Use of Low-cost Materials for Tar Abatement Process

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In the present work char, olivine and mayenite were used as bed materials to study ability to remove tar produced in biomass thermal processing. The tar gases formed from the pyrolysis reactions of the olive pomace biomass were forced to pass through the bed material. Nitrogen was used as carrier gas. The temperature of the bed was set at 660 °C and no oxidizing agent was added during the tests. The char was produced from the pyrolysis of olive pomace biomass. Olivine was used without any pre-treatment. Mayenite was synthesized in laboratory using $CaCO_3$ and Al_2O_3 as precursors. Among the tested materials, mayenite showed the best tar removal capacity and stability, with a total tar removal of about 60% after 60 min time on stream, while in the case of char and olivine the attained value was 15%. The measured average nitrogen-free gas flow value in the tests carried out with mayenite was 0.84 NL min^{-1}, whereas in the case of char and olivine the obtained average gas flow values were 0.65 and 0.55 NL min^{-1}, respectively. Accordingly, the higher average hydrogen amount was measured in the tests using mayenite as bed material (36%).

1. Introduction

Due to the worldwide concern about the depletion of fossil fuels and environmental problems associated with their use, renewable energy sources are getting increased attention. Among them, biomass have been recognized as one of the most attractive alternatives to fossil fuels, due to their availability all over the world and to their carbon neutral balance when used as fuel. Biomass exploitation as alternative to fossil fuels use in traditional combustion processes is however limited due to its low energy density and to its high water content. Gasification is one of the most promising technologies to upgrade this low quality fuel into a gaseous fuel (de Caprariis et al.,2014). In this process the solid biomass is transformed in high added-value gaseous product, called syngas, which has a higher energy density and is easier to handle and store. The main drawback that limits the spread of this technology is the production of tar along with the syngas. Tar is a complex mixture of condensable hydrocarbons comprising single-ring to 5-ring aromatic compounds plus other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAHs) (De Filippis et al., 2015). The presence of tar can cause operative problems to the gasification plants, such as pipe and filters obstruction and reduction of the heat exchange efficiency due to condensation in the colder downstream section. The minimum allowable limit for tar is highly dependent on the end user application.
Therefore, the most difficult challenge in designing a reactor for biomass gasification consists in minimizing the tar contamination within the syngas. Considerable efforts have been directed on tar removal from fuel gas, with tar reduction strategies consisting of primary measures, which reduce tar within the gasifier itself through optimization of design/operating conditions, and secondary measures, which remove the tar contained in the syngas by filtration, thermal cracking or catalytic reforming.
Thermal cracking and catalytic reforming allow the conversion of tar into lighter species such as CO, H_2 and CH_4 and are considered between the most interesting routes to tackle the problem, with the advantage of recovering the energy contained within the tar (Kosov et al., 2016).
Thermal cracking and catalytic reforming are endothermic processes, which need high temperatures to take place. Nickel supported over Al_2O_3 is the most widespread catalyst for catalytic reforming but it suffers from rapid carbon deposition. It is, therefore, crucial to select alternative materials having high resistance to coke deposition that can be used as first tar abatement step or as support for Ni.

In this work, tar removal is investigated in a fixed bed reactor where tar vapours are forced to pass through a bed filled with three different low-cost materials: olivine, char, and mayenite. Olivine is a non-porous natural silicate mineral containing magnesium and iron, whose tar removal capacity is known to improve upon calcination (Devi et al., 2005). Char is a low-cost material with a medium surface area. It is reported in literature that the source material and method of production of char affect its physical and chemical properties (Abu El-Rub et al., 2008; Volpe et al., 2016) and consequently, its tar abatement capacity. Mayenite is a calcium-aluminate framework of formula $12CaO \cdot 7Al_2O_3$,, in which 32 of the 33 oxygen anions are tightly bound, containing large cages, 1/6 of them being filled randomly by the remaining "free oxygen" (Li et al., 2009). The experimental tests were carried out in pyrolysis conditions in order to work with the maximum feasible tar concentration. The tar abatement efficiency was evaluated for the different materials as well as the gas composition. Deactivation tests were performed in order to evaluate the resistance of the materials to coke deposition.

