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BIO-SYNGAS COMPOSITION AND CONTAMINANTS THAT AFFECT SOFC AND RELATED GASIFIER PARAMETERS AND BED MATERIALS TO REDUCE SOFC HAZARDOUS EFFECTS

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1 EXECUTIVE SUMMARY

Experimental gasification campaigns were carried out with the aim of evaluating, in accordance with the purpose of Task 2.3 (Gasification tests on the lab scale fluidized bed gasifier), the effect of using calcined-dolomite and alkali carbonates (Na_2CO_3 and K_2CO_3) as primary additives in reducing the gas content of organic and inorganic contaminants directly in the gasification reactor.

After some hardware upgrading to the feeding system of the BFB gasification test rig to allow for a widen flexibility towards the type of feedstock, steam/oxygen gasification tests were carried out using three different matrices (i.e. low-grade corn grid, secondary solid fuel, olive pomace). Under similar operating conditions (i.e. ER $\approx$ 0.25, S/B $\approx$ 0.5, $T_{bed} \approx$ 830 - 850 °C) the experimental results provided positive evidence of the efficacy of the implemented solutions.

Specifically, the tests carried out with and without calcined-dolomite confirmed a general beneficial effect on the overall gasification performances and improvement of feedstocks conversion into gas products. Compared to olivine, a mixed bed olivine/calcined-dolomite 70:30, percentage by weight, indicated higher gas yields and carbon conversion percentages. For this latter, the comparison between representative values, indicated an increase from around 85 % to 95 % or higher. Consistently, the experimental data provided a significant reduction in the content of Tar. On a chromatographic basis, a content reduction of about 40 %-wt was estimated based on the total chromatographic tar value (23 g/Nm^3_{dry} vs 14 g/Nm^3_{dry}). Benzene and toluene remained the most abundant compounds among aromatics with a single ring, naphthalene among the aromatics with condensed rings. Some N- and and S- containing compounds were also considered (i.e. pyridine, quinoline, benzothiophene and dibenzothiophene). By using calcined-dolomite their contents were reduced by more than 50 %.

A content decrease was observed also regarding the inorganic contaminants H_2S, HCl and NH_3. For these compounds the use of calcined dolomite provided reduction above 70 %, 20 % and 10 %, respectively.

For HCl and H_2S, cutting in concentrations were attained also by the use of the alkali sorbents. The experimental data indicated that in the presence of Na_2CO_3 and K_2CO_3 in the bed inventory, for these two contaminants a reduction in the order of 35-40 % was achieved.

2 INTRODUCTION

The BLAZE project aims at the achievement of the overall objective of developing a technology for CHP application able to cover the production range from small (25-100 kWe) to medium (0.1-5 MWe) scale by using the widest fuel spectrum applicable, with high efficiencies (50% electrical versus the actual 20%), requiring low investment (< 4 k€/kWe) and operation (≈ 0.05 €/kWh) costs as well as almost zero gaseous and PM emissions, projecting electricity production cost below 0.10 €/kWh. To achieve this ambitious goal, the pathway proposed in BLAZE is based on a proper integration between a process based on gasification of solid feedstocks, especially including biowaste of low-grade/low-value, and an innovative system for the optimal exploitation of both the chemical energy and sensitive heat of the producer gas through the use of a solid oxide fuel cell (SOFC) unit coupled with a steam-driven high speed micro-compressor. An overview of the proposed approach is presented in Figure 1.

