

Article

Synergic Effects of Bed Materials and Catalytic Filter Candle for the Conversion of Tar during Biomass Steam Gasification

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Abstract: This work concerns the activities of the European project BLAZE that aims to integrate a pilot-scale gasifier unit with a Solid Oxide Fuel Cell (SOFC). The objective is to identify the optimal operating conditions for a gasifier and hot gas cleaning and conditioning unit to produce H₂-rich syngas with contaminants levels within the limits for the safe operation of the SOFC (750 mg/Nm³ and 75 mg/Nm³ for toluene and naphthalene, respectively). Experimental tests were carried out on a bench-scale gasification plant with a catalytic filter candle placed in the freeboard, to study the influence of temperature (1032 up to 1137 K), bed materials (olivine or olivine/dolomite 80/20%), and a nickel-based catalyst. The tests with a ceramic filter candle filled with catalyst and the mixture of olivine and dolomite in the bed gave the best results in terms of gas composition and gas yield, but the tar content was still higher than the limits for the SOFC. To increase the residence time of the gas in the catalytic bed a new metallic filter candle was tested. This candle, with almost the same external volume, allowed doubling the amount of catalyst used. Under these conditions, the content of toluene and naphthalene was reduced below 150 and 50 mg/Nm³, respectively.

Keywords: biomass gasification; SOFC; tar reduction; filter candle; hot-gas cleaning

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1. Introduction

The frequency and intensity of extreme weather phenomena are increasing due to global warming. If not countered, climate change will become irreversible, threatening all aspects of the society in which we live [1,2]. For this reason, the European Green Deal has set the ultimate goal of an economy with zero net greenhouse gas emissions by 2050. The EU climate neutrality affects all the activities of society (energy system, land and agricultural sector, industrial fabric and transport systems, and cities). In particular, the energy system based on the excessive use of fossil fuels causes more than 75% of the EU's greenhouse gas emissions [3].

The transition to a sustainable energy future will result in a largely decentralized system that uses locally available renewable resources (e.g., biomass, solar and wind energy) and the complete replacement of secondary energy sources with electricity and green hydrogen [4].

In this scenario, hydrogen, as an energy carrier, storage medium, and clean fuel, plays an increasingly central role for the decarbonization of the economy in all sectors (mobility, industry, household, and energy services) [5]. However, to date, 95% of hydrogen is produced from fossil sources [4]. Gasification is an effective process to obtain green hydrogen from biomass. This thermochemical process allows us to combine the exploitation of waste biomass and the production of a value-added product. In particular, small-to-medium combined heat and power generation (CHP) plants would allow the exploitation of the organic waste and agro-industrial residues produced locally, matching perfectly with a distributed energy system and reducing the transportation costs [6].

Gasification is considered an effective technology for the conversion of a great variety of solid biomasses, including many low-cost residues from forestry, agriculture, and organic waste. Gasification of biomass is performed by using air, oxygen and/or steam as gasifying agent to obtain a valuable fuel gas (mainly CO, CO₂, CH₄, and H₂) by partial oxidation at high temperature (1073–1273 K) and short residence time. However, some byproducts are generated during the process: particulate, ammonia, sulfur, halogens, base compounds and tar (mixture of condensable heavy hydrocarbons) [7,8]. The contaminants have to be removed before the use of gas, e.g., for the production of hydrogen [9,10] or fuel cell feeding [11–13].

Tars represent one of the main issues for the commercial breakthrough of the biomass gasification plant, causing several problems in the units downstream from the gasifier: blocking and fouling of engine, catalyst deactivation, and general malfunctions in the process equipment [14,15]. In addition, the presence of tar reduces gas yield and conversion efficiency [16]. The tar concentration in the raw syngas from a fluidized bed gasifier is typically in the range of 1 to 30 g/Nm³ [17,18]. This relatively high concentration is above the limiting concentration for most syngas applications [14,19,20].

As widely investigated in the literature, the reduction of the tar can be obtained by adjusting the operating conditions of the gasifier or using materials with catalytic activity [21–23]. Increasing the temperature and pressure enables reduction of the tar. Raising the steam to biomass ratio results in a lower amount of tar produced due to water gas shift, reforming, and cracking reactions, leading to higher H₂ yield and, therefore, better low heating value (LHV) for the gas. However, the energy requirements also increase [13,24].

The catalysts used can be divided as natural minerals (limestone, olivine, dolomite), metal alkalis (KOH, KHCO₃, and K₂CO₃), stable metals (nickel oxide), and noble metals [25]. Nickel-based catalysts have been demonstrated to be very effective in tar and methane steam reforming and are also suitable for NH₃ abatement [18,26]. However, sulfur and halogen compounds may deactivate or poison the catalysts [7,27,28].

Daiton [29] stated that the use of a nickel-based catalyst bed after a guard bed of calcined dolomite is a good option for effective tar removal and to improve the durability of the catalyst. Natural minerals can be used as bed material for primary tar reduction. Several authors report that the activity of olivine is much lower than that of dolomite, mainly due to the fact that the former is a non-porous material, and no internal surface is available. However, the latter is softer and gives rise to a large amount of fine matter in the produced gas [30–32].

This work concerns one of the experimental tasks of the European project BLAZE. The project aims to integrate a dual fluidized bed gasifier, hot gas cleaning and conditioning unit and industrialized solid oxide fuel cells (SOFC) to develop a CHP plant for the production of electricity and heat from renewable energy sources.

A system with biomass gasification and SOFCs offers the opportunity to generate sustainable and environmentally friendly energy. However, the gas contaminants present in the syngas (tars, sulfur, alkali, and halogens metals) could limit the performance of the SOFC and reduce its lifetime [33,34].

In particular, tars represent a potential issue for the operation of the SOFC, leading to phenomena of carbon formation and carbon deposition due to contact with the nickel particles on the SOFC anode. The rate of reactions leading to the formation of coke is faster than the reforming reactions and carbon gasification. Based on the rate of reactions, in the BLAZE project aromatic compounds were distinguished into slow and fast tars represented by naphthalene and toluene, respectively. In particular, the so-called slow tars tend to accumulate easily in the SOFC anode, decreasing the conversion of other hydrocarbons and damaging the microstructure of the anode.