2. Experimental section

2.1 Experimental set-up

The scheme of the experimental set-up is shown in Figure 1. The reaction system consists of two vertically positioned AISI 310L stainless steel tubes joined together, where, in the upper tube the pyrolysis of the biomass takes place, while the thermal cracking reactions occur in the lower one. Both tubes are 40 mm i.d. and 500 mm length. The tubes are externally heated by means of an electrical heater in order to sustain the endothermic reactions. The lower reactor is equipped with a steel net to support the fixed bed and a thermocouple to measure the temperature of the bed. The bed height was set at 80 mm and kept constant for all the materials tested. In the experimental runs, the fixed bed was heated at 700 °C and the measured internal temperature before the tests was about 660 °C. A layer of quartz wool is placed on top of the fixed bed in order to separate the cracking reactor from the pyrolysis one where the tar production takes place. The biomass was fed to the top of the reactor, by means of a piston feeding system, at time intervals selected in order to assure the continuity of the process. For each tests the total amount of fed biomass was 300 g divided into six runs in which 50 g of biomass were loaded. After each run, the amount of tar and gas produced was evaluated. Six separated runs were required in order to evaluate other than the tar abatement and the deactivation rates of the bed materials. The produced gas passes through a series of water-cooled traps to condense the unreacted tar whichi then analysed by a on-line analyser (Simens Ultramat 23) and an online mass spectrometer (Hiden QGA) to measure the concentration of CO, CH_4, CO_2 and H_2. In all the tests, a nitrogen flow of 0.4 NL/min was fed above the biomass bed. In Table 1 the list of the operative conditions is reported.

Table 1: Operative conditions set in the experimental tests.

Operative conditions	
Bed height (mm)	80
Biomass flow rate (g min^{-1})	0.67
Bed temperature (°C)	660
N_2 flow rate (NL min^{-1})	0.4
Pyrolysis temperature (°C)	700

All the experimental tests under identical conditions were carried out in duplicate to confirm the repeatability of the results. The reported values are averaged values.

2.2 Materials

The biomass used in all the tests was a residue of olive oil production, whose main properties are reported in a previous author work (de Caprariis et al., 2015), where it can be noticed that this kind of biomass has a high quantity of volatiles consisting in condensable species (tar + water) and gaseous compounds.
The olive pomace char, used as bed material was previously produced pyrolyzing previously ground olive pomace in a quartz reactor at 750 °C for 2 h in an inert atmosphere of N_2 (0.3 NL min^{-1})..
Mayenite was prepared grinding in Planetary Ball Mill (Pulverisette-7, Fritsch) for 15 min at a speed of 450 rpm a mixture of $CaCO_3$ and Al_2O_3 in stoichiometric ratio, followed by calcination at 900 °C over 4 h in air. The produced materials was then crushed and sieved to obtain particle sizes between 0.5-2 mm (Li et al., 2009). Olivine (bought from Nuova Cives s.r.l.) was used in the form of particles in the range of 0.1-0.2 mm.
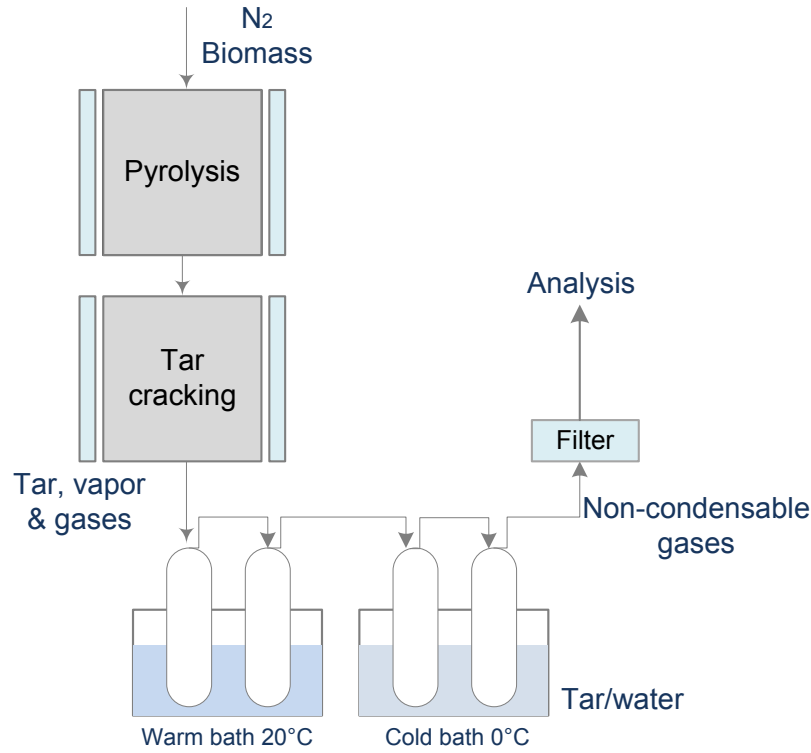
Figure 1: Scheme of the experimental set-up.

