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Biomass gasification in a catalytic fluidized reactor with beds of different materials

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ABSTRACT

The paper deals with fluidized bed gasification of a biomass for producing a syngas with optimized hydrogen yield thanks to in-bed catalysis. Four different bed materials have been adopted: inert quartzite as reference case, olivine and dolomite as natural catalysts, and Ni-alumina as artificial catalyst. The gasification tests have been carried out at steady state in a pilot-scale bubbling fluidized bed, under operating conditions typical for gasification as reported in the paper. The gas analyses have been performed with dedicated instrumentation, like continuous analyzers and gas chromatograph, and adopting a standard protocol for tar sampling and characterization. The influence of the catalytic materials on the concentration of stable gases (e.g. H_2, CO_2, CO, CH_4 and light hydrocarbons) as well as on the efficiency of tar conversion has been studied. In particular the artificial catalyst has the largest effectiveness in enhancing the H_2 yield as well as in tar reduction. The catalyst gives rise to an elutriation rate significantly lower than that observed for dolomite at comparable U/U_{mf} ratio, denoting a better mechanical resistance. A stable activity of the nickel–alumina catalyst has been observed for the whole duration of reaction tests suggesting that no deactivation phenomena occurred, due to coke deposition or morphological modifications of the particles.

1. Introduction

The biomass fuels represent an abundantly available, renewable energy resource with CO_2 neutral impact. Among different processes for their utilization, the biomass gasification is one of the best option in order to optimize the conversion of the chemical energy of the fuel [1]. However, the low energetic specific content of the biomass calls for utilization at local area to minimize the fuel transportation over long distance, so small scale processes and compact facilities are appealing [2]. The production of hydrogen-rich syngas is also very attractive for chemicals production or for direct utilization in fuel cells [3], provided that undesired species co-produced during the gasification are limited at very low levels. More specifically, the abatement of the condensable organic compounds, called tars, which can cause a number of malfunctions, is one of the major issues not completely resolved yet.

Catalytic tar decomposition is considered as a technology with the highest potential to contribute to the solution of this problem [4]. In addition, the use of a catalyst can enhance the gas yield and promote the reforming reactions of residual hydrocarbons [5]. Two approaches exist: hot gas cleaning downstream the gasifier (secondary methods) and catalytic conversion inside the reactor (primary methods) [6]. The secondary methods include tar cracking by structured catalysts, as well as mechanical separation using cyclones, filters or scrubbers. Although these methods are proven to be effective, the primary methods are gaining more attention since they are less complex and expensive, with evident advantages at small scale processes. In this framework the adoption of a catalytic fluidized bed is very promising, since it favors a fast heating rate of the biomass fuel and provides a good contact between the biomass and catalyst, both relevant factors for increasing the gas yield and cleanness [7].

For fluidized bed application, the catalyst requirements include not only high chemical activity but also good mechanical properties, availability and low price. Dolomite and olivine are acknowledged as suitable natural bed materials for fluidized bed gasification with appreciable catalytic activity [8]. Nevertheless, dolomite shows poor activity in modification of gaseous hydrocarbon concentrations and suffer from low mechanical strength undergoing comminution phenomena. Olivine has higher mechanical resistance, but a lower activity in tar cracking. A high efficiency in tar removal and hydrocarbon reforming is reported for nickel based artificial catalysts [8]. Commercial available catalysts are not suitable for fluidized beds where the attrition is significant [9]. In particular, Magrini-Bair et al. [9] reported for a naphtha reforming catalyst a relevant and not sustainable attrition rate. Therefore,

