

Hydrogen Rich Gas from Catalytic Steam Gasification of Biomass in a Fluidized Bed Containing Catalytic Filters

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Biomass gasification trials have been performed by using a fluidized bed made of used and fresh olivine particles, and Catalytic and Non-Catalytic filters of new type, placed in the freeboard of the gasifier. All tests were performed continuously at temperature of 800 °C in presence of steam. The optimum result has been obtained with the simultaneous presence into the gasifier of the used olivine particles and the Catalytic filter. When the Non-Catalytic filter is placed into the gasifier, in presence of used olivine as a bed inventory, the H₂ yield increases steadily during the four hours of gasification time, whereas in presence of Catalytic filter the yield of H₂ reaches the steady state value after only one hour of gasification time. The presence of a layer of char particles on the candle surface has a positive effect on tar, methane and ammonia conversion. The use of Filters inside the gasifier permits to improve the contact between the char particles and the mixture of gas and vapours produced during the biomass devolatilization process, as a result a cleaner gas is obtained, making this technological solution particularly attractive.

1. Introduction

To increase the security of energy supply and to reduce the carbon dioxide emissions as required by climate changes mitigation, the energy systems need to be oriented towards a mix of energy sources, in particular renewables and among these biomass. Biomass is an abundant energy source and it can be considered as the best form of storage of solar energy. Its transformation into energy produces an amount of CO₂ equal to that absorbed by the biomass during its growth with a net contribution to the atmosphere equal to zero. Compared to other renewable sources such as solar or wind, biomass presents less problems with energy storage because, in a sense, biomass itself is stored energy (Saidur et al., 2011).

Moreover, unlike fossil fuels such as coal and natural gas, biomass is a resource with low energy density and it is diluted on the territory, so that the contribution of transport to the final cost of energy produced is crucial. For this reason, it is necessary to use distributed, small to medium scale plants able to be fuelled with biomass, agro-industrial residues and organic wastes, produced locally.

Biomass can be converted in a fuel gas rich in hydrogen by thermo-chemical conversion processes such as the gasification process, that produces also carbon monoxide, with a significant content of methane and carbon dioxide. In the product gas are also present organic (tar – Topping Atmosphere Residuals) and inorganic (NH₃, and alkali metals) impurities, and particulate. Decreasing the amount of tar in the product gas is very important, not only to increase the efficiency of the transformation, but also to avoid gas scrubbing and a wastewater treatment plant which would be difficult to manage because tar is composed of organic molecules classified as vPvB (very persistent and very bio-accumulative (Trifirò, 2010)). Tar can be transformed in CO and H₂ by steam reforming reactions in presence of a suitable catalyst. The synthetic and natural catalysts are called primary when are placed into the gasifier bed (Caballero et al. 2000), secondary if

are placed in a secondary reactor downstream of the gasifier (Rapagnà et al. 2010). Most of the commercial Ni based catalysts have been developed for naphtha and methane reforming, so they are not suitable to be utilized into the gasifier bed, and even if placed in a secondary reactor, they require a hot filter to retain particulate. For this latter case, coke formation at the top and in the middle of the fixed catalytic bed is likely to occur due to the fact that tar and methane reforming reactions require heat; as a consequence, the temperature decreases along the catalytic bed. The supply of the heat at high-temperature complicates the whole process and makes it possible only for large gasification plants.

Moreover, the use of Ni based catalysts reduces the ammonia content allowing its complete elimination from the product gas by washing it with water. The elimination of particulate from the hot gas can be performed by using ceramic or metal filters able to assure separation efficiency of 99.999 %, with particle loadings <0.1 ppm (particle size <100 μm) in the outlet stream (Sharma et al., 2008).

The ceramic catalytic filters, inserted in the freeboard of the biomass gasifier, are able to convert tar to light gases, NH_3 to N_2 , as well as to produce a clean gas free of particulate (Heidenreich et al. 2013). This technical solution is suitable to be used by small biomass gasification plants, because it is necessary only one reactor vessel, reducing significantly the investment and operational costs.