The BLAZE project gives an indication on the concentration limits for naphthalene and toluene [35]:

- the toluene content lower than 750 mg/Nm³ even if it should be preferably <250 mg/Nm³;
- the naphthalene content lower than 75 mg/Nm³, even if it should be preferably <25 mg/Nm³.

Reducing the tar content below these limits is a key issue in coupling gasifiers and SOFCs. Hot gas conditioning and tar abatement is a very advantageous system that could make it possible to produce a clean fuel gas at a temperature as high as that required in high temperature fuel cells, reducing the thermal input and simplifying the process. The BLAZE project aims to assess the effectiveness of the gasification unit that also integrates into a single vessel the hot gas cleaning and conditioning. The ceramic filter candle is used for particulate removal, and elimination of trace elements reducing the thermal dispersion [33,36,37].

In this work, tests were performed in a lab-scale fluidized bed gasifier equipped with a filter candle filled in the inner hollow space with cylindrical pellets of a nickel-based catalyst. The effect of temperature on the gas composition and tar conversion has been analyzed to evaluate the performance of the system. Several process conditions were studied evaluating the catalyst activity in terms of tar conversion and NH_3 abatement. The tests were conducted using different bed materials (olivine, or olivine and dolomite) and with and without catalyst in the ceramic candle to highlight synergic effects. The objective is to identify the process conditions, such as to obtain clean syngas for the safe operation of the SOFC. In addition, a new metallic filter candle was tested. As far as the authors are aware, the use of the metallic filter candle represents a novelty for the hot gas conditioning that allows us to optimize the hollow space in the freeboard of the gasifier. In fact, this candle with the same footprint offers a greater internal volume than the ceramic one, maximizing the residence time of the gas in contact with the catalytic bed.

2. Materials and Methods

2.1. Experimental Materials

The biomass used is almond shells with Sauter mean diameter equal to $1060\ \mu\text{m}$. The proximate and ultimate analyses, and moisture are reported in Table 1.

Table 1. Characterization of almond shells [38].

Proximate Analysis (wt.%)		Ultimate Analysis (wt.% Dry Basis)	
Moisture	7.7	C	48.90
Ash	1.1	H	6.20
Volatile matter	71.7	N	0.18
Fixed carbon	19.5	O	43.50
		Cl	0.029
		S	0.026

The tests were carried out with a gasifier bed of olivine and a mixture of olivine and dolomite. The properties of the bed inventories are reported in Table 2. The bed height was almost 30 cm.

Table 2. Properties of olivine and dolomite particles.

Test	1-2-3	4-5-6-7		8	
Bed material	Olivine	Olivine	Dolomite	Olivine	Dolomite
wt. %	100	80.5	19.5	80	20
Sauter mean diameter [μm]	235	250.1	330.6	250.4	339.9
Particle density [kg/m^3]	3000	3000	1650	3000	1650

Gasification tests were carried out in a bubbling fluidized bed gasifier composed of a stainless-steel cylindrical vessel (ID 100 mm and height 850 mm) externally heated by an electric furnace. The filter candle is inserted in the freeboard of the reactor for in-situ gas conditioning. Two filter candles were used (Figure 1): a ceramic porous candle (supplied by PALL Filtersystems GmbH), with an external diameter of 0.06 m and length of the filter element of 0.5 m; and a highly porous stainless steel filter (supplied by GKN Sinter Metal), made of HASTELLOY X, with an external diameter of 0.06 m and a filter element length of

0.55 m. The stainless-steel filter is able to operate up to temperatures of 800 °C and 930 °C in oxidizing and reducing environments, respectively.



Figure 1. Metallic (a) and ceramic (b) filter candles.

The catalyst inserted in the filter candle was a commercial steam reforming catalyst (pellets with 3 mm diameter and height) containing approximately 15 wt.% of nickel, supplied by Johnson Matthey. No XRD, EDS, SEM and BET characterizations were performed on this catalyst due to an NDA (Non-Disclosure Agreement) signed with the catalyst supplier.

Nitrogen (grade 5.5) and air (grade 5.0) supplied by Rivoira SpA, and demineralized water were used as input streams for the tests.

2.2. Experimental Apparatus

A scheme of the experimental apparatus is reported in Figure 2.

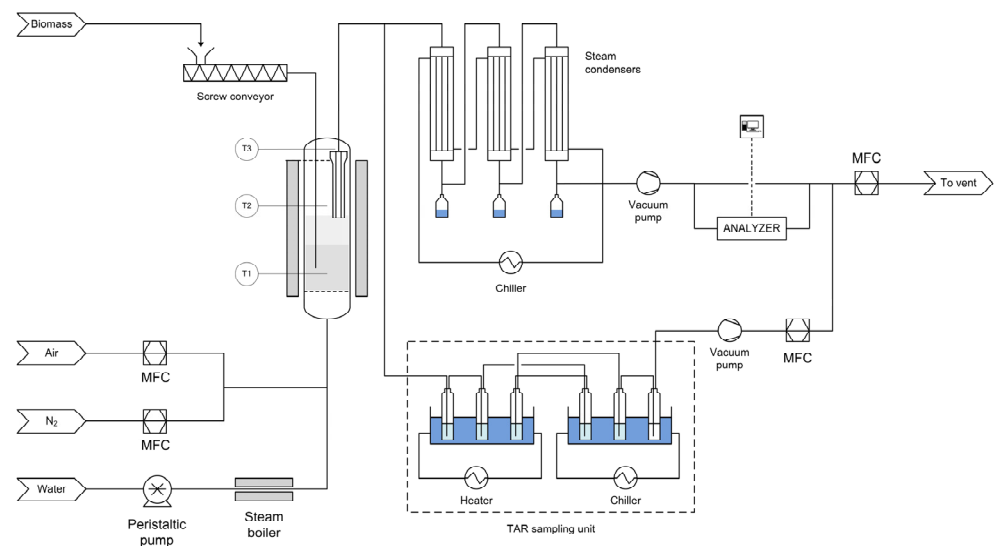


Figure 2. Simplified scheme of the bench-scale gasification test rig.