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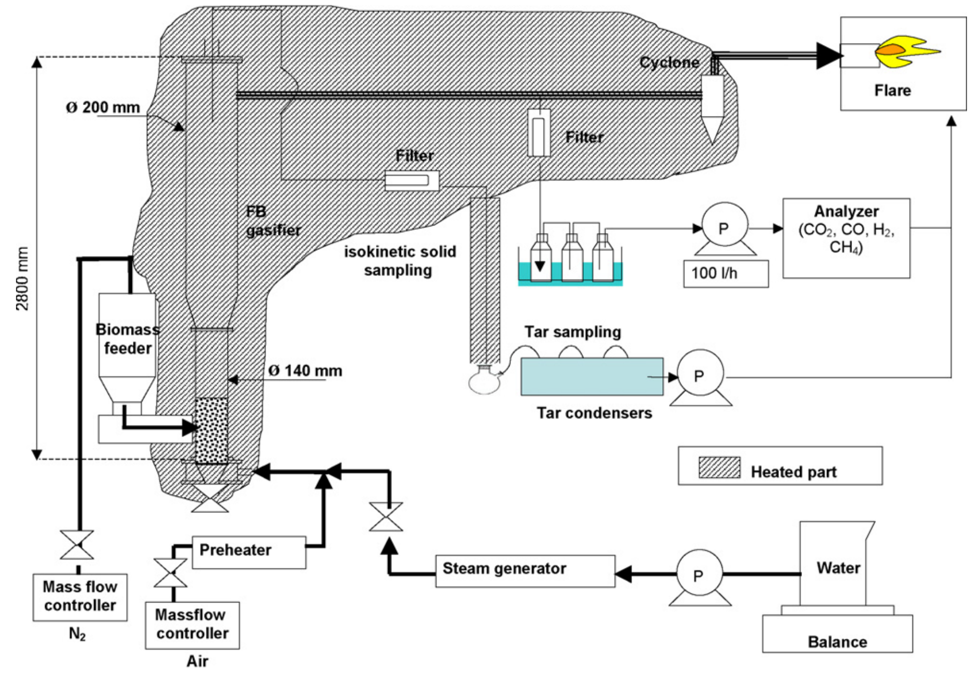

Fig. 1. Experimental apparatus used for gasification tests.

a catalyst to be used in a fluidized bed gasifier still requires investigation and development efforts.

The present paper deals with fluidized bed gasification of a biomass fuel and reports the results of an experimental research aimed at maximizing the hydrogen yield and tar reduction. A particular novel aspect of the research is the utilization as bed material of two natural catalyst (olivine and dolomite) and a purposely developed catalyst (Ni–alumina). With respect to the base case of an inert bed, the influence of catalytic materials on the concentration of stable gases (e.g. H_2, CO_2, CO, CH_4 and light hydrocarbons) as well as on the efficiency of tar conversion has been investigated in a pilot-scale fluidized bed gasifier. Results are reported and critically discussed in the paper.

2. Experimental

2.1. Experimental facility

The scheme of the gasification facility is shown in Fig. 1. The fluidized bed reactor is formed by two vertical stainless steel tubes having different size and connected by means of a conical adapter. The lower tube has an internal diameter of 140 mm and a height of 1010 mm whereas the upper tube is 200 mm i.d. and 1800 mm high. The gas distributor at the bottom of the fluidizing column has a conical shape and a total volume of around 1 l. The gas passes trough 72 holes, 1.5 mm i.d. that are arranged in 6 regular rows along the conical surface. The fuel is under-bed fed into the reactor by means of a screw conveyor, 130 mm above the conical distributor. The fuel flow rate is regulated by means of an additional screw feeder, rotating at changeable rate and directly connected to a sealed fuel hopper. A flare equipped with a LPG pilot flame burns the syngas coming from the gasifier upstream the chimney.

Distilled water is fed by means of a peristaltic pump with adjustable rate (0–1.8 L/h) to an electric tubular steam generator in order to produce steam at moderate gauge pressure (20 kPa) and temperature up to 400 °C. The steam directly enters the wind box of the gas distributor where it is mixed with the air flow, preheated up to 600 °C. An auxiliary nitrogen stream is used for inertizing the fuel feeding devices and enters into the gasifier together with the fuel.

Gasification products are sampled isokinetically inside the reactor and passed through a hot quartz fiber thimble to collect solid particles and in sequence through a condenser system to trap tars and water. The concentration of permanent gases are measured on-line by means of continuous analyzers for H_2, CO, CO_2, CH_4. Gaseous samples are also taken in 3 l bags and off-line subjected to a gas chromatograph FID analysis for determination of major hydrocarbon species.