Previous results have been reported considering two prototypes of Silicon Carbide hot gas filter elements: the first being modified by nickel impregnation (Rapagnà et al., 2009), and the latter by integration of a fixed bed of Ni catalyst grains into the hollow cylindrical space (Rapagnà et al., 2010). Silicon carbide filter elements, however, cannot be used under syngas conditions at temperatures of about 850 °C. Therefore, new filters made of an Al_2O_3 based grain-sintered porous material were prepared and tested as reported recently by Rapagna et al. 2012. In order to improve the performance of the biomass gasification process, further prototypes of catalytic candles have been developed by Pall Filter-systems GmbH Werk Schumacher. The results here discussed were achieved by testing two new filter prototypes under real gasification conditions. The product gas and tar compositions were monitored during each run, as well as the pressure drop through the catalyst element in the gasifier freeboard. Tar sampling was taken according to technical specification UNI CEN/TS 15439.

2. Experimental, Materials and Methods

2.1 Bench scale gasification plant

The biomass gasification tests were performed in a continuous bench scale gasification plant composed of a 0.1 m internal diameter bubbling fluidized bed gasifier made in AISI 310, externally heated by a 6 kW electric furnace. The reactor was manufactured so to house in its freeboard one ceramic filter. The biomass was delivered well inside the hot fluidized bed by using a probe connected with a continuous feeder unit able to contain about 10 kg of biomass. The exit of the reactor is connected with three condensers in series: the first, made of stainless steel, is cooled with tap water and the remaining two, made of glass, are cooled with refrigerated diethylene glycol. The flow of the dry and cold gas is measured by using both a mass flow-meter connected with PC and a mechanical gas flow-meter. A small portion of the total gas is sent to the gas analyzers in order to measure the volumetric percentage of H_2 , CO , CO_2 , CH_4 and NH_3 . The experimental data are stored as functions of time in a PC and permit to perform the material balance considering the values of the gas flow measured with the mass flow-meter.

Tar samples were collected in 2-propanol according to the UNI CEN/TS 15439 protocol and properly stored at 4 °C before the analysis by GC/MS - gas chromatograph/mass spectrometer technique.

The temperatures are monitored inside the bubbling bed, at the exit of the filter and in additional parts of the plant. Steam was generated from liquid distilled water fed, by means of a peristaltic pump, to a cylindrical, stainless steel evaporator encased in a 2.4 kW electric furnace.

2.2 Materials

Two bed inventories were utilized consisting of 3 kg of fresh and used olivine particles having an average diameter of 344-350 μm and particle density of 3000 kg m^{-3} . Olivine has been widely studied as a reactive bed-material for this process and the presence of iron can act as a catalyst for the decomposition of the tars produced during the gasification process. The biomass employed consists of ground almond shells, crushed and sieved to obtain a final average particle size of 1.1 mm. This type of biomass was chosen because it flows easily into the tube that connects the biomass feeder to the fluidized bed. Moreover, keeping the same type and size of biomass allows to compare the catalytic activity of filter candles having different characteristics. Two filters were used: a catalytic filter with integrated catalytic foam and a non catalytic filter. In particular, the first one was a catalytically activated Al_2O_3 based filter candle with new improved candle support with an Al_2O_3 outer membrane and with an integrated catalytic ceramic foam. A MgO-NiO catalytic layer system was applied on the catalytic filter candle support, whereas a MgO- Al_2O_3 -NiO based catalytic layer system was applied on the integrated catalytic ceramic foam. The effective filtration length was 0.389 m. The second one was a Al_2O_3

based Non-catalytic hot gas filter candle of new type, used for comparative purposes. Each filter was inserted in the freeboard of the gasifier; hot gas filter gaskets were inserted around the filter heads to prevent that the gas produced during the gasification process would bypass the filters.

2.3 Methods

In order to evaluate the performance of the filters, four tests were performed:

- 1- Catalytic filter in presence of fresh olivine: Test 109;
- 2- Catalytic filter in presence of used olivine: Test 112;
- 3- Non-catalytic filter in presence of used olivine: Test 116;
- 4- Non-catalytic filter in presence of used olivine: Test 117.