Biomass particles are fed from the top of the reactor by means of a screw-feeder operating at a constant feeding rate. Steam and nitrogen were fed from the bottom of the reactor percolating through a porous ceramic plate. The demineralized water is fed with a peristaltic pump to the electric steam generator at the defined flow rate. The flow rate of nitrogen was controlled by a mass flow controller (Bronkhorst®).

Temperatures inside the reactor were measured by three thermocouples installed in the fluidized bed (T1), in the freeboard (T2) and at the exit of the filter candle (T3).

The exiting gas passed through a series of glass condensers fed with a refrigerant liquid (glycol ethylene 10 wt.%) at about 274 K that flowed in counter current. In these apparatuses the gas was cooled down and the residual steam condensed, separated and recovered. At the outlet of the condenser a vacuum pump is present in order to extract the gas from the gasifier through the condensers and finally to transfer it to the gas analyzers. The total dry gas flow rate was measured with a mass flow meter, while the composition was measured in the online gas analyzers.

Furthermore, a slipstream of the product gas, approximately 1 Nl/min, was used for tar sampling. The gas flows through a series of impinger bottles filled with 2-propanol, in which tars condense, according to the technical specification CEN/TS 15439 (see Figure 2 for details). A vacuum pump positioned after the impinger bottle is utilized to assess a constant gas flow during the tar sampling procedure. At the end of the tar sampling (lasting approximately 30 min), the 2-propanol samples are collected and are successively analyzed with high-performance liquid chromatography (HPLC), for the identification and quantification of tar compounds.

The reactor was equipped with a porous candle inserted in the freeboard of the gasifier. To analyze the catalyst performances, the tests were carried out with empty candle and with candle partially filled with catalyst pellets (as reported in a previous work [28]). In order to use a greater amount of catalyst, a high porous stainless-steel filter was used.

The input conditions used in the gasification tests are summarized in Table 3.

Table 3. Process conditions of the gasification tests.

Test	1	2	3	4	5	6	7	8
Temperature [K]	1032	1085	1130	1081	1136	1093	1137	1123
Steam/Biomass _{dry}	0.50	0.51	0.51	0.53	0.52	0.51	0.50	0.58
Filter Candle	Ceramic filter with nickel-based catalyst			Ceramic filter without nickel-based catalyst		Ceramic filter with nickel-based catalyst		Metallic filter with nickel-based catalyst
Catalyst [g]		455			-		463	1027
Biomass [g/min]		11.28			10.84		10.84	11.10

Tests from 1 to 7 were carried out with the ceramic candle, and test 8 with the metallic filter candle.

At the end of each gasification test, the residual char in the gasifier was burned by feeding an air stream to the reactor. The flow rate of air was controlled by mass flow controller (Bronkhorst®). The produced CO and CO₂ were measured to quantify the amount of unconverted char in the bed.

2.3. Analysis of Products

A slipstream of dry product gas was fed to the online gas analyzers ABB URAS, ABB CALDOS, ULTRAMAT 6 Siemens to measure the composition in terms of H₂, CO, CO₂, CH₄, and NH₃.

The 2-propanol samples collected in the tar sampling unit were analyzed offline by means of HPLC (Hitachi “Elite LaChrom” L-2130) to identify and quantify the tar compounds in the product gas. The HPLC apparatus was equipped with an UV detector (Hitachi UV-detector L-2400) set at 254 nm. The reversed phase C18 column (Alltech “Apollo C18 5 µm”) protected with a guard column was used for the chromatographic separation of the tar fraction. Finally, water conversion, gas and char yield, carbon conversion and GHSV were calculated using the same relationships adopted in the work of Savuto et al. [28].

The water conversion η_w during the gasification test was calculated as:

$$\eta_w = \frac{\dot{m}_{w,in} - \dot{m}_{w,out}}{\dot{m}_{w,in}} \times 100 \quad (1)$$

where $\dot{m}_{w,in}$ is the mass flow of the water input as moisture of the biomass and steam, and $\dot{m}_{w,out}$ is the mass flow of the water output collected in the flasks connected to the steam condensers.

The measure of dry gas flow rate and its composition, allow us to calculate the gas yield Y_{gas} and the carbon conversion X_C by means of:

$$Y_{gas} = \frac{Q_{dry,N2Free} (Nm^3/h)}{Q_{Biomass} (kg/h)} \quad (2)$$

$$X_C = \frac{\eta_{CO} + \eta_{CO_2} + \eta_{CH_4}}{\eta_{C_{in}}} \times 100 \quad (3)$$

where $Q_{dry,N2Free}$ is the dry gas flow without nitrogen, η_i are the moles of CO, CO₂ and CH₄ in the product gas and $\eta_{C_{in}}$ represent the total moles of C in the biomass.

Furthermore, the overall gas flow rate is used to calculate the gas hourly space velocity (GHSV):

$$GHSV = \frac{Gas\ flow\ rate_{wet} (Nm^3/h)}{Catalytic\ bed\ volume (m^3)} \quad (4)$$

The amount of un-reacted char in the gasifier was evaluated by the analysis of the CO and CO₂ contents in the gaseous product during the post-combustion step. Then the yield of char Y_{char} was calculated as:

$$Y_{char} = \frac{m_{char} (g)}{m_{Biomass} (kg)} \quad (5)$$

where m_{char} is the mass of the residual char and $m_{Biomass}$ is the mass of the biomass fed during the gasification phase.

3. Results and Discussion

The reactor configuration allows to integrate gasification and gas cleaning and conditioning in a single vessel. In particular, the installation of a candle in the freeboard of the gasifier allows the hot gas produced to be forced to pass through the catalytic bed to exit the reactor (candle temperature calculated as the arithmetic average between the freeboard temperature and the gas temperature at the exit of the reactor).