2.2. Materials

Four different materials, namely quartzite, olivine, dolomite and a Ni dispersed on γ-alumina (Al_2O_3) catalyst, have been selected for the bed. Their properties are reported in Table 1. For the catalyst we have reported the properties of support. With exception of quartzite, all materials exert catalytic activity relevant to biomass gasification [10]. The Ni-based catalyst has been prepared by wet impregnation of γ-alumina particles. Nickel nitrate is dissolved in water and added to a suitable amount of γ-alumina powder (PURALOX SCCA-150/200, Sasol. Surface area 160 m^2/g). The sus-

Table 1
Properties of bed materials.

Bed material	Density (kg/m^3)	Average size (μm)	Minimum fluidization velocity (cm/s)	Terminal velocity (m/s)	Attrition rate constant k	Geldart's group
Quartzite	2600	250	2.2	2.3		B
Olivine	3200	250	2.7	2.7		B
Calcined dolomite	1600	400	3.0	2.7	70.5×10^{-7}	B
γ-Alumina	1800	150	0.6	1.1	2.5×10^{-7}	A–B

Table 2
Properties of the biomass fuel and operating conditions of the experiments.

Fuel	Spruce wood pellets
Moisture (% by mass)	8.4
Volatiles (% by mass)	74.2
Fixed carbon (% by mass)	17.1
Ash (% by mass)	0.3
Carbon (% by mass dry)	49.3
Hydrogen (% by mass dry)	5.9
Nitrogen (% by mass dry)	<0.1
Oxygen (% by mass dry)	44.4
Stoichiometric air (kg/kg)	5.4
Low heating value (MJ/kg)	18.5
Operating conditions	
Pressure (kPa)	101
Bed height (m)	0.18–0.30
Bed temperature (°C)	780
Fluidization velocity (m/s)	0.3
Equivalence ratio	0.17
Steam/fuel ratio	0.65

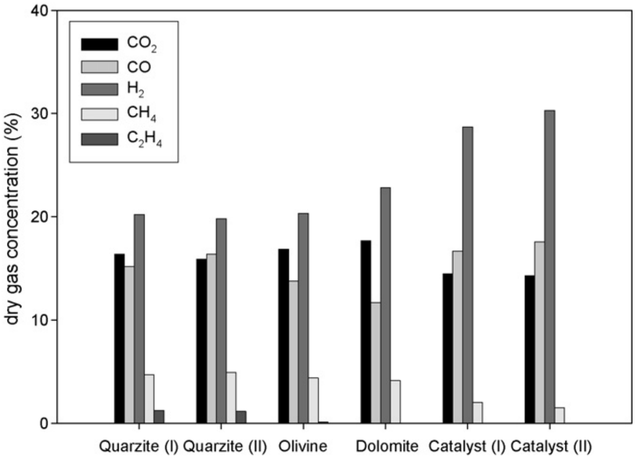

Fig. 2. Dry gas composition at the exit of gasifier for different bed materials ($T = 780\,^{\circ}C$, $\phi = 0.17$, $\Psi = 0.65$, $U = 0.3$ m/s).

pension is dried under vacuum at 60 °C. The impregnated powder is calcined for 3 h in air flow at 800 °C in order to promote the formation of $NiAl_2O_4$. The Ni content (5.5% by weight) of the catalysts was determined by ICP-MS using a Agilent 7500CE instrument after dissolving the Ni–alumina complex in HCl/HNO_3 solution at 80 °C. The catalyst shows a surface area of 156 m^2/g, measured by N_2 adsorption at 77 K with a Carlo Erba 1900 Sorpomatic instrument. The redox behavior of the catalyst was determined by performing H_2 temperature programmed reduction (TPR) experiments using a Micromeritics 2900 TPD\TPR analyzer. A main peak at high temperature has been observed in the TPR profile that can be attributed to the reduction of Ni^{2+} ions in the lattice of the spinel ($NiAl_2O_4$) [11] that are more difficult to be reduced than NiO [12]. This evidence is in agreement with the formation of the nickel–aluminate phase.

Spruce wood pellets have been used as fuel, whose properties are reported in Table 2. It is worth to underline the somewhat high particle density, the low ash content and the limited moisture content, all factors that are beneficial for the studied process and its reliability.

