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Biomass Gasification with Dolomite and Olivine Particles as a Bed Inventory in Presence of Ceramic Filters

Sergio Rapagnà*, Giacomo Spinelli

Faculty of Bioscience, Agro-Food and Environmental Technology, University of Teramo, Campus universitario di Coste Sant'agostino, via R. Balzarini 1 64100 Teramo
srapagna@unite.it

Biomass gasification trials were carried out continuously in a bench scale gasification plant where the main component has been a fluidized bed reactor containing in its freeboard alternately, non-catalytic and catalytic ceramic filters already used in other gasification tests. The ceramic filters were delivered by Pall Schumacher. The fluidized bed inventory was composed of olivine particles contains alternately 10 % and 20 % by weight of dolomite particles. The fluidization gases were air and steam mixed with nitrogen to assure a good fluidization quality. The experimental tests have shown the beneficial effect of the presence of basic materials such as dolomite, which catalyses the hydrocarbons cracking reactions produced during the devolatilization/pyrolysis process of the biomass particles. The simultaneous presence of the iron content in the olivine particles and the nickel deposited on the ceramic filter, allowed to reduce the amount of tar in the product gas at a smaller concentration of 57 mg for normal cubic meter of dry and nitrogen free gas.
The results demonstrate the goodness to carry out biomass gasification process in presence of a mixture of olivine and dolomite particles contained in a fluidised bed with a catalytic ceramic filter inserted in the freeboard of the gasifier. This plant configuration that use only one reactor, allows a significant simplification of the whole gasification process.

1. Introduction

The use of biomass as a source of energy offers an opportunity for regional development because they will contribute to the solution of the problem of electric power delivery to large area of less developed regions, where biomass sources are abundant and electrification is poor. In contrast to the centralised power generation system established for fossil energy sources, bio-energy is amenable to local production and output, close to areas of biomass availability. To avoid transportation cost of the biomasses, it is preferable to utilize small transformation plants be fuelled with biomasses produced around them. Biomasses are mainly utilized to produce heat (<0.1 MW), and electrical energy (>10 MW), by means of combustion processes.
Biomasses account for more than 35 % of the primary energy consumption in the development countries. In the near future, most of the World population will live in these countries and biomass will be one of the main renewable energy sources of the future. The use of biomass as a renewable energy source, will contribute to achieve the World target to decrease the emission of CO_2 to the atmosphere.
In the EU-28 the overall CO_2 emission in the year 2013 has been lower of about 24% respect of the year 1990. However for the same years, the CO_2 emissions from the transport and international aviation have been increased of 13 % and 93 %. To decrease the CO_2 emission from the transport sectors, it is necessary to produce synthetic fuels obtained from biomass.
In the early industrial revolution biomass has been an important source of chemical products, by providing dyes, paints, inks, solvents, etc. (Morris 2001).
Today, the best available technology to produce an energy vector rich of hydrogen, to be efficiently transformed in a liquid fuel, is the biomass gasification process.

