CHEMICAL ENGINEERING TRANSACTIONS

VOL. 43, 2015

A publication of AIDIC

The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216

DOI: 10.3303/CET1543067

Air-Steam Biomass Gasification in a Fluidised Bed Reactor in Presence of Ceramic Filters

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Steam and air-steam biomass gasification tests, were performed in a fluidized bed gasifier in absence and in presence of catalytic and non-catalytic ceramic filters, delivered by Pall Filter-systems GmbH Werk Schumacher. Auto thermal conditions were achieved for the air to fuel ratio divided by the air to fuel ratio for the stoichiometric combustion ER equal 19.6 %. The catalytic filter shows is effectiveness to reduce tar, CH_4 and NH_3 in the producer gas, when only steam is utilized. By performing biomass gasification tests in presence of the mixture air-steam, the amount of organic compounds heavier than naphthalene increases considerably and account for more than 20 % of the total tar. These high molecular weight organic compounds are more difficult to be transformed in light gases. For these tests, in presence of non-catalytic and catalytic filters the reduction of tar was 22% and 54%.

1. Introduction

Renewable energy sources can play a major role in the future of world economy due to the necessity to decrease the CO_2 emissions to the atmosphere as well as to decrease the dependence on imported fossil fuels. To reach this goal it is very important to decrease the fossil fuel consumption of the transportation sector that is responsible for the 18 % consumption of primary energy worldwide (Gonzàlez et al. 2008). The fuel consumption for transport will increase in the coming years because it is expected that vehicle ownership will double in the next two decades, with most of the increase occurring in non-OECD countries (International Energy Outlook, 2014), and it is quite unlikely to powered all of these vehicles with batteries.

Among the available renewable energy sources, solar and wind energy sources, are strongly dependent on the weather conditions, as a result of which they are not able to assure the continuity of energy production over time. Power plants fuelled with fossil fuel are then required, in order to produce energy when the solar and wind plants are not able to supply the required energy, as a consequence of which the overall costs of the energy production increase. To reduce this negative behaviour, electrolytic hydrogen can be produced.

Hydrogen can be stored, transported by using pipes and efficiently transformed in electrical energy by using fuel cells (do Sacramento et al., 2013). However, the continuity of energy produced by renewables energy sources can be achieved by using biomass transformation plants.

Nowadays biomasses account for more than 35% of the primary energy consumption in the development countries. Due to the fact that, it is estimated that in the near future, most of the world population will live in these countries, biomasses will be one of the main renewable energy sources of the future. To avoid transportation cost of the biomasses and to utilize agro-industrial residues and organic wastes, produced locally, it is preferable to utilize small transformation plants able to be fuelled with biomasses having different physical properties and moisture contents.

Biomass gasification process produces hydrogen rich gases that can be the building block to produce liquid fuels by means Fischer Tropsch (FT) synthesis, as well as to produce pure hydrogen by separation processes. In this latter case the hydrogen production can be integrated with the electrolytic hydrogen

Please cite this article as: Rapagna S., Spinelli G., 2015, Air –steam biomass gasification in a fluidised bed reactor in presence of ceramic filters, Chemical Engineering Transactions, 43, 397-402 DOI: 10.3303/CET1543067

produced by using solar and wind energy sources. However, biomass itself is the best solar energy accumulator.

The biomass transformation plants produce also heat that can be used in the vicinity of the plants, to decrease the need of biomasses used for heating, which present some problems concerning their traceability and the environmental implications of their use, because of the emission into the atmosphere of fine dust and organic compounds, considering the fact that most of the stoves have low energy efficiency and high emission values. The use of innovative gasification plants that do not emit solids and pollutant compounds in atmosphere, would result in a significant improvement in air quality in the areas where they would be located.

The biomass gasification process can be performed by using fluidised bed reactors, due to their ability to operate continuously, at high temperatures, and to utilize catalysts into the reactor and outside it to drastically reduce tar, NH_3 and other pollutants in the producer gas.

The fluidising agent could be air, steam or pure oxygen. Air, that it is necessary to assure temperature level inside the gasifier above 800 °C, gives the production of a gas with low heating value due to the presence of large amount of nitrogen. Oxygen can be the best solution, but the high operating costs associated with its production, made this gas not suitable to be utilised in small biomass gasification plants (Wang and Chen, 2013). The presence of steam into the gasifier is desirable in order to permit the reforming reaction of organic compounds, produced in the devolatilization process of the biomass particles, and for the gasification of char particles inside the gasifier.