2.3. Operating conditions

The operating conditions of the gasification tests are reported in Table 2. The bed temperature T, the fluidization velocity U, the equivalence ratio ϕ, and the steam/fuel ratio ψ have been kept constant at changing the bed materials. Two different bed heights have been adopted for quartzite and catalyst.

2.4. Test procedure

Steady state tests of gasification have been carried out following a standard experimental procedure. The reactor is heated up to the desired temperature (700–800 °C) thanks to the air pre-heater and the electrical resistances in presence of an air stream of around 8 kg/h through the distributor and the bed. Generally, the plant is ready for gasification in 2–3 h. Then, the fluidization air flow is set at the assigned value, the steam generator is turned on and the water is pumped to produce the desired steam flow rate at around 400 °C. Afterwards, the biomass feeding is started, together with an inertizing nitrogen flow of 0.75 kg/h.

Under steady conditions of the monitored variables, namely temperatures and gas molar fractions, the measurements are taken and recorded. Concerning sampling, a 15 mm i.d. stainless steel probe is introduced in the reactor from the top (1 m inside), and the tube is kept at 450 °C by a heating tape from the sampling point to a ceramic hot filter, able to retain particles as small as 200 nm. Then, the gaseous and condensable species are sent through a two step-condenser, the first one at ambient temperature for heavier tars, the second one at −10 °C for lighter ones. A high precision pump is used for the suction of the sampled gas, aerosol and solid.

The solid particles in the hot filter and the sample at the cyclone are weighed after the experiments; their size distribution is determined off-line by means of a laser granulometer. The liquid phase products are weighed, separately with respect to their dew point. Then, both the condensate at ambient temperature and at low temperature are dissolved in dichloromethane, to separate water from tar. The speciation of the condensed heavy tars (dew point higher than 20 °C) is performed by a HP 9600 series gas chromatograph equipped with a HP 35 PhenylEthylMethyl Siloxane, linked to an Agilent Technologies Chemstation Rev.A.10.01 (1635). The analysis is restricted only to the family of chemical species that are prescribed by the tar protocol of the CEN/TS 15439 normative [13].

A sample of the syngas is also analyzed off-line line by a micro-gas chromatograph AGILENT equipped with TCD detectors in order to determine the presence of light hydrocarbons.

3. Results

Fig. 2 shows the average concentrations of CO_2, CO, H_2, CH_4 and C_2H_4 in the syngas for gasification tests carried out with the four different bed materials. Two bed heights have been adopted for quartzite and catalyst, namely 0.18 and 0.30 m (I and II, respectively), the other operating variables being the same, as reported in Table 2. The average concentrations of gas species are also reported in Table 3, as well as the gas yield (Y_{gas}), the water conversion (X_W) and the carbon load (ξ_C). The gas yield has been evaluated on the basis of a mass balance assuming the conservation of N_2 and is expressed as kg of gas produced per kg of dry-biomass. The water conversion is referred to the total amount of water entering the gasifier. The carbon load has been computed by time integration of CO and CO_2 profiles during burning in air the accumulated char after each test; it is defined as the mass fraction of the total fed fixed carbon. The inert bed of quartzite is assumed as reference case for the other conditions; as expected, it gives the worst performance in term of syngas quality (e.g. H_2 concentration). The use of olivine slightly improves the hydrogen content in the syngas and significantly contributes to tar conversion in lighter hydrocarbons, both effect being emphasized with dolomite as bed material. The catalyst exerts the largest role in improving the gasification per-

Table 3
Composition of dry gas computed by thermodynamic equilibrium, composition of dry gas, gas yield (Y_{gas}), water conversion (X_w), carbon load (ξ_c) and tar concentration obtained during the biomass gasification tests.