The dolomite fine particles elutriated from the bed are retained inside the reactor by the filter candle, producing a dust free syngas. In addition, the trapped particles build up a cake around the filter surface which contributes to the further conversion of the tar.

The experimental results are summarized in Table 4, while the tar content is reported in Table 5. The results refer to the data collected during the tar sampling (Figure 3) when the gasifier is at the steady state. The temperature and gas composition of all the tests are reported in Appendix A.

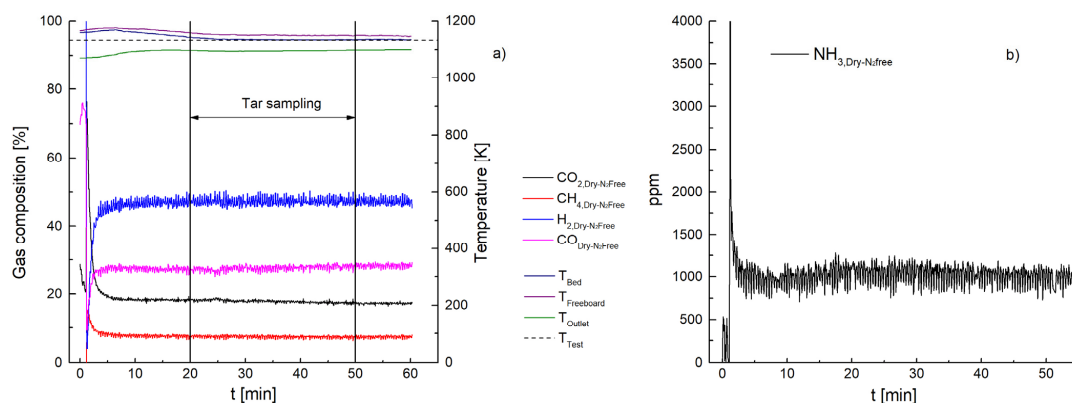


Figure 3. Temperature and gas composition (a) and ammonia content (b) during test 5.

Table 4. Experimental results.

Test	1	2	3	4	5	6	7	8
Bed material	Olivine		Olivine—Dolomite					
Gas yield [Nm ³ /kg _{Biomass}]	1.4	1.4	1.4	1.4	1.6	1.8	1.9	1.9
Char residue [g _{Char} /kg _{Biomass}]		78.1		101.7	67.1	80.6	60.4	55.9
Tar [mg/Nm ³]	7116.0	3730.7	678.2	6217.3	3252.3	798.0	432.8	225.2
H ₂ O conversion [%]	37.8	43.7	54.7	38.5	42.7	50.0	54.8	58.2
GHSV [h ^{−1}]	4153	4102	3922	—	—	4168	4227	2324
H ₂ [%vol _{dryN2free}]	53.4	53.5	54.2	46.3	46.8	55.3	55.1	53.3
CO [%vol _{dryN2free}]	25.7	27.0	28.4	23.6	26.9	28.8	31.4	34.7
CO ₂ [%vol _{dryN2free}]	18.3	16.4	14.4	20.7	17.7	13.9	12.1	11.3
CH ₄ [%vol _{dryN2free}]	2.6	3.1	2.9	9.4	8.6	2.0	1.4	0.6
NH ₃ [ppm]	447	260	66	1499	1032	112	87	57
Average candle temperature [K]	1022	1066	1113	1096	1124	1076	1108	1114
Mass balance closure [%]	1.1	1.7	5.2	1.3	4.6	2.5	2.2	0.6

Table 5. Tar content in the product gas (mg/Nm³-N₂free).

Test	1	2	3	4	5	6	7	8
Toluene	1856.3	1383.1	167.3	2001.5	1096.9	390.0	239.5	146.1
Naphthalene	861.3	636.0	186.0	1620.1	1366.4	254.0	136.7	47.5
Phenol	568.7	223.1	48.6	86.0	0.0	0.0	0.0	0.0
1-ring compounds	2311.7	1546.5	185.6	2489.0	1263.7	432.4	256.3	154.8
2-ring compounds	571.8	274.5	58.9	609.6	228.9	53.4	24.6	15.0
3- and 4-ring compounds	2803	1050	199	1412.6	393.3	58.3	15.2	7.9

Using dolomite-olivine mixture in the bed with the empty candle (tests 4 and 5), both composition of the gas and tar content are worse than those obtained with the addition of nickel-based catalyst. Several studies with olivine and dolomite report the low catalytic activity of this material, but its use as primary catalyst allows the cracking and reforming of tars preventing coking of the secondary catalyst [39]. In particular, the high surface area and oxide content of the calcined dolomite promote the tar decomposition increasing the H₂ content and the H₂/CO ratio in the producer gas [40].

The effect of the dolomite on tar composition will be discussed in Section 3.2.

The nickel, as a group VIII metal, catalyzes the steam reforming reactions of methane and tar. Using a commercial nickel-based catalyst in the filter candle, the yield and the quality of the producer gas is enhanced. The results of tests 1, 2, 3, 6, 7, and 8 show a lower amount of CH₄ and methane at the same temperature level. Due to the conversion of hydrocarbon the gas is characterized by the increase of H₂ and CO content, and higher H₂O conversion.

The operative temperature plays a central role in the gasification process. The results show that by raising the temperature, other conditions being equal, the gas yield is increased, the residual char decreases and the gas composition is improved. In particular, the H₂O conversion and H₂ content are improved, while the CH₄ and tar content are strongly decreased. These results are related to various phenomena that occur on increasing the temperature: the pyrolysis, the first step of the process, is made faster by increasing the amount of gas produced; the endothermal water gas reaction of the char is favored; the cracking and steam reforming of heavier hydrocarbons and tars are enhanced [41].