By using a mixture of steam and air it is possible to assure the desirable gasification temperature and to improve significantly the quality and the quantity of the gas without high operating cost. To further increase the yield and quality of the product gas, suitable catalysts have been utilised to transform the hydrocarbons produced during the gasification process in permanent gases.

These catalysts, when are placed into the bed inventory are called primary catalysts, otherwise when they are located in a secondary reactors after the gasifier, are called secondary catalysts.

However, the primary catalysts, due to attrition phenomena are easily lost by elutriation from the gasifier. On the other hand, it is necessary to supply heat at high temperature at the vessel that contains secondary catalysts, due to the endothermic reforming reaction of the hydrocarbons.

Dust and fine char particles should be also removed at high temperature before they reach the secondary catalysts. As pointed out by Sharma et al. 2008, the major obstacle to the commercialization of advanced gasification plants to produce hydrogen is the gas cleaning process at temperature above 600 °C. It has been estimated that by performing gas filtration at temperature of 850 °C instead of 550 °C, the production cost of FT liquid from forest residue is reduced by 5 %, and the overall efficiency increases of same value (Tuomi et al. 2015). Recently, it has been proposed to utilize catalytic and non catalytic ceramic filters, placed in the freeboard of the fluidised bed biomass gasifier, to perform the steam reform of hydrocarbons as well as to eliminate dust (Rapagnà et al., 2014). The effectiveness of catalytic ceramic filters to improve the gas quality has been tested and described elsewhere (Rapagnà et al. 2010).

The results reported in this work, have been obtained by performing biomass gasification trials in a fluidised bed reactor, by using a mixture of air and steam as a fluidising medium, in presence of ceramic filters inserted in the freeboard of the gasifier, delivered by Pall Filter-systems GmbH Werk Schumacher.

2. Materials and method

2.1 Materials

A continuous bench scale fluidised bed biomass gasification plant has been utilized to perform experimental tests at temperature of 750-830 °C. The detailed description of the plant has been reported elsewhere (Rapagnà et al. 2009).

Almond shells from Southern Italy was used for the gasification experiments having a mean particles size of 1.1 mm. The main elementary composition of the raw materials in % by wt was: C, 46.65; H, 5.55; O, 38.74; volatile matter, 72.45 and ash content of 1.16. The Low Heating Value (LHV) of the raw biomass was 18350 kJ/kg (Rapagnà et al. 2000). From these data, the dry ash free biomass, can be represented by the pseudo-fuel having the formula $C_{16}H_{23}O_{10}$. The standard enthalpy of formation of this pseudo-fuel ($\Delta H°_{C16H23O10}$) can be calculated as reported in eq. (1) and eq. (2):

$$C_{16}H_{23}O_{10} + 16.75\ O_2 = 16\ CO_2 + 11.5\ H_2O + 7567\ kJ \qquad (1)$$

$$\Delta H°_{C16H23O10} = 16\cdot \Delta H°_{CO2} + 11.5\cdot \Delta H°_{H2O} - 7567\ kJ = 1515\ kJ/mol \qquad (2)$$

The air sent to the gasifier in the last three tests, was 10.6 L/min at ambient conditions. In the gasification processes it is usually to report the equivalence ratio ER that is defined as the air-to-fuel ratio divided by

the air-to-fuel ratio for the stoichiometric combustion, %. In our case the value of ER was always 19.6%.
The bed inventory was made of olivine particles having diameter of 344-350 μm and particle density of 3000 kg m^{-3}. It is widely accepted that the use of olivine particles improve significantly the production of gas and its activity depends on its iron oxides content (Lancee et al. 2014).
Catalytic and non-catalytic ceramic filters have been inserted in the freeboard of the gasifier. They are similar of those described elsewhere (Nacken et al. 2012). The non-catalytic filter was made of a grain-sintered Al_2O_3 with a pore volume of 45 %. The catalytic filter was obtained by applying a MgO-NiO catalytic layer to the non catalytic filter and inserting into the hollow-cylindrical space of 40 mm in diameter a MgO-Al_2O_3-NiO based catalytic layer system.
The gas produced during the biomass gasification process was forced to pass through the ceramic filter by means a clamping system able to compensate the different thermal expansions of the stainless steel and the ceramic materials. On-line gas analysers coupled with PC were utilised to determine the dry gas composition such as H_2, CO_2, CO, CH_4 and NH_3. The total flow rate of the dry gas was always measured at room temperature, by using a mass flow meter connected with PC. The tar content in the produced gas was determined according with UNI CEN/TS 15439 protocol and properly stored at 4 °C, before to perform HPLC quantitative analysis carried out by external calibration using at least six levels of PAHs concentration, to cover the range measured in the various samples. Each point of the calibration curves was repeated at least three times. Standards and tar solutions were analyzed by HPLC (Hitachi "Elite LaChrom" L-2130). The injection volume was 20 μL. The detection was carried out at 254 nm (Hitachi UV-detector L2400). The column used to separate tar molecules was a C18, 150 x 4.6mm (Alltech "Apollo C18 5 μm"). A gradient elution was applied using methanol/water at a flow rate of 1 ml min^{-1} (Rapagnà et al. 2012).