	Equilibrium values at 780 °C		1	2	3	4	5	6
	C	$C-C_{fix}$	Quarzite (I)	Quarzite (II)	Olivine	Dolomite	Catalyst (I)	Catalyst (II)
CO_2 (%)	12.56	14.94	16.40	15.90	16.90	17.70	14.50	14.30
CO (%)	21.19	17.55	15.20	16.40	13.80	11.70	16.70	17.60
H_2 (%)	35.34	37.8	20.20	19.80	20.30	22.80	28.70	30.30
CH_4 (%)	$3.66e^{-4}$	0.02	4.70	4.90	4.40	4.10	2.02	1.49
C_2H_4 (%)			1.25	1.11	0.15	0.04	0.02	0.02
C_2H_6 (%)			0.11	0.11	0.11	–	–	–
Y_{gas} (kg/kg)			1.12	1.14	1.02	1.01	1.14	1.21
X_w (kg/kg)			0.31	0.32	0.43	0.43	0.57	0.52
ξ_c (kg/kg)			0.21	0.23	0.33	0.30	–	0.38
TAR_I (g/Nm^3)			14.60	12.80	10.5	8.90	8.40	7.60
TAR_{II} (g/Nm^3)			4.60	5.20	2.70	2.50	0.60	1.00

formance: the H_2 molar fraction attains the largest value 28.7% among the tests carried out with the shallow bed. The presence of catalyst increases the hydrogen concentration and slightly the total gas yield, as can be noted from the data reported in Table 3. Furthermore, the comparison of the gas concentrations attained with different bed materials shows that the hydrocarbon steam reforming reactions (CH_4 and C_2H_4) are largely accelerated by the presence of the catalyst, whereas the dolomite mainly enhances the reaction path of the water gas shift reaction, by increasing H_2 and CO_2 level in the syngas. The analysis of carbon load data reveals that the fixed carbon is not completely converted, the highest conversion being 79% for quartzite. Table 3 also reports the thermodynamic equilibrium composition of the system at temperature of 780 °C and pressure of 101 kPa that has been evaluated by using the software tool CEA-Chemical Equilibrium with Application [14], purposely adapted to fluidized bed gasification [15]. Equilibrium data obtained by subtracting the amount of fixed carbon in the biomass are also reported in Table 3. It clearly appears that the real system is not at thermodynamic equilibrium in all gasification tests. More specifically, an higher CO_2 and CH_4 concentration and lower H_2 and CO concentration than that previewed by equilibrium have been found. However, the difference between theoretical and measured concentrations significantly decreases in the case of $C-C_{fix}$ calculations, indicating that the fuel char accumulates in the bed without undergoing chemical conversion. The tests carried out with the catalyst are the most close to the equilibrium, thanks to the faster reaction kinetics. In contrast, the mixing phenomena between reactants and catalyst are still relevant and limit the global gasification kinetics. It is likely that the presence of the bubbles in the bed favors the establishment of local air rich pockets, leading to partial combustion of biomass volatiles. Thus, CO_2 is produced in excess with respect to equilibrium and only slowly depleted via the dry hydrocarbon reforming reaction that is characterized by a very slow kinetics [16]. This mechanism as well as the limited char conversion would increase the actual equivalence ratio and in turn explain the larger value of CO_2 concentration obtained during all the experiments with respect to thermodynamic equilibrium estimates.

The tar concentration in the syngas evaluated on the basis of both condensation steps (i.e. at room temperature and at −10 °C) is reported in Fig. 3. It is worth to note that the concentration of light tar (TAR II) is always significantly lower than that of heavy tar (TAR I). When olivine bed is used the amount of tar is only slightly reduced, while a more marked effect is observed using dolomite. A tar reduction up to 50% is observed in presence of catalyst, which gives rise to the lowest tar level (8.40 g/Nm^3). The measured values are in agreement with the data reported by Gil et al. 1999 [17] obtained under rather similar gasification conditions in inert bed with a gasification ratio [($H_2O + O_2$)/biomass] = 0.90 and H_2O/O_2 = 3, instead of 0.8 and 2.3 used in this work.

From the comparison of tests 1, 2, 5 and 6, it appears that the bed height has a marginal influence on the gas composition and tar reduction, the largest effect being appreciable only for H_2 concentration that increases of around 1% with the tall bed of catalyst. This result indicates that the residence time of the gas in the bed and the amount of catalyst are high enough, even for the shallow bed, but bed bypass phenomena may occur.