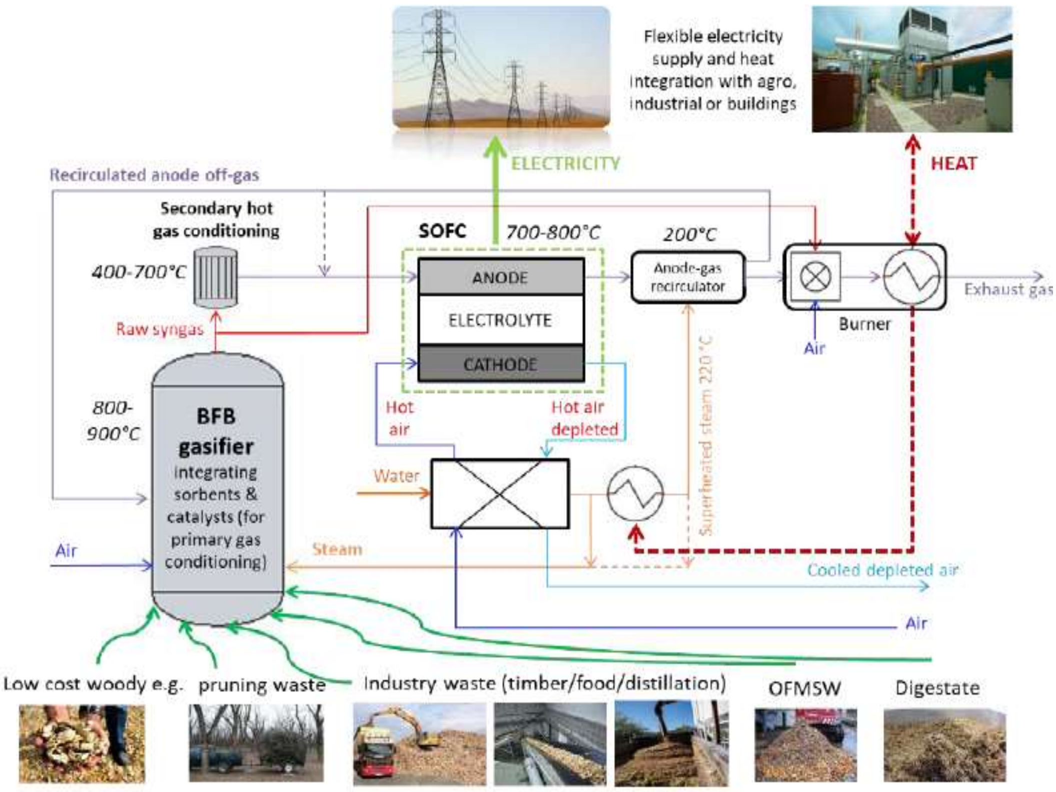


Figure 1. BLAZE biomass CHP plant concept

Among others, a key aspect to achieve the stated targets is the quality of the producer gas to be addressed to the SOFC unit, with particular regard to the load of contaminants. For a smooth and long-last operation of the SOFC the producer gas needs to have a quite high level of purity. Therefore, organic and inorganic compounds such as tar, HCl and H_2S, typically present in a producer gas, are particularly hazardous. In the BLAZE project, to achieve the limit specifications for all these contaminants, a finest integration of both primary (or in-bed) and secondary (or downstream) methods for gas cleaning and upgrading were considered.

The study of the performance of solutions pertaining to the first type of methods has been addressed in Task 2.3 “Gasification tests on the lab scale fluidised bed gasifier”.

2.1 Objectives and scope of the document

Deliverable D2.2 presents the activities carried out in the BLAZE project in relation to the aims of WP2 “Gasification and conditioning tests”, Task 2.3. More specifically, the activities were focused on the characterization of the gasification process in terms of overall performances and quality of the produced gas in the presence of low-value additives for gas conditioning, in accordance with in-bed/primary methods, such as calcined-dolomite and alkali carbonates (e.g. Na_2CO_3, K_2CO_3). [1-17]

Calcined-dolomite and carbonates are both known in the literature for having beneficial effects on the quality of the producer gas, in particular regarding organic and inorganic contaminants.