2.2 Methods

Biomass gasification tests were performed in order to achieve auto thermal conditions in the gasifier. To evaluate the effect of ceramic filters inserted into the freeboard of the gasifier, the following tests were conducted:

Catalytic filter in presence of steam and N_2: Test 120;
Catalytic filter in presence of steam and air: Test 124;
Non-catalytic filter in presence of steam and air: Test 125;
Blank test without filter in presence of steam and air: Test 126.

In all the tests, before to deliver the biomass to the gasifier, the bed inventory of olivine particles was heated up externally with a cylindrical furnace, in presence of air. For test 120, when the bed temperature was 840 °C, air was replaced by steam and 10.6 L/min of N_2 in order to assure the desired filtration velocity. After 10 minutes from the start of the biomass gasification process, the bed temperature has stabilized at 830 °C, meanwhile the reactor exit temperature, from the starting value of 790 °C increases slowly during the gasification time reaching a stable value of 804 °C, after 2 h.
For the last three tests, biomass gasification runs started when the bed temperatures were in the range of 740-785 °C at which the correspondent reactor exit temperatures were in the range of 640-740 °C.
These two temperatures reached in less than 1 h constant values that are reported in Table1. In the biomass gasification test 120, the furnace temperature set point was 120 °C higher than those set for the last three tests.
A continuous dry gas flow of 3 L/min was sent to the gas analyzers, to measure the gas composition, during the biomass gasification time, as well as during the subsequent combustion of char, which were performed at the end of the gasification runs, by sending only air into the hot gasifier.

3. Results and Discussion

In Table 1 are summarized the operating conditions at which the four tests were performed, as well as the gas yields and compositions, the char yields and the total and single material balances for the elements C, H e O.
By performing the mass balance for carbon and hydrogen, considering all the currents entering and leaving the reactor, for the first tests, the variation is between +10 and +15 %, meanwhile for the three tests performed with air, the balances vary from +5 to + 10%. The oxygen balances is +5 % for the first test and about -4.5 for the last three tests. However, considering the overall balance of all the elements that enter and leave the reactor, with the exception of nitrogen and ash which remains inside the gasifier, even for the first test there is

an acceptable variation of 8 %, for the tests performed with air and steam the material balances are quite perfect.

In presence of air and steam the overall biomass gasification reaction can be written as shown in eq. (3):

$$C_{16}H_{23}O_{10} + aO2 + cH2O = dCO_2 + eH_2O + fCH4 + gH2 + hC10H8 + iChar \qquad (3)$$

Naphthalene has been considered as the representative compound of the tar. For the four gasification tests, the stoichiometric coefficients of the above reaction are deductible from Table 1, and permits to calculate the heat of reaction at temperature of 25 °C and atmospheric pressure per kg of raw biomass, indicated as $\Delta H°_R$.