Fig. 4 reports the chromatograms obtained by GC analyses of the heavy tar (TAR I) for the tests carried out with different bed materials and shallow bed. It is worth noting that different Y-scales have been used in the four panels, 800 pA for quartzite and olivine and 140 pA for dolomite and catalyst. This is motivated by the increased tar dilution in the solvent (dichloromethane) for the tests giving rise to a lower tar content. Moving from the first diagram (quartzite) to the last one (catalyst) a progressive reduction of the chemical species detected in the tar can be noted. The produced tar is a very complex mixture where a large number of different species can be detected. Using quartzite and dolomite as bed material, the more abundant products are napthalene, acenaphthylene, fluorene, phenanthrene, fluranthene, indene and pyrene. This result is in agreement with that reported by Pfeifer et al. [18], using a bed of olivine and similar steam/biomass ratio in a temperature range 750–900 °C. As shown in the chromatographs of Fig. 4, the tar nature is also affected by the presence of the catalyst. In particular, no hydrocarbons with five rings are present because they are probably converted in hydrocarbons with three or four rings, while hydrocarbons with a single or double ring, such as phenol and indene, are completely reformed.

Limited generation and in turn elutriation of fine particles, evaluated by weighing the solid collected at both the cyclone and filter,

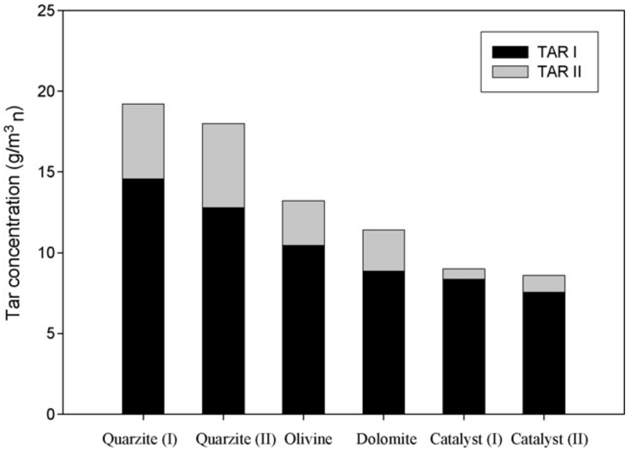

Fig. 3. Tar concentration in the syngas for different bed materials (T = 780 °C, ϕ = 0.17, Ψ = 0.65, U = 0.3 m/s.