Tests 3 and 4 are similar in order to confirm the experimental results. The gasifier is externally heated up to the desired temperature with the olivine bed fluidized by air. Before starting the biomass delivery into the hot fluidized bed, air was replaced by steam and about 10 L/min of N₂ in order to assure the desired filtration velocity and to facilitate biomass particles smooth flow in the feeding pipe, from room temperature to the gasification temperature. During the gasification tests, a small amount of gas at the exit of the gasifier is made to pass through a set of ampoules containing isopropyl alcohol, according to the CENT specification for tar measurements. The flow of the permanent gases at the exit of the ampoules was measured by means of a flow-meter in order to permit the calculation of tar concentration in the dry, N₂ free product gas. This small amount of gas that represents about 8 % of the total gas, was not measured by the mass flow meter and recorded by the PC,, for this reason the total flow of the different gas species is slightly lower during the tar sampling periods. At the end of each gasification test, the quantity of char at the end of the whole gasification process was determined measuring the concentration of CO₂ and CO in the exit gas, obtained by burning under air stream the whole carbonaceous residue trapped into the gasifier.

3. Results and Discussion

The main biomass gasification conditions as well as the results obtained in the four tests are summarized in Table1.

Table 1. Biomass gasification conditions and results

Test number	109	112	116	117
Bed temperature, °C	800	814	800	801
Biomass feed rate, g/min	10	10	10	10
Steam flow rate, g/min	7.73	9.57	9.15	9.36
Steam/biomass dry	0.92	1.12	1.08	1.1
Total gasification time, min	240	300	240	176
Results				
Reactor outlet temperature, °C	777	807	774	757
Water conversion %	37.7	41	25	24.5
Gas yield, Nm ³ /kg _{daf}	1.58	1.84	1.42	1.37
Tar content g/Nm ³	1.31	0.14	----	7.92
Char residue g/kg _{daf}	----	23.55	70.81	69.78
H ₂ (vol.% dry N ₂ free)	51	55.5	50	49
CO ₂ (vol.% dry N ₂ free)	22	20	24	24
CO (vol.% dry N ₂ free)	22	21.5	19	19.5
CH ₄ (vol.% dry N ₂ free)	5	3	7	7.5
Filtration velocity, m/h	----	114	----	110

As expected the results show that the Catalytic filter perform much better than the Non-catalytic one, and used olivine plays a positive role to improve the production of permanent gases and to reduce the tar content in the product gas.

These results have to be related to the fact that during the biomass gasification process a calcium-rich layer is formed on olivine particles. This Calcium-rich layer increases tar conversion and enhances hydrogen production. As reported by Lancee et al. (2013), this layer builds up in time and contributes to enhance the water gas shift (WGS) and gasification reactions. Deposition of calcium oxide on olivine can be catalyzed by Fe, which is present at the particle's surface (Kimbauer, et al. 2012). To better evaluate the effect of the used

olivine to increase the permanent gases, in Figure 1 we report the yield of different gas species produced during the gasification process as a function of time.