3. Results and discussion

3.1 Tar removal capacity of the three different bed materials

In the first set of experiments, the reactor was used as a simple pyrolyzer in order to measure the amount of tar produced from the olive residue biomass. The resulting amount of 16 % wt with respect to the fed biomass represents the tar starting value for the further calculations. After this characterization step, experimental tests with the fixed bed constituted by the three selected materials were performed.

The tar abatement capacity of the bed materials was calculated from Eq(1), Eq(2) and Eq(3). In these calculations, it is necessary to take into consideration the tar removed by the bed of char which is accumulated in the pyrolysis section after each run. The height of this char bed, produced after the pyrolysis of 50 g of biomass was measured to be 29 mm The capacity of the fixed bed was calculated according to:

$$C_i = (X^i_{tar,in} - X^i_{tar,out})/H_{bed} \tag{1}$$

$$X^i_{tar,in} = (X_{tar,0} - \sum_{k=1}^{i-1} X^*_{tar,k}) \tag{2}$$

$$X^*_{tar,k} = C_{char,i-1}H_{char}; \quad C_{char,0} = 0 \tag{3}$$

where C_i is the tar removal capacity in each run i (g cm^{-1}), $X^i_{tar,in}$ and $X^i_{tar,out}$ (g) are the amounts of tar entering and exiting from the cracking bed reactor, respectively, H_{bed} (cm) is the height of the bed and $X_{tar,0}$ is the amount of tar produced from the pyrolysis when no craking process takes place. $X^*_{tar,k}$ is the tar removed by the bed of char produced in each run having a capacity of tar removal of $C_{char,i-1}$ and a height H_{char}. The $C_{char,i-1}$ is calculated from the Eq(1), when char is used in the cracking bed, assuming that for the first run the char produced by the pyrolysis does not have any influence on the tar abatement ($C_{char,0} = 0$). This calculation is based on the hypothesis that the removal capacity of the added char bed in each run i is equal to the removal capacity of the fixed bed in the previous run i -1.

The tar removal capacity for the three tested materials, in terms of grams of tar removed per height of bed, is reported in Figure 2a. Mayenite presents the higher performances in tar removal capacity as a function of time

studied in the tests. It is interesting to note that after 40 min the tar abatement capacity of mayenite is ca. 0.5 g cm^{-1}, a value double with respect to those observed when olivine and char were used. This result could be ascribed to the high "free oxygen" restored property of mayenite, which plays a central role in the carbon resistance and sulphur tolerant properties of this material (Li et al., 2008).