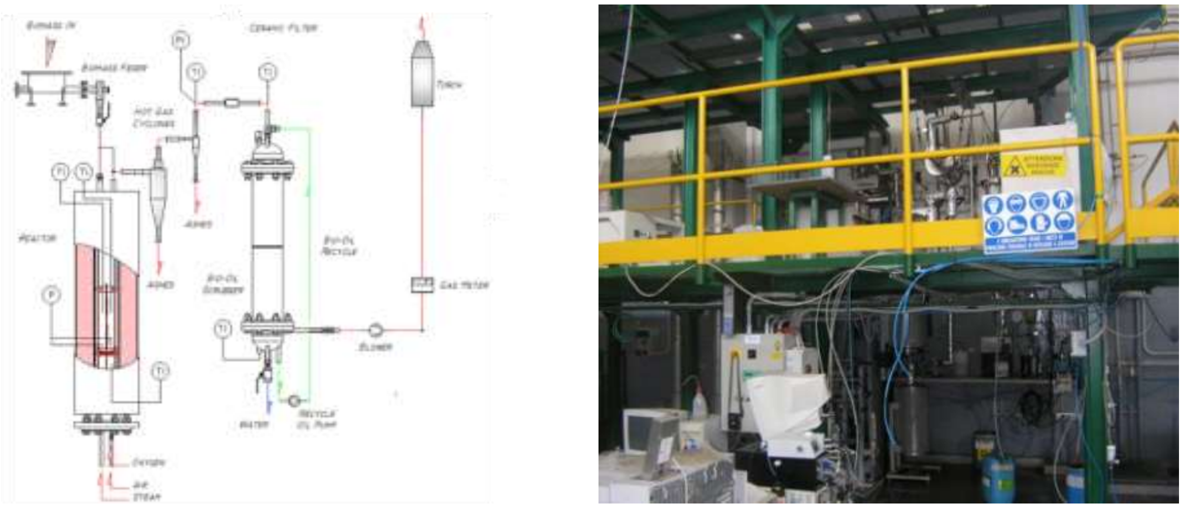
With the objective of collecting data relevant to the implementation of the gasification process in fluidized bed according to the specific approach of the BLAZE project, after some hardware modifications to the bench scale facility and checks of operability, gasification experimental campaigns were carried out on some topical biomass feedstocks. For the selection of the most interesting materials, the data of physicochemical characterizations (Task 2.2) were taken into account.

3 EXPERIMENTAL GASIFICATION TEST CAMPAIGNS

3.1 Experimental setup

The main facility of reference to carry out the activity of gasification within the aim of Task 2.3 is a bench-pilot scale gasification plant based on a Bubbling Fluidized Bed (BFB) gasifier. The reactor has an internal diameter of 134 mm and height of 791 mm. To drive the thermochemical process, several gasifying agents can be supplied (e.g. air, enriched air/oxygen, steam and their mixtures) to the reactor. From the outlet of the gasifier, the produced gas flows through two cyclones for particles removal, then get into a scrubber for tar removal. Piping and equipment from the gasifier outlet to the inlet scrubber are carefully insulated to avoid thermal dispersion and tar condensation. The plant can be operated in order to test the effect of most relevant process parameters, such as steam/biomass (S/B) and equivalence (ER) ratios. Effect of the nature of the bed inventory can be explored as well by choosing among the sand-like materials (e.g. silica sand, olivine), dolomite and their mix. The produced dry gas is measured by a gas meter located downstream the wet scrubber and analyzed on-line at a GC-TCD system for gas composition (i.e. H_2, CO, CO_2, CH_4, light hydrocarbons). Points for gas sampling are also set up on the pipelines to allow the monitoring of particulate, organic and inorganic contaminant loads (e.g. Tar, H_2S, HCl and NH_3) along the plant.

In Figure 2 an overview of the gasification test rig and plant site is presented.



a) b)

Figure 2. Bench-scale facility for feedstocks gasification in bubbling fluidized bed (BFB) reactor: a) schema of the plant, b) picture of the site.