Table : Gasification mass balance

Test number	120	124	125	126
Operating conditions				
Bed temperature, °C	830	820	825	820
Biomass feed rate, g/min	6.8	11.62	11.62	11.62
Steam flow rate, g/min	6.7	8.02	8.39	8.45
Steam/biomass dry	1.15	0.83	0.86	0.87
N_2 flow rate, L/min	10.6	-	-	-
Air flow rate, L/min	-	10.6	10.6	10.6
Total gasification time, min	240	244	163	90
Results				
Reactor outlet temperature, °C	804	710	730	720
Water conversion %	40	21.14	15.78	20.17
Gas yield, Nm^3/kg_{daf}	1.74	1.51	1.41	1.37
Tar content g/Nm^3	0.283	3.95	6.67	8.6
Char residue g/kg_{daf}	38.2	2.31	1.91	3.17
H_2 (vol.% dry N_2 free)	57.5	42	40	39
CO_2 (vol.% dry N_2 free)	20	34.5	36	35
CO (vol.% dry N_2 free)	21	18	18	20
CH_4 (vol.% dry N_2 free)	1.5	5.5	6	6
NH_3 (ppmv dry N_2 free)	200	1,050	2,000	2,000
Filtration velocity, m/h	85.7	102	112.4	--
$\Delta H°_R$, kJ/kg raw biomass	2,390	-3,740	-3,930	-3,740
ΔH_R, kJ/kg raw biomass	5,850	-802	-383	-826
Mass balance				
g In per kg of raw biomass fed to the gasifier				
C	466.5	466.5	466.5	466.5
H	172.6	141.0	144.5	145.1
O	1,324.4	1,326.1	1,354.4	1,359.0
g Out per kg of raw biomass fed to the gasifier				
C	395.2	433.6	421.6	419.8
H	155.7	132.7	135.0	134.4
O	1251.2	1,392	1,423.5	1,416.7
$\frac{C_{in} - C_{out}}{C_{in}} \times 100$	15.3	7.0	9.6	10
$\frac{H_{in} - H_{out}}{H_{in}} \times 100$	9.8	5.9	6.6	7.4
$\frac{O_{in} - O_{out}}{O_{in}} \times 100$	5.5	-5.0	-5.1	-4.2
$\frac{C_{in} + H_{in} + O_{in} - C_{out} - H_{out} - O_{out}}{C_{in} + H_{in} + O_{out}}$	8.2	-1.3	-0.7	0

To check if the amount of air is sufficient to assure auto thermal condition in the reactor, the heat of reaction ΔH_R per kg of raw biomass was also calculated at bed temperature, considering that the steam and the air temperatures inlet in the gasifier are 500 °C and 20 °C. The constants to calculate the isobaric heat capacity, as well as the standard enthalpy of formation for the ideal gases at 25 °C, have been taken from Reid et al. (1988).

For the gasification tests performed with air, the values of ΔH_R per kg of raw biomass, are in the range of 10-20 % of the heat of reaction at temperature of 25 °C and atmospheric pressure, and represent the heat loss outside the gasifier. From these data, it is possible to assure that with the operation conditions reported in Table 1, by using a well thermal isolated gasifiers, it is not necessary to perform air-biomass gasification tests with ER greater than 0.2. As far as the gas yields and tar concentrations in the producer gases are concerned, in this work the best values have been achieved with test 120, according to previous results obtained at similar conditions with similar catalytic filter (Rapagnà et al. 2014).

The comparison of the results obtained for tests 125 and 126, confirms previously observation (Rapagnà et al. 2014) that the presence of the filter inside the gasifier enhances the gas production and decreases the tar content in the gases, due to the presence on the surface of the candle of char and fine particles of olivine that catalyze the char gasification as well as the steam reforming of hydrocarbons. No effect on ammonia concentration has been observed in presence or absence of non-catalytic filter. The decrease of tar content in the producer gas is about 23 % when non-catalytic filter is inserted in the gasifier, and can’t be due only to the smaller temperature differences between the two tests 125 and 126. Similar results have been reported by Tuomi et al. (2015), that performed gasification of biomass in presence of air (ER=19.9 %) and steam (Steam/biomass daf= 0.21), with sand or dolomite as bed inventory. They recorded, that with the bed made of sand at temperature of 851 °C. The total tar conversion ranging from 38% to 28% during the six hours gasification time. The higher tar conversion compared with our results, can be due to the higher bed temperature as well as the type of tar compounds produced by the different biomasses utilized, such as wood and almond shells.

The measured concentrations of organic compounds greater than benzene are reported in Figure 1.