3.1. Ammonia Content

As shown in Table 4, the bed composition, the nickel-based catalyst and the process temperature influence the ammonia content in the gas. In the temperature range investigated, an effective catalyst is necessary for the decomposition of the ammonia, due to the high activation energy required [40]. Without the nickel-based catalyst, high NH_3 values are obtained, highlighting that the use of the olivine-dolomite bed has a minor influence on ammonia reduction. In fact, tests 4 and 5 showed considerably greater quantities of ammonia in the produced gas (up to 13 times) than those obtained under the same conditions with the use of the nickel-based catalyst (tests 6 and 7). Simell et al. observed that dolomite suffers by the presence of competing components such as CO , CO_2 , N_2 and H_2 in the decomposition of ammonia [42].

As the temperature increases, the amount of ammonia decreases. Using only olivine as bed material, a 75% reduction in ammonia content is observed; when varying the average candle temperature between 1066 and 1113 K, this value increases up to 85% if also the test at 1022 K is considered.

From the comparison between the nitrogen contained in the biomass and the ammonia, it can be observed that in the tests with a nickel-based catalyst and a higher temperature, the greatest conversion occurs. In particular, from the comparison of tests 3-7-8 (process temperature ≈ 1123 K) the ammonia residue in the gas represents about 3% of the nitrogen content of the biomass (as reported in Table 1).

Test 6 shows that the conversion of ammonia is enhanced by using both a mixture of dolomite and olivine particles and a ceramic filter filled with nickel catalyst. The NH_3 content obtained at 1076 K represents about 4% of the nitrogen content of the biomass. This result highlights the synergetic effect of the concurrent use of dolomite-olivine bed mixture and nickel-based catalyst. In fact, the latter is less effective in the NH_3 decomposition in the presence of tars.

3.2. Tar Content

Table 5 reports the results for tar compounds gathered in lumps, as suggested by Corella et al. [43].

3.2.1. Ceramic Filter Candle (Test 1–7)

Temperature and catalyst have a considerable influence on the tar conversion. Tests with a mixture of dolomite and olivine particles in presence of an empty ceramic filter candle (tests 4 and 5) compared with tests where the ceramic filter candle is filled with nickel-based catalyst (tests 6 and 7) show the strong positive effect of the presence of the nickel catalyst in reducing the tar content in the produced gas.

The nickel-based catalyst allows us to considerably reduce the activation energy of the steam reforming reactions, improving the tar conversion, even if no dolomite is added in the bed (as shown in tests 1, 2 and 3): in particular, the residual toluene concentration, for the tests at the higher temperatures (Test 3), is below the preferable limit for a correct operation of the SOFC ($<250 \text{ mg/Nm}^3$, see introduction), even if the naphthalene concentration is still too high ($>75 \text{ mg/Nm}^3$). The tar content and gas composition in terms of H_2 , CO , CO_2 and CH_4 are strictly related to the temperature. In particular, the endothermic steam reforming reactions of tar and methane are favored at elevated temperatures. Using the nickel-based catalysts further enhances these reactions, leading to considerable reductions of tar as in test 3.

Tests 4 and 5 show the worst composition in terms of tar content. The results confirm that the calcined dolomite is very active for decomposition of phenols, that are reduced more than in tests with nickel catalyst.

Tests 2, 4 and 6 were carried out at the same temperature level of approximately 1080 K. Test 2 was performed with only olivine bed particles and nickel catalyst in the ceramic filter candle, while test 4 was performed with a bed inventory made of a mixture of olivine and dolomite particles in presence of an empty ceramic filter. Both a mixture of

dolomite and olivine particles and a ceramic filter filled with nickel catalyst were used in test 6. Comparing the results from tar analysis of these three tests (Table 5), the highest values of toluene, naphthalene and 2- and 3- ring compounds were obtained in test 4, when nickel catalyst was absent. Test 6 showed a strong reduction of the tar contents compared to tests 4 and 2. Similar considerations can be made for tests 3, 5 and 7, performed at a higher temperature of 1130 K.

Tests 6 and 7 showed that the tars content was further reduced with respect to tests 2 and 3 due to the synergic effect of the simultaneous use of dolomite particles inside the bed and nickel-based catalyst in the ceramic filter candle.

These conditions were chosen for further investigation. The ceramic filter candle was replaced with the metallic one, and a double amount of catalyst was tested, as described in Section 3.2.2.

3.2.2. Metallic Filter Candle (Test 8)

About 1 kg of nickel-based catalyst pellets, that is, double the amount of catalyst utilized into the ceramic candles in previous tests, was inserted into the metallic filter. The gasification test performed at temperature of 1123 K by using this filled metallic filter and a mixture of olivine and dolomite particles gave better results compared to the other tests. In particular, compared to test 7, the CH_4 and NH_3 concentrations, and the tar content decreased by 57%, 34% and 48%, respectively. Furthermore, the H_2O conversion was slightly higher.

The metallic filter candle allows us to double the gas residence time on the catalyst compared with when the ceramic filter is utilized. In this way, the contact with the active site of the catalyst is improved, with a positive effect on the total amount of hydrocarbon such as tar and methane, as well as the ammonia content. With these arrangements, the naphthalene and toluene concentrations of 48 and 146 $\text{mg}/\text{Nm}^3_{\text{N}_2 \text{ free}}$ were obtained, respectively, which are lower than the requirement for SOFC utilization.

4. Conclusions

In this work, steam gasification tests were carried out in a bench scale fluidized bed gasifier. The aim was to obtain the optimal conditions for the effective syngas conditioning and for the reduction of tar content, in order to reach the limits required for feeding an SOFC.

The results highlight the high conversion efficiency of tar and ammonia obtained using the filter candle filled with nickel-based catalyst in the freeboard of the reactor. The residual tar content was about 5 times lower ($678 \text{ mg}/\text{Nm}^3$) than that obtained with the use of an empty candle ($3252 \text{ mg}/\text{Nm}^3$), even if a dolomite-olivine mixture was used as bed. The best results in terms of gas composition, gas yield and tar content were obtained in tests with a bed inventory made of a mixture of dolomite and olivine particles and nickel-based catalyst in the candle ($\text{GHSV} = 4227 \text{ h}^{-1}$), at the higher operating temperatures.