To better match with the aim of Task 2.3, some hardware modifications were implemented to the bench-scale facility to allow a larger flexibility to the reactor feeding system with respect to the size of the particle feedstocks and to improve the particle removal section. In Figure 3 a comparison of the

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related plant section before and after the work of upgrading is presented. Cold and hot tests were then conducted to verify the operability and reliability of the structure without problems (e.g. gas leakages, feedstock feeding rate, gasifying agents feeding rate).

a) b)

Figure 3. Pictures presenting the hardware modification implemented at the feeding system of the BFB gasification plant: a) view of the section before the upgrading, b) details of the components after the upgrading

3.2 Materials and methods

3.2.1 General overview

To collect the data of relevance for the evaluation aimed in Task 2.3, two gasification experimental campaigns were planned. The first campaign was focused on the evaluation of the effects of calcined-dolomite on the quality of the produced gas in mix with olivine, bed material usually used at the bubbling fluidized bed facility, with respect to tar and inorganic contaminant loads. In the second campaign, in addition to verifying the effectiveness of the calcined-dolomite, attention was paid to evaluating the effectiveness of sorbents with known efficacy towards HCl and H_2S removal, such as Na_2CO_3 and K_2CO_3.

In all the tests carried out in the presence of calcined dolomite, a natural specimen from a local cave was adopted. To evaluate the performance of the gasification process, tests were arranged to collect data using only olivine and an olivine/calcined-dolomite mix. For this latter, according to the literature [11, 2], the olivine to calcined-dolomite ratio 70:30 by weight was selected.

The calcined-dolomite was prepared directly in-place by keeping the mixed inventory at 850 °C, starting from the natural material. The absolute amount of non-calcined dolomite to be used was calculated considering a weight loss of 47.5%, as experimentally determined at 850 °C. To facilitate the removal of

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the CO_2 produced during the Mg and Ca carbonates decomposition, the calcination process was carried out under a slight flushing of N_2. The CO_2 concentration in the N_2 stream was monitored over time and the process was considered complete when values < 0.2 %-v were observed.

Concerning the use of Na_2CO_3 and K_2CO_3, the commercially available products in powder form (purity >99 %-wt) were considered. To allow an easy handling and facilitate the dosing operation, granular materials were then prepared and, after sieving, the fraction in the range 0.85÷1.7 mm was taken. In each test a single batch of 10 times the amount required on the basis of the stoichiometric reactions [4, 1] and the amount of feedstock supplied in 1 h was added to the bed inventory before starting the feedstock supply.

As far as the biomass feedstock is concerned, in the first gasification campaign a low-grade corn grit was selected. This feedstock was chosen being already known, at the time of the tests were started, its physicochemical characteristics (e.g. proximate and ultimate analysis), and in particular its relatively high content of chlorine and sulfur, so as to facilitate the evaluation of the effect of using calcined dolomite also towards the reduction of H_2S and HCl contents in the producer gas. In the second gasification campaign two further feedstocks selected from the complete set of materials characterized in Task 2.2 were considered. In this case the selection was oriented considering the data about availability assessed in Task 2.1 and the chemical-physical properties. In accordance with the characterization data collected, feedstocks with low ash melting points were excluded, while the preference towards material with relatively high content of Cl and S was still considered as a key element to allow an easy evaluation of the performance of the primary methods adopted for in-bed gas cleaning and conditioning. In the second gasification campaign olive pomace and a secondary solid fuel (*subcoal*) were chosen.

Depending on the specific needs of evaluation, the gasification performances were evaluated by on-line and off-line measurements. Specifically, the dry gas yields were calculated on the basis of the data collected over time at a gas meter; carbon conversions were evaluated by taking into account the amount of residual char accumulated in the gasifier until the end of each test and the one accumulated in the cyclones at the exit of the reactor. The carbon in the char accumulated in the gasifier was quantified by burning the residue and evaluating the flow of CO_2 evolved during the combustion, while the carbon in the char collected in the cyclones, by the weight reduction from its burning in oven. The data of the whole material collected in the cyclones were adopted to also estimate the content of entrained particulates.

Dry gas composition was monitored online by GC-TCD analysis. Concerning the contaminant loads, the tar content was measured by sampling the gas according to the technical specification CEN/TS 15439 and evaluating concordantly the gravimetric and chromatographic (via GC-MS and HPLC technique) values. Finally, regarding the contents of inorganic contaminants, most of the species were measured by sampling the producer gaseous stream with acidic or alkaline aqueous solutions. Specifically, HCl was quantified by gas sampling in 5 %-wt NaOH solutions, while NH3 in 5 %-wt H_2SO_4; the solutions were then analyzed via high-pressure liquid chromatography (HPLC). The hydrogen sulfide, H_2S, was quantified online via a GC system coupled with a Flame Photometric Detector (FPD).