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The biomass gasification processes are carried out at elevated temperatures, the first step is the pyrolysis or devolatilization of the solid that is the transformation of a compound into other substances, through the action of heat alone. Subsequent upgrading steps involve reactions of the produced gases and char with steam and hydrogen. The final products composition is a function of many variables such as the temperature, the biomass particle size, the biomass composition and the reactor configuration.
Among different type of gasifiers, bubbling and circulating fluidised bed reactors are able to utilize all kind of biomasses having different particle sizes, moisture and composition and for these reasons they are more and more utilized worldwide.
The heat required by the gasification process can be supplied by feeding in the gasifier air or pure oxygen or by using two interconnected fluidised beds in which are performed separately the gasification of biomass and the combustion of char. With this latter configuration, it is possible to use only steam in the gasifier and air in the combustion zone, as a result of which, high calorific value of the producer gases are obtained.
However, for the gases containing nitrogen, able to be fuelled to the Internal Combustion Engine to produce electricity and heat, and even more for the gases free of nitrogen that are suitable to be transformed efficiently in a liquid fuel, it is necessary to eliminate the solid and organic impurities.
For the gas able to produce liquid fuels, the presence of tar and dust may preclude the subsequent steps to improve the CO/H_2 ratio for the Fischer-Tropsch synthesis, such as the water gas shift reaction, and the CO_2 removal by absorption processes.
For all the biomass gasification processes, in presence or in absence of nitrogen in the producer gas, it is preferable to remove powders and tar at a high temperature. This permits to increase the energy efficiency of the overall gasification process, as well as to avoid the production of water polluted by polycyclic aromatic hydrocarbons, that are difficult to remove by normal purification systems, that use activated sludge. Nevertless, by performing the hog gas cleaning, is possible to utilize the steam contained in the producer gas necessary to reform the hydrocarbons and to further produce H_2 by the shift of CO. The elimination of the hydrocarbons at high temperature also entails the elimination of NH_3 present in the gas.
Many catalysts have been tested inside and outside the gasifiers. They are called primary catalysts, when are placed into the bed, and secondary catalysts when are placed in a secondary vessel after the gasifier.
As primary catalysts the most widely used are dolomite and olivine. Calcined dolomite, limestone or magnesite have been found able to reduce drastically the tar content in the producer gas (Delgado et al., 1996) but a large amount of fines are produced. Olivine shows a slightly lower activity in biomass gasification and tar reforming, but higher attrition resistance than dolomite. The olivine activity or more specifically olivine activation depends on its iron oxide content (Rauch et al., 2006). To increase the catalytic effect of the iron oxide, Fe/olivine catalyst has been prepared and tested (Rapagnà et al., 2011), in bubbling and dual fluidized beds. The results showing a considerably tar reduction compared with the bed of only olivine, as a result of which, the inexpensive and non-toxic Fe/olivine catalyst is a material suitable for use as primary catalyst in a fluidized bed gasification of biomass (Virginie et al., 2012). When the bed inventory is composed of olivine particles, the catalytic activity increases with the gasification time due to the formation of a layer of CaO on the bed particle surfaces. Compared to fresh olivine, a CaO-coated olivine bed material it is able to decrease tar content in the product gas by 82 % (Kirnbauer et al., 2012).
Even Ni -based reforming catalysts utilized inside the fluidized bed, have shown high activity and selectivity for tar conversion to hydrogen rich gas, the intense abrasion and attrition typical of the fluidized and circulating beds, leads to the formation of fine containing Ni. These fines mixed with the ashes, make these dangerous for the environment, and expensive to dispose of.
It has been also observed that the catalytic activity of the bed material to reduce tar, increases with the gasification time, only when olivine particles are used. For all the other materials utilised as a bed inventory their catalytic activities are severely restricted by the abrasion and attrition effects typical of the bubbling and circulating fluidized bed gasifiers.
For this reason, secondary catalysts have been placed after the gasifier, in one or two vessels.
Ni/Al_2O_3 (Aznar et al., 1993), dolomite (Corella et al., 1996), Ni/monolith (Simell et al., 1996), Ni-perovskites catalyst (Rapagnà et al., 2002), have been used as secondary catalyst placed into a secondary vessels. As far as secondary gas treatments are concerned, the use of monolith modules placed at the gasifier outlet, seems quite satisfactory, however the major drawback for their use on a commercial scale is their rapid deactivation (Toledo et al, 2006). To avoid catalyst deactivation by H_2S and carbon deposition, high temperature level is required (900 - 920 °C) throughout the system by re-heating of the gaseous stream at the expense of its chemical energy (Simell et al., 1996).
From the economic point of view, the use of gasifier downstream units, will significantly impact on the costs, contributing to the overall investment, especially in small-biomass gasification plants.

In order to simplify the whole biomass gasification process and make it feasible even in small plants, and at the same time make it as efficient as possible, it has been proposed, to utilize catalytic filter candles inserted in the freeboard of the gasifiers (Heidenreich et al., 2008).

The filters eliminate all the solids transported by the gases, and the char fine particles that adhere on the surface of the filters, catalyse the tar reduction that are further reduced by the catalyst contained into the filters (Rapagnà et al. 2009). The hot gas that leaves the gasifier is free of solid particles and contains low amount of high organic compounds (Rapagnà et al., 2014).

To decrease the amount of tar that reaches the ceramic filters, dolomite and olivine particles have been utilised as bed inventory. The catalytic and non-catalytic filters utilised in this work, have been developed by Pall Filtersystems GmbH Werk Schumacher, their technical features have been extensively described elsewhere (Nacken et al., 2015).