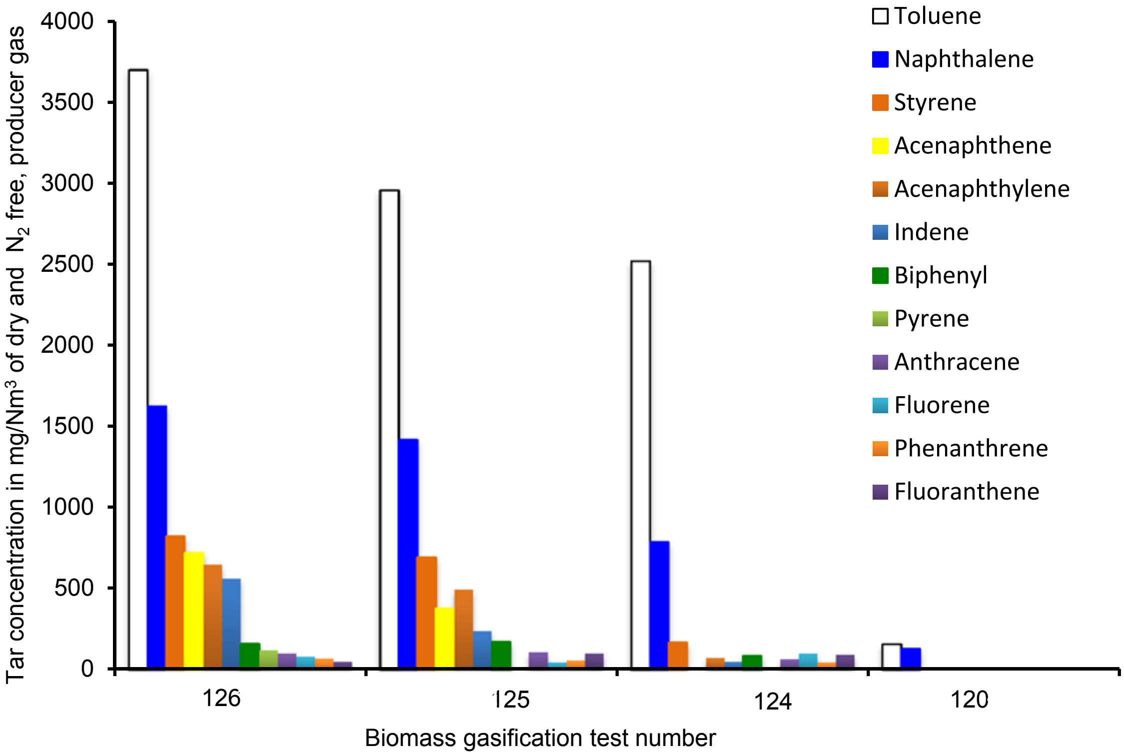

Figure 1: Concentration of organic compounds detected in the producer gases of the four tests.

For the group of light tars that are heavier than benzene up to naphthalene the conversion is 23%, meanwhile for naphthalene and the group that is heavier than it, the conversions are 12.8 % and 29.7 %. The organic compound heavier than naphthalene represents the tar compositions of the last three tests confirm that by performing the gasification of biomasses in presence of air, increases the amount of organic compounds heavier than naphthalene. In a previous work (Rapagnà et al. 2014) we have reported that by performing the biomass gasification test in a steam atmosphere, in presence of a non-catalytic filter (test 117) the sum of the organics heavier than naphthalene represents only 4 % of the total amount of tar. In this work the sum of the similar compounds account for more than 20% for the tests 125 and 126 and more than 11 % for the test 124. These data explain why by using the catalytic filter inside the gasifier the tar concentration in the producer gas is 3.95 g/Nm^3 meanwhile in the atmosphere of only steam the concentration is 0.283 g/Nm^3.

As far as the pressure drop through the filters are concerned, for the non catalytic filter the overall gas pressure drop attains a constant value of 2,400 Pa, after about 1.5 h of gasification. Greater gas pressure drop are measured when catalytic filters are used. For the test 120, performed with only steam, the gas pressure drop is quite constant during the 4 h gasification time ad equal of about 4,500 Pa. Higher gas pressure drop of 5,700 Pa was measured for test 124. This last value is a good indication that the high tar content in the producer gas can’t be due to the gas that by-pass the catalytic filters, but to the nature of the refractory organic compounds produced when air is present into the gasifier.

4. Conclusions

In the air-steam biomass gasification process performed by using bench scale fluidised bed apparatus, auto thermal conditions were achieved with an ER ratio of 19.6 %. The presence of filters inserted in the gasifier enhances the gas production and tar conversion. The organic compounds produced during the air-steam biomass gasification process are heavier than those produced when only steam is used as a gasifying agent. In order to decrease the tar content in the producer gas, further work is in progress with dolomite particles mixed with the bed of olivine particles. The production of dolomite fines, due to attrition phenomena, should increase the effectiveness of the catalytic and non-catalytic filters present into the gasifier.

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