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3.2.2 First experimental gasification campaign

Data concerning the operating conditions adopted in the tests without and with calcined-dolomite, characterizing this first gasification campaign, are summarized in Table 1. The main data of chemical-physical characterization relevant to the considered biomass feedstock (i.e. low-grade corn grit) are presented in Table 2.

Table 1. Operating conditions adopted in the 1st gasification experimental campaign

Parameter	Value of reference
Equivalence ratio (ER)[a)]	0.25
Steam/Biomass (S/B, wt/wt)	0.5
Feeding rate (kg_{ar}/h)[b)]	0.8-1.0
$T_{gasif.}$ (°C)[c)]	830-850
Bed material	Olivine (OLV); Olivine/Calcined Dolomite (OLV:c-DLM = 70:30 by weight)

a) the ER parameter is defined as ratio with respect to the amount of oxidant required in a process of complete combustion;

b) the «ar» abbreviation stands for «as received»;

c) average temperature referred to the bed inventory.

Table 2. Main chemical-physical characterization of the low-grade corn grit

Parameter	
Humidity (%-wt)	5.0
Proximate analysis (%-wt)	
Ash	1.74
Volatile Matter (VM)	84.4
Fixed Carbon (FC)	14.0
Ultimate analysis (%-wt)	
Carbon (C)	46.1
Hydrogen (H)	7.3
Nitrogen (N)	1.15
Chlorine (Cl)	0.04
Sulfur (S)	0.09
Oxygen (O)	43.5
Heating Values (MJ/kg_{dry})	
Higher Heating Value (HHV)	16.31
Lower Heating Value (LHV)	15.71

3.2.3 Second experimental gasification campaign

The gasification tests carried out during the second gasification campaign used samples of olive pomace and of a secondary solid fuel (subcoal) as feedstocks. Data about their full characterization are reported in the project deliverable D2.1 «Biomass selection and characterization for small-to-medium scale gasification - SOFC CHP plants». For convenience, in Table 3 only data of ultimate analysis are recalled in order to have available the Cl and S element contents that, among others, are the most relevant with respect to the aim of this gasification campaign.

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Table 3. Data of ultimate analysis for samples of olive pomace and subcoal

Feedstock	%-wt					
	C	H	N	S	Cl	O
Olive pomace	51.8	7.1	2.8	0.06	0.08	32.1
Subcoal	53.7	9.0	2.3	0.1	1.0	18.3

The operating conditions adopted in the tests without and with calcined-dolomite, characterizing this second gasification campaign are summarized in Table 4.

Table 4. Operating conditions adopted in the 2nd gasification experimental campaign

Parameter	Subcoal	Olive pomace
Equivalence ratio (ER)[a)]	0.25	0.25
Steam/Biomass (S/B, wt/wt)	0.5	0.5
Feeding rate (kg_{ar}/h)[b)]	0.8-1.0	0.5-0.6
$T_{gasif.}$ (°C)[c)]	830-850	830-850
Bed material	Olivine (OLV)	Olivine (OLV); Olivine/Calcined Dolomite (OLV:c-DLM = 70:30 by weight)
Sorbents	--	Na_2CO_3, K_2CO_3 (addition in batch; granular form)

a) the ER parameter is defined as ratio with respect to the amount of oxidant required in a process of complete combustion;

b) the «ar» abbreviation stands for «as received»;

c) average temperature referred to the bed inventory.

4 RESULTS AND DISCUSSION

4.1 First experimental gasification campaign: olivine vs olivine/calcined-dolomite

Data collected from the gasification runs using low-grade corn grit indicated a general positive effect of the presence of calcined-dolomite compared to the tests carried out with only olivine. Specifically, in accordance with the known catalytic effect towards the tar contaminants, the organic load in the produced gas was found around 70 % lower, based on the values measured in the gravimetric mode. A significant content reduction was observed also with respect to inorganic species such as H_2S, HCl and NH_3. For these three gas contaminants the reductions were evaluated around 75 %, 20 % and 40 %, respectively. As the calcined-dolomite is more brittle to attrition than olivine, an increase in the particulate entrained by the producer gas was observed at the same time. In particular, in the gaseous stream at the exit of the gasifier, the dust content was estimated to be about 4 times higher in the test carried out with calcined-dolomite compared to test with only olivine.