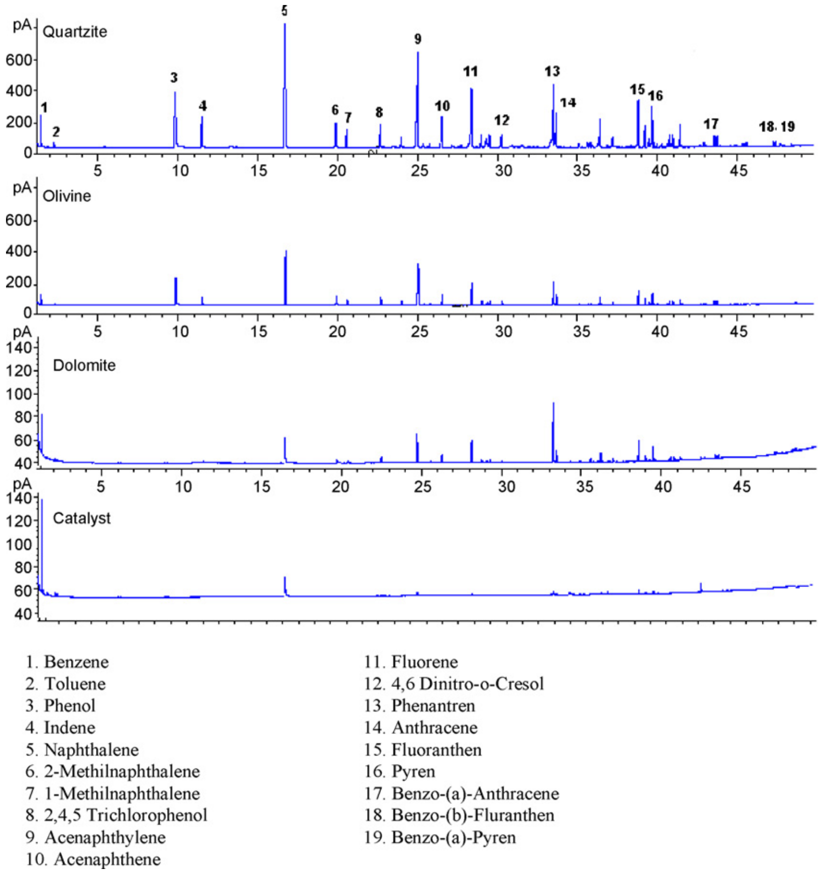

Fig. 4. Chromatograms of tar analysis for different bed materials ($T = 780\,^\circ$C, $\phi = 0.17$, $\Psi = 0.65$, $U = 0.3$ m/s).

respectively, have been observed using quartzite and olivine as bed materials. More in detail, the dimensionless elutriation rates evaluated with respect to dry fuel feeding rate are 6.3×10^{-3} and 1.1×10^{-2} for quartzite and olivine, respectively. The elutriated particles are predominantly composed by residual char, as confirmed by the elemental analysis showing that the carbon content is 75% and hydrogen 1.5% by weight. This result confirms the high mechanical resistance reported for both quartzite and olivine [10]. Higher elutriation rates, evaluated by a mass balance on the bed material before and after the gasification test, have been obtained for both dolomite and catalyst, 1.3×10^{-1} and 3.7×10^{-2}, respectively. The larger elutriation rate of dolomite with respect to the catalyst is congruent with a significantly higher attrition constant, as reported in Table 1 denoting a better mechanical resistance and suitability for fluidized bed process of the catalyst.

It is worth to note that the U/U_{mf} ratio adopted in the gasification tests for catalyst is largely higher than that of other materials. Since the attrition and elutriation rates are strongly enhanced by increasing U/U_{mf} ratio, a larger elutriation rate could be expected. Congruently, the samples collected at the filter and cyclone for the catalyst have a lower carbon content, less than 10% by weight.

A stable activity of the catalyst has been observed for the whole duration of the reaction tests, up to 120 min, suggesting that no deactivation phenomena occurred, due to coke deposition or morphological modifications. In order to reinforce this finding, the catalyst has been also characterized by electronic microscopy after the use in the gasifier. The value of the surface area of the used sample measured by BET analysis is the same of that obtained for the fresh catalyst (156 m^2/g). This result indicates that nor particle sintering neither nickel migration and agglomeration along the alumina surface may occur, under reaction conditions. Furthermore, for a sample of catalyst taken during a gasification test the SEM analysis and the elemental analysis highlight no formation of carbon fibers on the catalyst surface and a low carbon content, less than 1%. These good features can be ascribed to the strong interaction between nickel and support, as confirmed by TPR analysis showing the presence of nickel aluminate phase, which limit the nickel sintering and coking in agreement with finding reported by Pfeifer et al. [18].

4. Conclusions

The biomass gasification tests carried out in a pilot scale fluidized bed with different bed materials confirm that the composition of the syngas as well as the tar concentration are appreciably modified in presence of catalytic materials. The olivine slightly improves the hydrogen content in the syngas and contributes to tar conversion in lighter hydrocarbons. The dolomite has a more marked effect, whereas the Ni-based catalyst exerts the largest role in improving the gasification performance.

The tar concentration is reduced of around 50% with the nickel–alumina catalyst with respect to the reference test carried out in quartzite. The tar nature is also affected by the presence of the catalyst, a simplification of chemical species detected in the tar (e.g. hydrocarbons with five rings) being revealed by the chromatographic analysis.

The catalyst gives rise to an elutriation rate about 3.6 times lower than that observed for dolomite at comparable U/U_{mf} ratio, denoting a better mechanical resistance. Therefore it could be considered as a more suitable material for fluidized bed process.

A stable activity of the catalyst has been observed for the whole duration of the reaction tests, up to 120 min, suggesting that no deactivation phenomena occurred, due to coke deposition or morphological modifications.

The poor char conversion as well as the role played by the bed fluid-dynamics, as revealed by the low effect of the bed height, are also relevant in order to improve the gasifier performance. This matter deserves further investigation with both experimental and theoretical approaches.

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