regulate the gaseous flows entering and leaving the plant are connected to a PC for data storage.

The concentration of tar in the producer gas is determined according to the technical specification CEN/TS 15439, by bubbling the gas leaving the gasifier equal to a flow of 1 l/min of dry gas, inside ampoules containing isopropyl alcohol for a period of 30 minutes. HPLC instrument is then utilised for the qualitative and quantitative determination of the organic compounds present in the alcoholic solution.

At the end of each gasification step, the char inside the reactor is burnt-out with a mixture of air and nitrogen with the foresight not to increase the bed temperature above the value reached during the gasification test. From the data of the volumetric fractions of CO and CO₂ and the exhaust gas flowrates it is possible to calculate the char yields.

4. Results and discussion

The operating conditions of the tests, the amount of catalyst placed into the ceramic candle as well as the results, are summarised in Table 1.

For the three tests, the biomass has been always almond shell particles. Three thermocouples placed into the hot fluidized bed, in the freeboard of the reactor at half the length of the candle, and at the outlet of the candle, were utilised to measure the temperatures. The gasification temperature is the average between the temperature at the outlet of the candle and the average obtained between the temperature into the bed and the temperature in the freeboard.

The first test, carried out with only the filter candle without catalyst, at an average gasification temperature of 814 °C works as a blank test.

The second and the third gasification tests, performed with a ceramic candle containing 462 g of catalyst pellets placed in the same space filled by the powder catalyst shown in Figure 1, were been carried out at gasification temperatures of 796 °C and 831 °C.

The tar concentration in the cold and dry producer gas for the blank test is 6639 mg, similar of these reported in the literature for fluidized bed gasifiers at the same temperature level.

The other two tests, carried out with the same quantity of catalyst but at different gasification temperature levels, produce a gas with tar concentrations of 854 mg and 448 mg for the second and third tests respectively. In the gasification of biomasses, the quantity of tar decreases as the temperature increases. Since the gasification temperature of the second test is lower than that of the blank test, the tar conversion is certainly higher than that obtained by the following calculation:

$$\text{Tar conversion in \%} = \frac{\text{Tar}_{in} - \text{Tar}_{out}}{\text{Tar}_{in}} \times 100 = \frac{1.37 \frac{\text{Nm}^3}{\text{kg}_{\text{daf}}} \cdot 6639 \frac{\text{mg}}{\text{Nm}^3} - 1.8 \frac{\text{Nm}^3}{\text{kg}_{\text{daf}}} \cdot 854 \frac{\text{mg}}{\text{Nm}^3}}{1.37 \frac{\text{Nm}^3}{\text{kg}_{\text{daf}}} \cdot 6639 \frac{\text{mg}}{\text{Nm}^3}} \cdot 100 = 83\%$$

Same calculation for the third test gives:

$$\text{Tar conversion in \%} = \frac{\text{Tar}_{in} - \text{Tar}_{out}}{\text{Tar}_{in}} \times 100 = \frac{1.37 \frac{\text{Nm}^3}{\text{kg}_{\text{daf}}} \cdot 6639 \frac{\text{mg}}{\text{Nm}^3} - 1.86 \frac{\text{Nm}^3}{\text{kg}_{\text{daf}}} \cdot 448 \frac{\text{mg}}{\text{Nm}^3}}{1.37 \frac{\text{Nm}^3}{\text{kg}_{\text{daf}}} \cdot 6639 \frac{\text{mg}}{\text{Nm}^3}} \cdot 100 = 91\%$$

For the last test, tar conversion will be lower than the value of 91%, because the gasification temperature is higher than that of the blank test.

Table 1: Biomass gasification conditions and results

Test number	I	II	III
Catalyst weight, g	0	462	462
Biomass feed rate, g/min	10.84	10.84	10.,84
Steam flow rate, g/min	5.4	5.4	5.4
Steam/biomass dry	0.54	0.54	0.54
Total gasification time, min	52	68	60
Bed temperature,	810	820	864
Freeboard temperature	848	839	878
Reactor outlet temperature, °C	800	763	792
Condensate, g/min	3.73	2.94	2.53
Water conversion %	31	45	53
Gas yield, Nm ³ /kg _{daf}	1.37	1.8	1.86
Tar content, g/Nm ³	6639	854	448
Char residue g/kg _{daf}	110	88	67
H ₂ (vol.% dry N ₂ free)	47	55	55
CO ₂ (vol.% dry N ₂ free)	21	14.3	12.5
CO (vol.% dry N ₂ free)	24	29.1	31.7
CH ₄ (vol.% dry N ₂ free)	8	1.7	0.9
Ppm of NH ₃ in N ₂ free	1500	40	35
Filtration velocity, m/h	94	102	106
$\frac{\text{in-out}}{\text{in}} \times 100$	2.44	-1.15	0.66

However, both tests have shown that it is possible to lower the concentration of tar in the producer gas to levels similar to those obtained by using adsorption plants such as the OLGA process.

All the benefits deriving from such plant configuration are quite evident in terms of simplicity of operation, no use of organic solvents and increasing energy efficiency of the whole gasification process.

In addition to reducing tar concentration, the catalyst drastically lowers ammonia and methane concentrations in the producer gas, with significant advantages for the subsequent gas treatment phases.

Furthermore, tar concentration will decrease by increasing the amount of catalyst contained into the ceramic candle by increasing the length of the candle or by increasing their number in the gasifier freeboard. These solutions are difficult to make in the laboratory scale. Porous metal candle with the same length and diameter of the ceramic candle, but with more internal volume capable of hosting a quantity of catalyst, even double that contained in the ceramic candle, could be the solution.

5. Conclusions

Commercial ceramic candle filled with commercial catalyst pellets, placed in the freeboard of biomass gasifier is able to transform about 90% of the produced tar in light products, as a result of which high calorific value of the producer gas is attained.

This process configuration is able to produce a gas containing low tar concentration as well as very low concentration of NH_3 and CH_4 , making subsequent gas treatment processes less expensive

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