An overview of the results observed in relation to the several sources of producer gas contamination is presented in Table 5.

Table 5. Overview of the removal efficiency of the calcined-dolomite towards the organic and inorganic contaminant species in the 1st gasification experimental campaign (feedstock: low-grade corn grit)

Gas contaminant	Olivine	Olivine/Calcined-Dolomite
Tar (g/Nm^3_{dry})[a)]	11.8	3.5
Particles (g/Nm^3_{dry})	1.3	5.6
HCl (mg/Nm^3_{dry})	235	180
H2S (mg/Nm^3_{dry})	150	36
NH3 (mg/Nm^3_{dry})	5000	3100

a) data referred to the gravimetric method.

Although small, effects of the use of calcined-dolomite were confirmed also throughout the data relevant to the feedstock conversion in producer gas (i.e. gas yield and carbon conversion) and its related composition. In particular, the online GC analysis indicated a change in the gas composition with a slight reduction in the content of CH_4 and light hydrocarbons with a consequent enrichment in H_2. In Figure 4 a comparison on the average composition is shown.

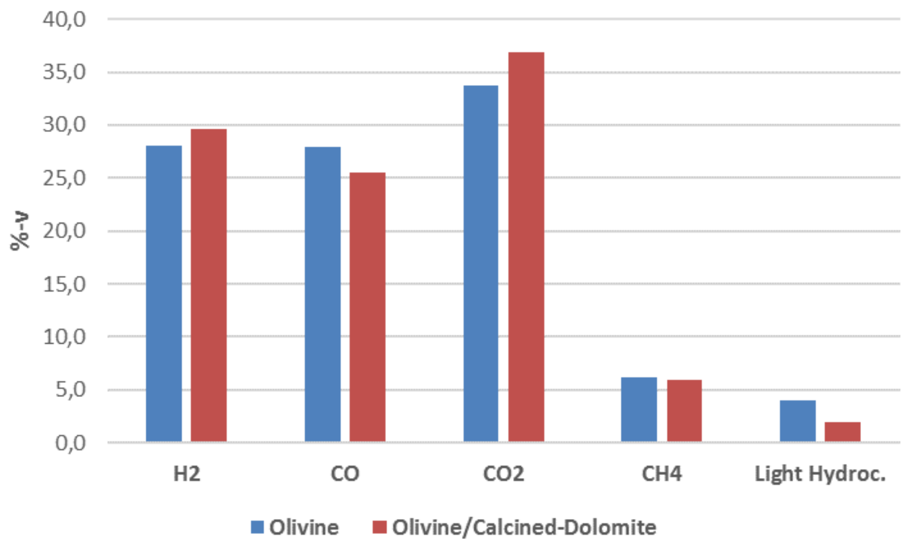

Figure 4. Comparison of the gas composition in gasification tests carried out with Olivine and with Olivine/Calcined-Dolomite 70:30 ratio, percentage by weight. Feedstock: low-grade corn grit.

In Table 6 an overview of the overall process performances is presented.

Table 6. Overview of process performances in the gasification of low-grade corn grit

Gas contaminant	Olivine	Olivine/Calcined-Dolomite
Gas Yield ($m^3_{dry}/kg_{biom, dry}$)	1.25	1.30
LHV (MJ/Nm^3_{dry})	9.2	8.7
Residual Char ($g/kg_{biom, dry}$) c)	18	16
CGE (Cold Gas Efficiency, N_2-Free; %) b)	~ 75	~ 70
Carbon Conversion (%) c)	~ 90	~ 95

a) calculated as a percentage between the unconverted carbon remained in the reactor and the carbon supplied with the feedstock;
b) calculated as: Gas Rate[Nm^3_{dry}/h]*LHV [kJ/Nm^3_{dry}]/(Biomass feeding Rate[kg_{OP}/h]*LHV [kJ/kg_{dry}])*100;
c) calculated as a percentage between the total carbon in the gaseous products (i.e. CO, CO_2, CH_4, light hydrocarbons) and the carbon in the supplied feedstock;