Although the simultaneous use of dolomite-olivine bed and nickel-based catalysts allowed us to further improve the conditioning performance, the gas obtained still did not satisfy the necessary requirements for feeding the SOFC. Therefore, a new metallic filter candle was tested which allows a greater quantity of catalyst inside the cavity with the same overall external dimensions of the filter. Under the new conditions ($\text{GHSV} = 2324 \text{ h}^{-1}$) the gas obtained showed toluene and naphthalene contents equal to 146 and 48 mg/Nm^3 , respectively, finally within the limits imposed for the SOFC, and a negligible methane concentration, confirming the best efficiency in terms of steam reforming reactions.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

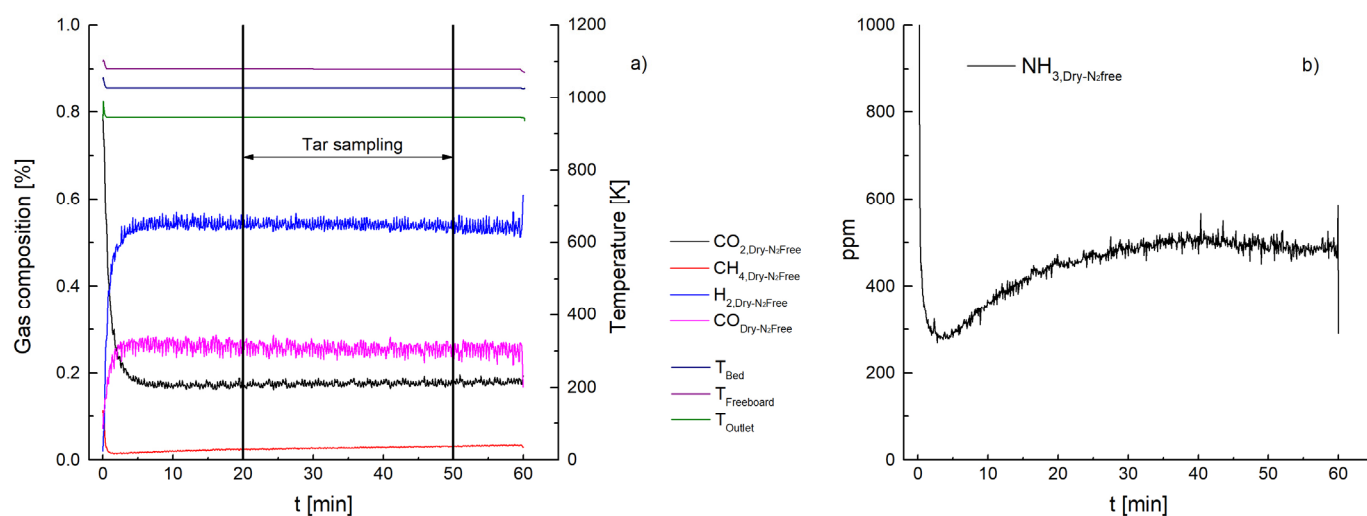


Figure A1. Temperature and gas composition (a) and ammonia content (b) during test 1.

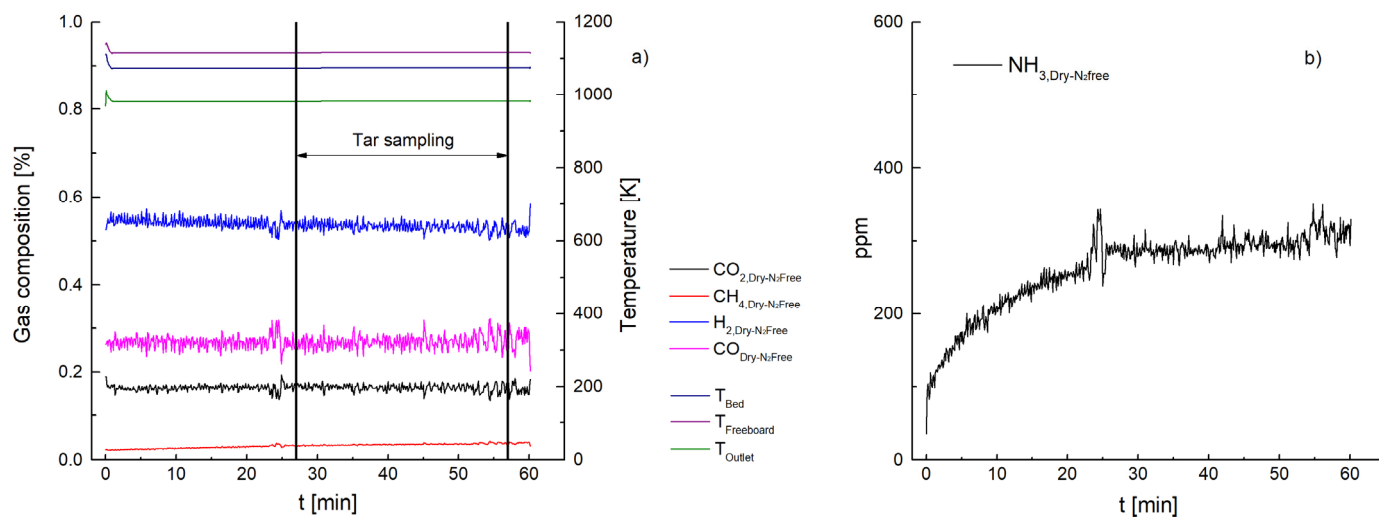


Figure A2. Temperature and gas composition (a) and ammonia content (b) during test 2.