With this arrangement, the dolomite particles will act both as primary catalyst, because are part of the bed inventory, and as a “freeboard catalyst”, because their fines are present on the surface of the ceramic filters.

2. Experimental

A bubbling fluidised bed reactor with an inner diameter of 0.1 m has been utilised to perform continuous biomass gasification tests. In order to evaluate the catalytic influence of the different bed materials, it has been utilised always the almond shells particles having the same mean particle size of 1.1 mm. Original almond shells were ground in a mill and sieved in order to obtain a biomass mean particle diameter of 1.1 mm. As described elsewhere the biomass particles are delivered well inside the hot fluidized bed by a tube connected with a biomass feeder (Rapagnà et al., 2015). Using a bed inventory composed of olivine and dolomite particles has performed experimental tests. In the freeboard of the gasifier, filters were inserted alternatively: ceramic catalytic filter and non-catalytic ceramic filter, delivered by the Pall Schumacher, that were used to perform experimental trials reported in a previous papers (D’Orazio et al., 2015).

Table 1 shows the experimental conditions used for the biomass gasification tests conducted in continuous in order to assess the effect of dolomite particles mixed with olivine particles as a bed inventory. For both the ceramic filters, the gasification trials have been performed in presence of air and in presence of steam with two different amount of dolomite in the bed inventory. The air was supplied by the compressor, meanwhile nitrogen from a cylinder. The two gases, were mixed together before entering into the mass flow meter that was set at 16 l/min. The volumetric ratio between the two gases it was controlled by varying the output pressure from the nitrogen cylinder to stabilize the bed temperature at the requested value of the gasification test.

However, the air pressure at the inlet of the mass flow meter is not constant with time. The volumetric capacity of the compressor tank is not high so that the pressure with which the air comes out from it is greater during the compression phase. For this reason the ratio air/N_2 it is not constant during the biomass processes and influences the gas composition of the producer gas.

The tar content in the gas that leave the reactor has been determined according to technical specification UNI CEN/TS 15439. HPLC/UV method has been utilized to characterize the tars present in the samples.

The producer gas was cooled to ambient temperature, by using heat exchangers, and a flow rate of 1 l/min were analyzed to determine the volumetric composition of H_2, CO, CO_2, CH_4 and NH_3. At the end of each gasification test, air was send to the gasifier to burnt-off the char accumulated inside the gasifier, and by recording the amount of CO and CO_2 evolved during the combustion phase, char yield is calculated.

Table 1: Experimental condition for the biomass gasification tests

Test number	128	129	130	131	133	134	136	137
Symbol	▲	■	●	◆	□	△	○	◇
Catalytic Ceramic Filter	Yes	Yes	Yes	Yes				
Non-Catalytic Ceramic Filter					Yes	Yes	Yes	Yes
Dolomite particles in the bed, g	312	312	701	701	312	312	701	701
Olivine particles in the bed, g	2,805	2,805	2,805	2,805	2,805	2,805	2,805	2,805
Air flow rate at ambient conditions, L/min	----	5.4	----	5.4	5.4	----	----	5.4
Nitrogen flow rate at ambient conditions, L/min	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6
Steam feed rate, g/min	8.58	----	8.32	-----	-----	8.38	8.42	----
Biomass feed rate, g/min	11.62	11.62	11.62	11.62	11.62	11.62	11.62	11.62

3. Results and discussion

The purpose of these tests was to quantify the catalytic activity of dolomite particles, by varying their amount in the bed. The results are very interesting considering that they have been obtained by using a single reactor that operates at temperature slightly above 800 °C, and at atmospheric pressure.