4.2 Second experimental gasification campaign

This experimental campaign was focused on evaluating the performance of the gasification process in a BFB gasifier in relation to the primary methods of gas upgrading (i.e. calcined dolomite and sorbents) when using the low-value feedstocks *subcoal* and olive pomace, chosen from those identified in the assessment about biomass availability (T2.1). Its main objective was to get feedbacks for a better integration with the second gas upgrading methods (i.e. HT catalytic and sorbent fixed beds), under assessment in Tasks 2.5 and T2.6, towards the overall goal of ultimately producing a syngas with specifications such as to enable a continuous and smooth operation of the SOFC unit.

4.2.1 Gasification tests of Subcoal

The second experimental gasification campaign was started using *subcoal* first. This material was supplied in pellets of standard sizes (i.e. Ø 8 mm, length < 40 mm), after a rough grinding to reduce the size at a dimension compatible with the plant feeding system, a fraction with dimensions in the range 4-8 mm was considered. During the tests the feeding system supplied the material to the reactor as expected and no screw stoppage occurred. However, the investigation with this material overall did not progress properly and smoothly; the experimentation had to be stopped several times because of unusual gasifier performances (e.g. gas composition, T_{bed}). Works of plant O&M were also required (e.g. maintenance of gasifier, dismantling of piping for inspection and cleaning).

Due to the relatively low bulk density, the material supplied probably accumulated on the surface of the bed inventory providing results not representative of a regular gasification process. In an effort to improve the dispersion of the feedstock inside the bed material, thus facilitating the interaction among the *subcoal*, the bed particles and the gasification agents, nitrogen was added to the steam/oxygen medium in order to increase the fluidization of the bed inventory. Nonetheless, the overall results did not improve very significantly the process operation, so that the trial with *subcoal* was stopped at the stage of testing with only olivine. In Table 7 a representative gas composition, on dry basis, is presented. These data were considered unreliable for tests performed in the presence of vapor, a condition where H_2/CO> 1.1 is more typical [10, 18-20]. Unusual was also the concentration of CH_4 considered relatively too high for runs carried out at temperature higher that 800 °C.

Table 7. Gas composition of the producer gas from the test with *subcoal* using olivine as bed material

Gas component	%-v (dry basis)
H_2	11.3
CO	10.9
CO_2	23.7
CH_4	8.3
Light hydroc.	< 0.2
N_2	45.7

Nevertheless, based on the collected data an estimation of the process performance was undertaken. A summary for the test with olivine in presented in Table 8.

Table 8. Overview of process performances in the gasification of *subcoal* in the presence of only olivine.

Gas contaminant	Olivine
Gas Yield ($m^3_{dry}/kg_{sc, dry}$)	1.6
Gas Yield «N2-free» ($Nm^3_{dry}/kg_{SC, dry}$)	1.0
LHV (MJ/Nm^3_{dry})	5.1
Residual Char ($g/kg_{biom, dry}$) c)	~ 20
CGE (Cold Gas Efficiency, N_2-Free; %) b)	~ 40
Carbon Conversion (%) c)	< 50

a) calculated as a percentage between the unconverted carbon remained in the reactor and the carbon supplied with the feedstock;
b) calculated as: Gas Rate[Nm^3_{dry}/h]*LHV [kJ/Nm^3_{dry}]/(Biomass feeding Rate[kg_{OP}/h]*LHV [kJ/kg_{dry}])*100;
c) calculated as a percentage between the total carbon in the gaseous products (i.e. CO, CO_2, CH_4, light hydrocarbons) and the carbon in the supplied feedstock;

According to the data on the produced gas and residual char a gas yield of 1.6 $Nm^3_{dry}/kg_{Subcoal, dry}$ and a carbon conversion in gas-phase products below 50 %-wt ($Carbon_{gas}/Carbon_{Subcoal}$) were estimated. Also in this case, considering gas yield >2.2 $Nm^3_{dry}/kg_{Feedstock, dry}$ and carbon conversion >85 %-wt as representative comparison values in similar operating conditions [16], the particularly low data confirmed a non-representative gasification process.