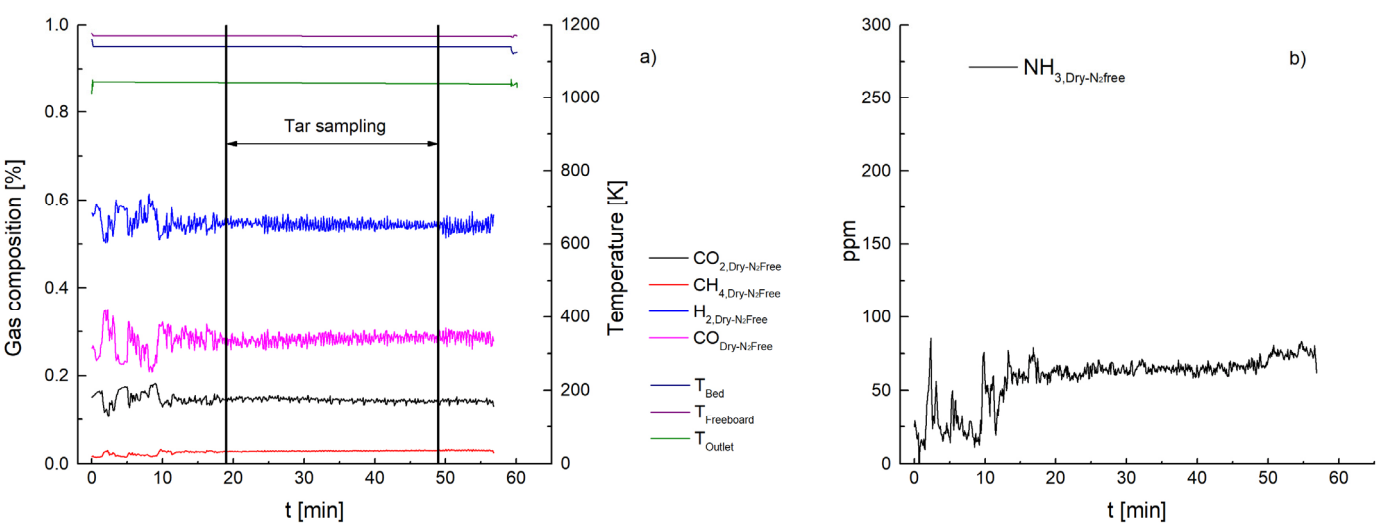


Figure A3. Temperature and gas composition (a) and ammonia content (b) during test 3.

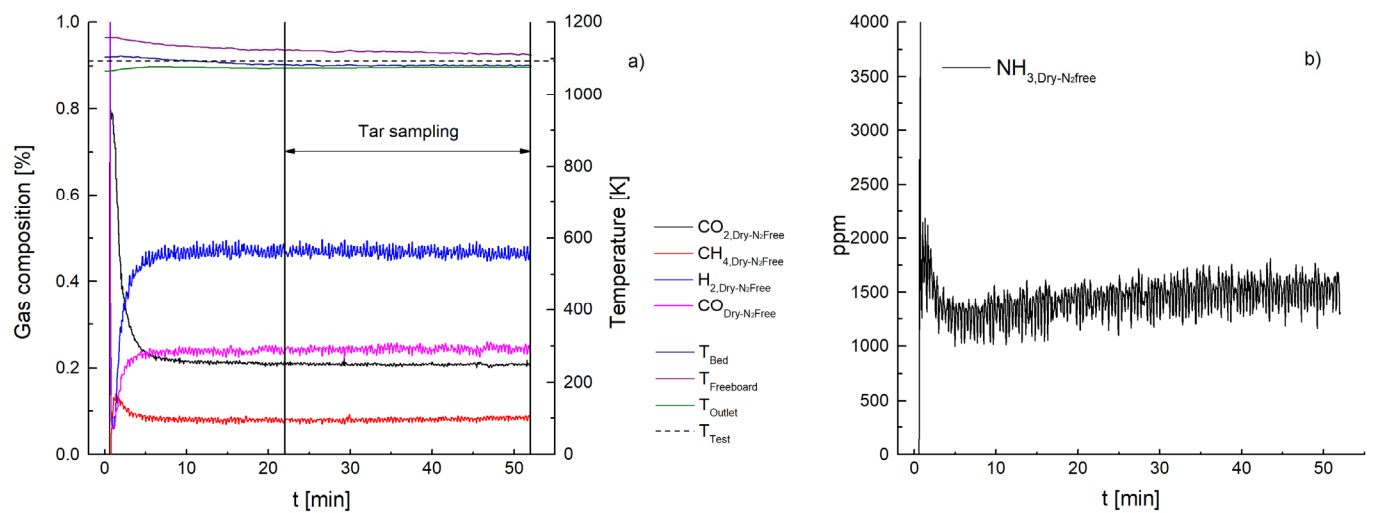


Figure A4. Temperature and gas composition (a) and ammonia content (b) during test 4.