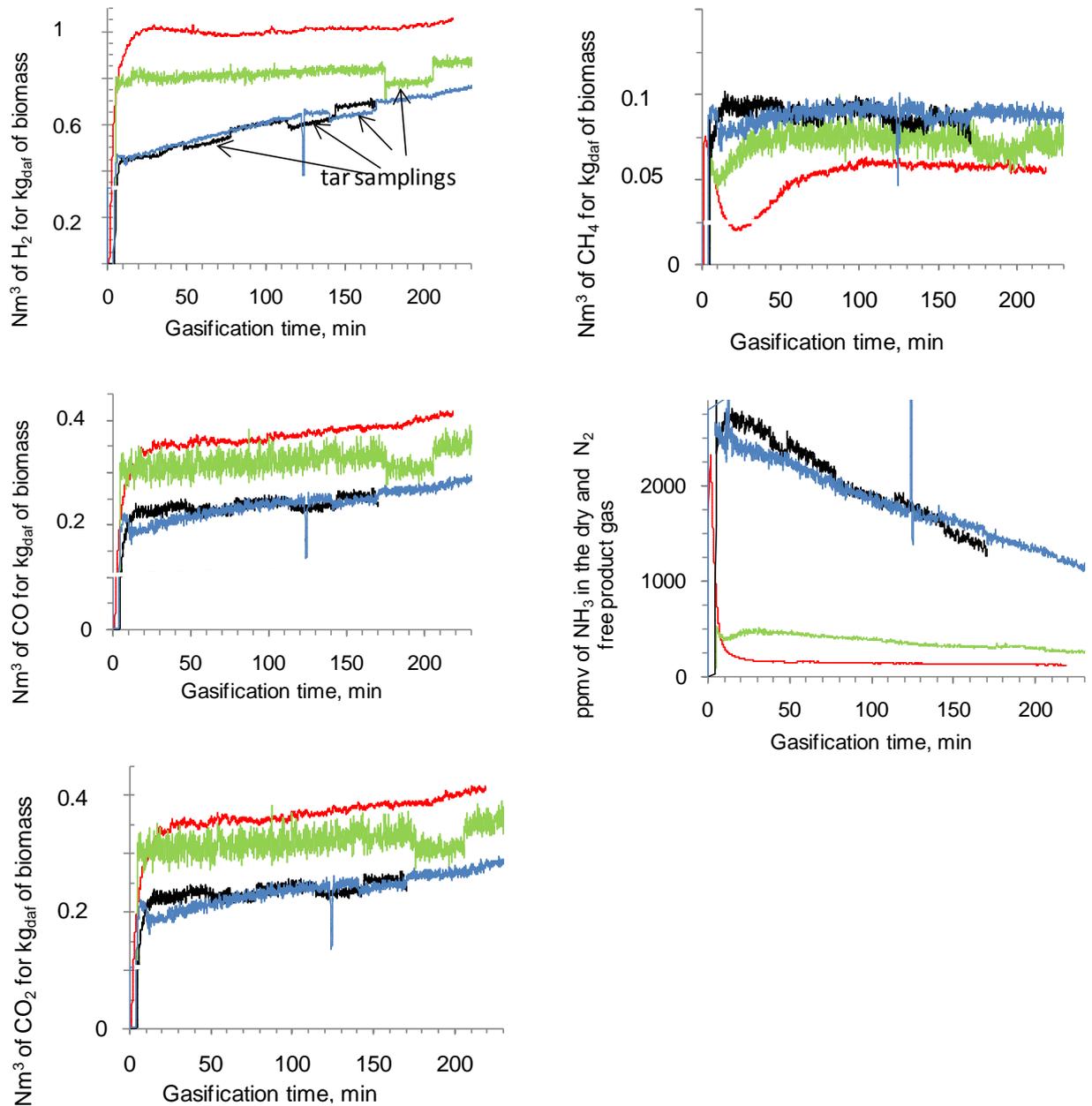


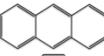
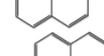
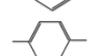
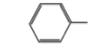
Figure 1. gas yields as a function of the gasification time for the four tests: 109 (green), 112 (red), 116 (black) and 117 (blue)

In presence of the Catalytic filter in the freeboard of the gasifier, the H_2 yield per kg_{daf} biomass in the case of used olivine is 20 % greater compared to the case of fresh olivine. The presence of the Calcium layer on the olivine particles catalyses the steam gasification of the carbonaceous materials present into the bed, as a result of which more CO and CO_2 are obtained. Except at the beginning of the gasification process, when the amount of CH_4 is very low, the final CH_4 production is slightly less than that produced when fresh olivine particles are used, and this difference can not be due to the presence of the Calcium on the surface of the olivine particles. In fact the CH_4 yield is similar to the case of Non-catalytic filter utilized in presence