As can be seen from Figure 2a, after 60 min the tar removal capacity of all the three materials reached a plateau, in the case of olivine and char the values are close to zero, while the attained value with mayenite is about 0.3 g cm^{-1}. Both olivine and char present an abrupt decrease in their tar removal capacity after 30 min that is after 100 g of biomass fed. For the char, this phenomenon could be interpreted as the swift saturation of the active sites and fast clogging of its porous structure. In the case of olivine several studies point out that Fe and Fe oxides are the catalytic active phases (Abu El-Rub et al., 2008). Before the reaction Fe is in the form of magnetite Fe_2O_3 and when exposed to a reducing atmosphere, as the one used in the experiments, is transformed into metallic Fe which is recognized as the active phase in the Boudouard and cracking tar decomposition. It was also observed that metallic Fe is the phase that mainly suffers carbon deposition and this behaviour can explain the rapid deactivation of this bed material (Fredriksson et al., 2012).
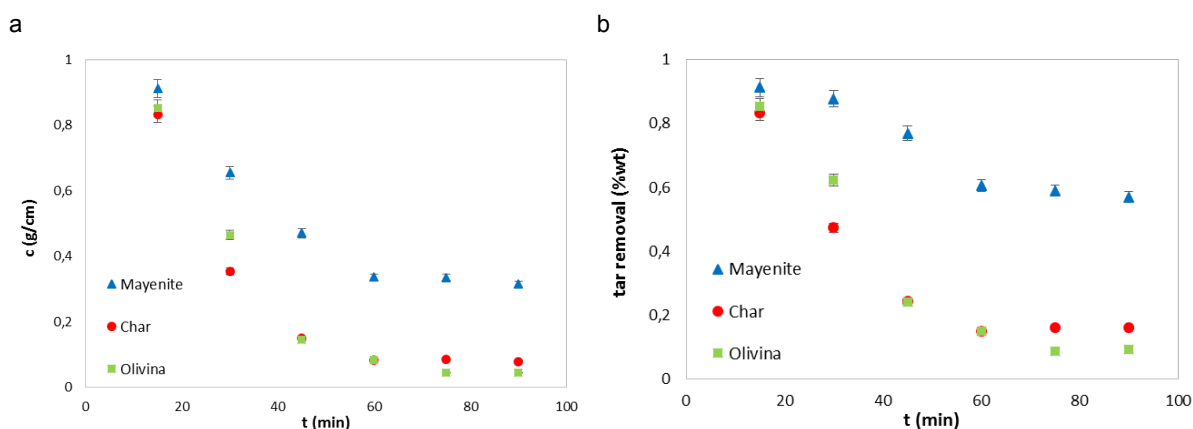
a

b

Figure 2: a-Tar abatement capacity as a function of time; b-Total tar removal (% wt).

In order to have a clearer vision of the performance of the tested bed materials, the total tar removal as a function of time is depicted in Figure 2b. It can be noticed that after 40 min time on stream the total tar removal obtained for mayenite is ≈75 % wt., in sharp contrast with the value obtained using char and olivine (≈24 % wt.). Moreover, after 60 min, the attained tar removal value for mayenite is close to 60 % wt, emphasizing the good tar removal and carbon resistance properties of this calcium-aluminate synthetic material.

The amount of coke deposited on the surface of the used bed material in the tests conducted with olivine and mayenite were obtained gravimetrically after the regeneration of catalysts in a muffle furnace for 4 h at 700 °C. In Table 2 the values of the percentage of the coke deposited on the surface of the materials with respect to the total fed biomass are reported. As expected, the deposited coke on the surface of mayenite is much lower in comparison with the obtained value for olivine.

Table 2: Coke deposited.

	Coke deposited (% wt)
Char	n.d.
Olivine	4.3
Mayenite	1.4

3.2 Deactivation rates of the three materials

The deactivation rates of the bed materials were measured using the data of tar abatement capacity of the first three runs. In Table 3 the deactivation rate obtained bylinear regression of the data shown in Figure 3 for the three materials are reported. Mayenite showed the lower deactivation rate among all the three tested materials, while char and olivine present similar values. The values of the tar removal capacity reported in Figure 3, for olivine and mayenite can be satisfactorily regressed as a straight line, contrarily, in the case of