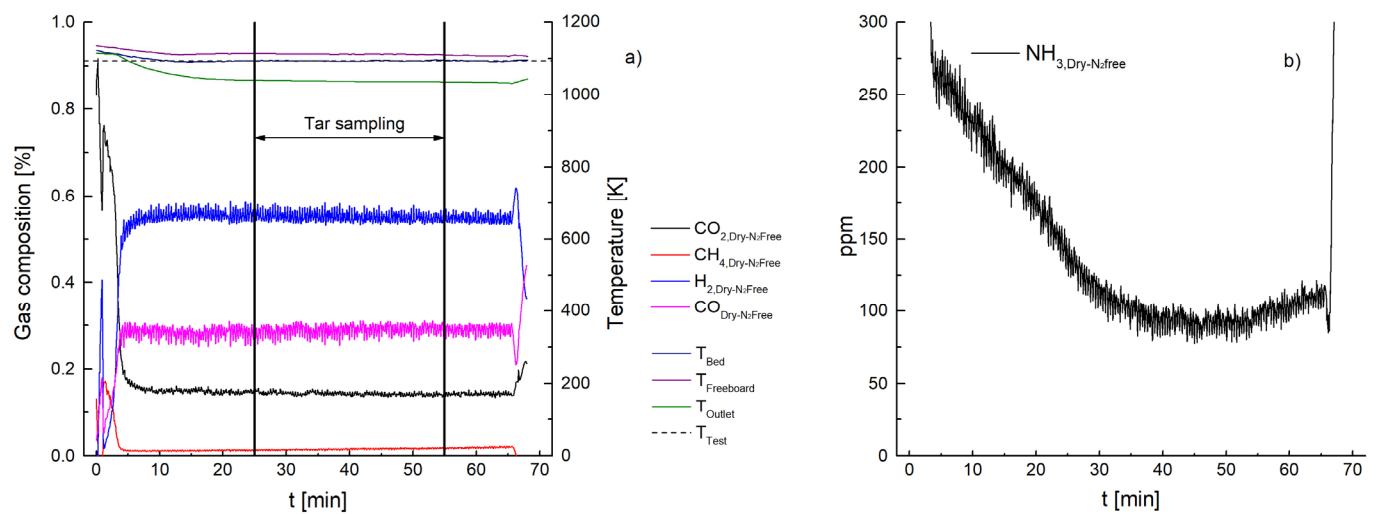


Figure A5. Temperature and gas composition (a) and ammonia content (b) during test 6.

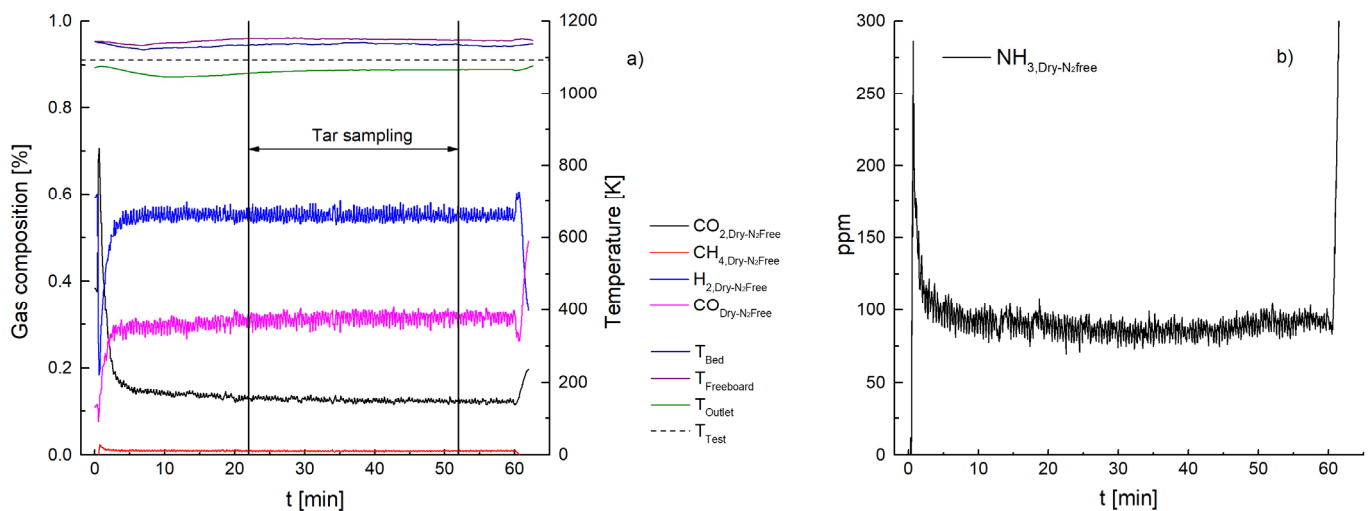


Figure A6. Temperature and gas composition (a) and ammonia content (b) during test 7.

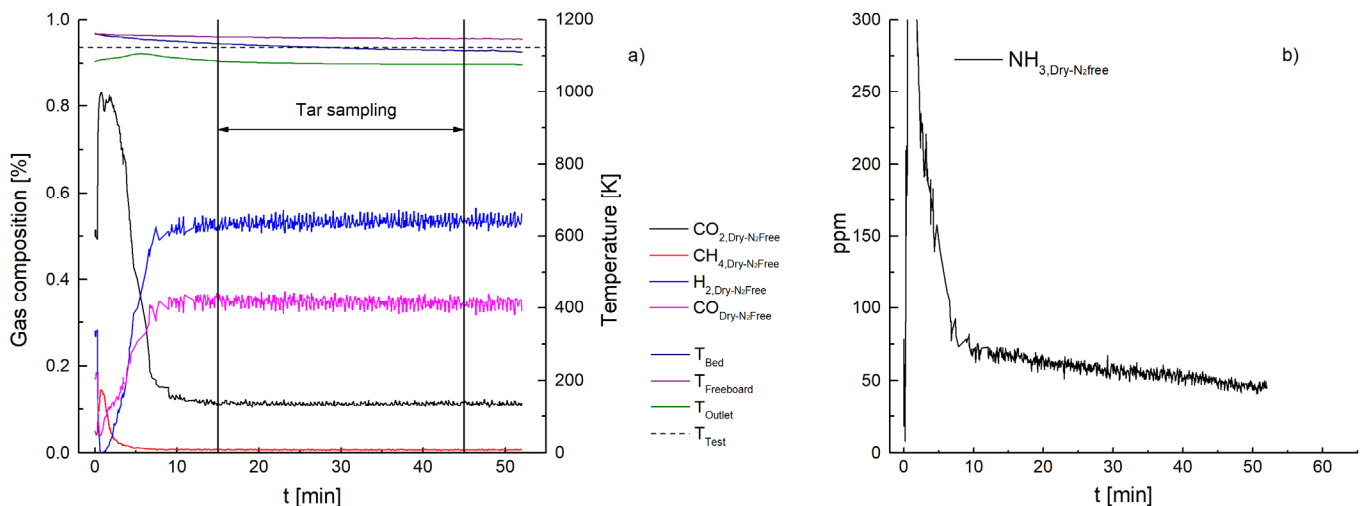


Figure A7. Temperature and gas composition (a) and ammonia content (b) during test 8.

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