of used olivine particles and Calcium can not catalyze the steam reforming of CH_4 and can not destroy NH_3 as it is also shown in Figure 1. Char obtained from the devolatilization step progressively accumulates into the gasifier and reacts mainly with steam to produce CO and H_2 . For this reason it is expected that the amount of H_2 should increase with time. It has been also demonstrated that char is able to catalyze the conversion of hydrocarbons such as tar and methane. As reported by Abu El-Rub et al. (2004), the catalytic activity of char depends on the pore size, the surface area and ash or mineral content. The first two characteristics are dependent on char production conditions, such as fuel particles heating rate and pyrolysis temperature. The last factor depends mainly on the char precursors. The use of ceramic filters in the freeboard of biomass gasifiers allows to improve contact between char particles and the product gas, maximizing the hydrocarbon catalytic reforming reactions.

It is quite interesting to note that for tests performed with the catalytic filters, the yield of H_2 is definitely higher and remains quite constant with time, in contrast with the behavior just noticed with a Non-catalytic filter. When catalytic filters are utilized, the prevailing mechanism for tar reforming and hydrogen production has to be ascribed to reactions inside the ceramic candle more than to those promoted by the build up of a char cake at its surface. The yield of tar compounds obtained for three different tests are reported in Table 2.

Table 2. Yield of tar compounds for tests 109, 112 and 117, referred to biomass feedstock

Tar compound	Molecular structure	g/kg _{daf} of biomass		
		109	112	117
1 Acenaphthylene		0.0158	0.00736	0.323
2 Fluorene		0.00948	0.00368	0
3 Phenanthrene		0.0363	0.0110	0.1206
4 Anthracene		0.00632	0.0110	0.1206
5 Pyrene		0.00474	0	0
6 Phenol		0	0	0
7 Naphthalene		0.736	0.0681	4.75
8 Styrene		0.0711	0	0.893
9. Xylene		0.0632	0	0.374
10. Toluene		1.13	0.160	4.27
Total tar		2.07	0.261	10.8

The continuous increase of H_2 content in the product gases when Non-Catalytic Filters are inserted into the gasifier is probably due to the catalytic reforming of tar performed by the char particles deposited on the filter surface and by char gasification. The catalytic activity of the char is also able to destroy part of the NH_3 formed during the gasification process, as a result of which its quantity in the product gas decreases with the gasification time. However, the char catalytic activity is not comparable with the catalytic activity of Ni particles present into the Catalytic Filter. The tar yield is forty times lower in presence of the Catalytic Filter, compared with tar yield obtained for the Non-Catalytic filter test. Similar behavior is observed for the NH_3 content in the product gases. However, the yield of NH_3 when Non-Catalytic Filters are used, steadily decreases with time, suggesting that the char catalytic activity increases with time, due to the increasing amount of char particles deposited on the Filter outer surface. Further work, considering longer biomass gasification tests, in presence of the Non-Catalytic Filter, will provide more accurate information about the yield of NH_3 , H_2 and tar reached at steady state conditions.

4. Conclusions

Catalytic filters inserted in the freeboard of the fluidized bed gasifier are able to convert 98 % of the total tar recorded when they are replaced by Non-Catalytic filters. Used olivine perform much better than fresh olivine as a bed inventory, as a result of which the total tar yield decreases of about 87 %. The H₂ yield increases monotonously with the gasification time even after 4 h when Non-Catalytic filters are used, indicating that the layer of char and olivine dust particles, progressively accumulated at the surface of the filter catalyses the steam reforming of the tar compounds produced during the biomass devolatilization process. It can be concluded, from the results obtained in these tests, that there are three combined effects: the used olivine bed inventory, the char particle layer on the outer surface of the filters and Ni particles into the filters. These three catalytic conversion steps are performed simultaneously in only one vessel, which permits a biomass gasification process easily to operate and economically attractive even in small to medium scale.

Acknowledgment

The research leading to these results was funded with the contribution from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° [299732] 10, in the framework of the project: "UNIfHY – UNIQUE gasifier for hydrogen production".

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