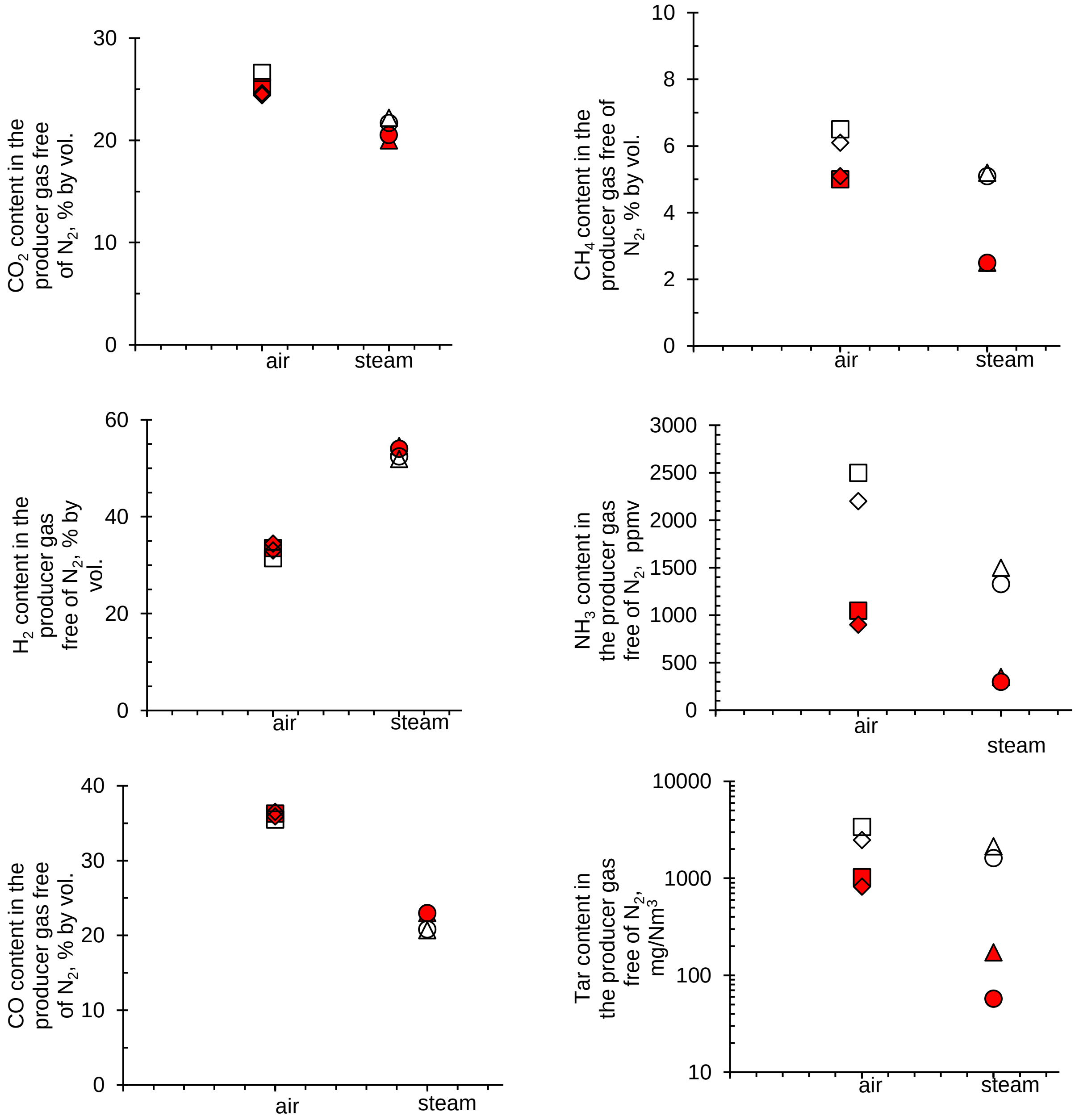

Figure 1: Volumetric percentage of H_2, CO, CO_2 and CH_4 in dry and free nitrogen producer gases, as well as the tar and NH_3 contents. The symbols indicate the test numbers described in Table 1

For all the tests carried out, the temperatures of the fluidized bed during the gasification tests ranged between 820 °C and 816 °C. Different have been the temperatures measured at the output of the gasifier. For the tests carried out with the catalytic ceramic candle, the outlet temperatures from the reactor varied between 800°C and 825 °C when steam is used, while with air were 730 ° C.

With the non-catalytic ceramic candle, in presence of steam the outlet temperatures ranged between 775 °C and 763 °C, while with air were about 60 °C lower.