char, the second calculated value is much lower than expected from a linear trend leading to a coefficient of determination equal to 0.95.
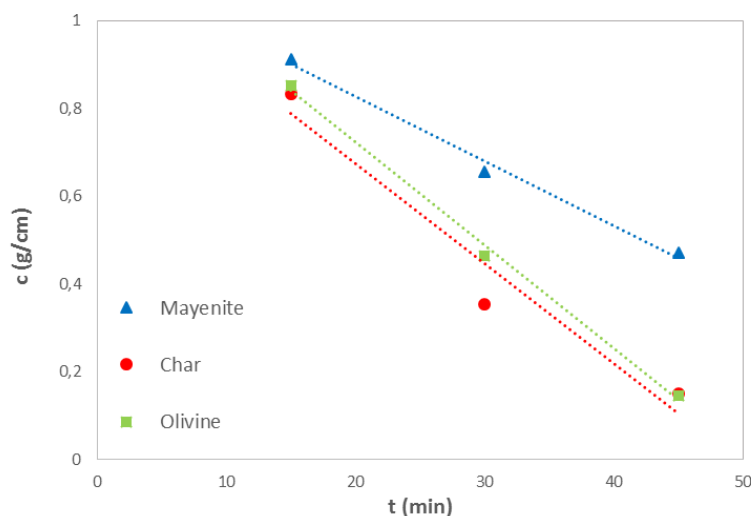

Figure 3: Tar abatement capacity as a function of time and linear regression to evaluate the deactivation rate.

Table 3: Deactivation rate.

	Deactivation (g cm^{-1} min^{-1})	R^2
Char	0.024	0.95
Olivine	0.023	0.99
Mayenite	0.016	0.99

3.3 Gas flow rate and concentration of the main non-condensable gases

The gas flow rate on a dry nitrogen-free basis and the concentration of the main non-condensable gas are reported in Table 4. The reported values represent the average values of the six runs. As expected from the tar removal capacity results, the average gas flow rate measured in the tests realized with mayenite as bed material is greater than those obtained for olivine and char. The slightly higher gas flow rate value obtained when char was used as bed material with respect to olivine could be ascribed to the occurrence of the gasification reactions of the char in the bed, which produce H_2 and CO_2 (Shen Y., 2014). Furthermore, the highest hydrogen and carbon monoxide values were obtained when mayenite was used as bed material, and the H_2/CO ratio obtained for this material was 2.3. It should be noted that the CO_2 concentration in the tests using mayenite reached a value of 22 % vol, the lowest carbon dioxide concentration value among all of the tested materials in the present work. This interesting result could be correlated with the well-known CO_2 sorption property of the CaO-$Ca_{12}Al_{14}O_{33}$ synthetic material (Chengxiong et al., 2016). The sorption of CO_2 by means of the CaO present on the mayenite structure could shift the WGS thermodynamic equilibrium toward H_2 formation for a limited time.

Table 4: Average produced gas flow rate in N_2 free basis and average concentration of the main non-condensable gases

	Gas flow rate (NL min^{-1})	CO (% vol)	CO_2 (% vol)	CH_4 (% vol)	H_2 (% vol)
Char	0.65	12	34	10	28
Olivine	0.55	14	27	9	22
Mayenite	0.84	15	22	11	36

4. Conclusions

The harsh conditions applied in this study could represent a worst-case scenario of a downdraft gasifier where no partial oxidation of the produced tars takes place or of a staged gasifier where the pyrolysis reactions occur separately from the gasification reactions. Thus, the results obtained represent valuable information about the performance of low-cost materials such as char and olivine when exposed to real tar gases. Olivine and char lost very fast their tar removal capacity, which is halved after 30 min time on stream and completely lost it after 60 min. On the other hand, mayenite showed both greater tar removal capacity and slower deactivation rate than the low-cost materials tested. The total tar removal after 60 min time on stream in the case of mayenite was 60%. The higher gas flowrate and hydrogen concentration obtained in the tests with this synthetic material confirmed the good tar cracking/reforming capacity of mayenite. The coke deposited on the surface of mayenite with respect to the total fed biomass presents the lowest value, highlighting the excellent carbon resistance ability of mayenite. The experimental tests showed the promising tar removal capacity of mayenite. Owing to its good performances, even if lower than those obtained with mayenite, the char coud be used for a first step of tar abatement in a gasification plant, with the advantage that it is produced within the plant itself and thus its use does not implicate an extra external cost.

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