When catalytic candle is used, the temperature inside the gasifier tends to drop down, due to the steam reforming reactions, as a results of which the oven tends to give more thermal power to the reactor, which increases the gas output temperatures. In presence of air, the oven temperatures are fixed at 5 ° C lower than the fluidized bed temperatures. These lower temperatures of the oven influence the temperatures of the exit gases which are lower than those of the bed. Same behavior can be applies to the non-catalytic candle. In this latter case, the steam reforming reactions inside the gasifier are less extended than the previous case, and then less heat is required from the oven that influences the gas output temperatures, that are smaller than in the case of catalytic candle are considered.

The main results of these tests is that the presence of dolomite particles inside the fluidized bed improve considerably the quality of the producer gases in term of tar and ammonia contents.

Previous tests performed with the same ceramic filters in presence of only olivine particles as a bed inventory, and air and steam as gasification gases, showed that the tar content in the producer gas is greater than in the case of only steam is used (Rapagnà et al., 2015).

The results of this work confirmed this observation, but the amount of tar in the producer gases, are considerably less than that measured in the previous tests, due to the catalytic effect of the dolomite particles present inside the bed.

For the non-catalytic filter, the tests carried out in presence of air, with two different amount of dolomite particles into the bed (tests 133 and 137) showed a tar content, in the dry and nitrogen free gases of 3,381 mg/Nm^3 and 2,480 mg/Nm^3. When steam is used for the tests performed with both beds, the tar contents in the producer gases are 2,131 mg/Nm^3 and 1,609 mg/m^3. These data clearly shown the positive effect of the dolomite particles to decrease the tar. This effect doesn't change with time, because the fine dolomite particles produced in the fluidized bed for the attrition ad abrasion phenomenon, are carried out to the surface of the filter enhancing their catalytic effects. Comparing these data with the previous one, obtained by performing the biomass gasification in a bed of olivine particles, in steam and air atmosphere (Rapagnà, 2015), the tar reductions in the dry and free nitrogen final gases are 49 % and 63 % in air atmosphere and 68 % and 76 % in steam atmosphere.

As was expected, better results are obtained by utilizing catalytic ceramic filter inserted in the freeboard of the gasifier. In presence of air, the tar contents in the producer gases, by using the two bed inventories with 10 % and 20 % of dolomite, have been 1,026 mg/Nm^3 and 818 mg/Nm^3, meanwhile in a steam atmosphere the tar contents drop down to 172 mg/Nm^3 and 57 mg/Nm^3.

Comparing these last results with the data obtained at the same operating conditions, with the same catalytic ceramic filter and in presence of only steam, but in absence of dolomite, the tar reductions are 40 % and 80 %. These results are due to the effects of contemporary subsequent catalytic steps that progressively reduce the concentration of organic compounds produced by the devolatilization/pyrolysis of the biomass particles feed well inside the hot bed. The bed inventory, make a significant tar reduction through cracking and reforming reactions of the evolved organic vapours before they leave it together with solid fines, such as dolomite and olivine particles, char and ashes.

The layer composed of the elutriated solids deposited on the surface of the ceramic filters, able to further reduce the tar content in the gases, can be considered as a catalytic fixed bed,.

After this second catalytic step, the dust free gases and vapours pass through the catalytic filter with integrated catalytic ceramic foam (Nacken 2015). The presence of Ni inside the filter catalyses the steam reforming of hydrocarbons to produce CO and H_2. From Figure 1, it is possible to observe that the methane content in the producer gas is a function of the steam contents, but its concentration do not depends of the amount of the dolomite particles present into the bed. Same trend is for ammonia. These data, clearly show, that the methane and ammonia compounds, present in the producer gases, are reformed by the nickel contained in the catalytic ceramic filters. As far as the tar is concerned, its concentration in the producer gas, is a function of steam and the amount of dolomite particles present into the bed. We can assure that the tar destruction is due to the combining cracking and reforming reactions catalyzed mainly by the basic materials and the metallic nickel particles.

3. Conclusions

From all the results obtained by using dolomite in the bed mixed with olivine particles, it is possible to asses that the tar is reduced from 50 to 80 % respect the tests performed without dolomite. The producer gases that contain very low amount of tars, are free of tar and suitable to be utilized to further processes necessary to upgrade the gases to produce bio-fuels.

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