4.2.2 Gasification tests of olive pomace

The test with olive pomace were carried out confirming the use of a N_2 flow addition to the gasification medium in order to allow a better fluidization of the bed material and the dispersion of the feedstock particles within it. The N_2 flow was also beneficial in keeping the temperature of the bed reactor in the selected range 830-850 °C (see Table 4). Starting from the supplied raw material, in order to have a process performance as uniform as possible, a fraction in the range 1.7÷4 mm was considered. This fraction was chosen as it was the most abundant in percentage by weight (> 70 %), and therefore representative of the entire batch.

After a preliminary check on the operability of the facility with the considered fraction, the gasification experimentation was carried out in accordance with the intended programme. An overview is summarized in Table 9.

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Table 9. Overview of the gasification tests with olive pomace: additives considered and process monitoring

Characterization to performance assessment	Bed Materia		Sorbents		Method
	OLV	OLV + DLM	K_2CO_3 a)	Na_2CO_3 a)	
Gas Analysis	√	√	√	√	On-line, gas stream
Residual Char	√	√	--	--	On-line (@end of test)
Entrained particulate	√	√	--	--	Off-line, cyclones
Tar	√	√	--	--	Off-line, Isopropanol sampling solution
HCl	√	√	√	√	Off-line, NaOH water solution
H_2S	√	√	√	√	On-line, gas stream
NH_3	√	√	--	--	Off-line, H_2SO_4 water solution

a) The sorbent was added in batch mode per amounts corresponding to 10 times the value required on the basis of the stoichiometric reactions and the amount of feedstock supplied in 1 h.

4.2.2.1 Overview of the process performances

About gas yields, residual char and carbon conversion, all experimental data gave evidence of the beneficial effect of the use of calcined-dolomite in improving the overall process performance as it can be inferred by the comparison of data presented in Table 10

Table 10. Overview of process performances in the gasification of olive pomace

Parameter	OLV	OLV + c-DLM
Gas Yield (Nm^3dry/$kg_{OP, dry}$)	2.1	2.3
Gas Yield «N2-free» ($Nm^3_{dry}/kg_{OP, dry}$)	1.2	1.4
Residual Char (%) a)	~ 10	< 5
CGE (Cold Gas Efficiency, N_2-Free; %) b)	50-60	> 70
Carbon Conversion (%) c)	85-90	> 95

a) calculated as percentage ratio between the carbon remained unconverted in the reactor and the carbon supplied with the feedstock;
b) calculated as: Gas Rate[Nm^3_{dry}/h]*LHV [kJ/Nm^3_{dry}]/(Feeding Rate[kg_{OP}/h]*LHV [kJ/kg_{dry}])*100;
c) calculated as percentage ratio between the total carbon in the gaseous products (i.e. CO, CO_2, CH_4 and light hydrocarbons) and the carbon in the supplied feedstock;

Effect of the presence of calcined-dolomite was gathered also from the composition of the producer gas based on the permanent gas component (Table 11).

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Table 11. Gas composition of the producer gas from the test with olive pomace using olivine and olivine/calcined-dolomite mix (70:30 %-wt) as reactor bed materials

Gas Component	%-v, dry basis	
	OLV	OLV + c-DLM
H_2	18.2	18.0
CO	15.1	14.0
CO_2	22.1	20.2
CH_4	5.5	4.9
Light hydroc.	2.2	2.2
N_2	37.0	41.0

The data collected via GC analysis indicated an H_2/CO ratio of 1.2 and 1.3, in tests with only olivine and with olivine in mix with calcined-dolomite, respectively. These values are significantly higher than 1 as expected, being the gasification carried out with steam and in the presence of a catalyst, i.e. calcined-dolomite, able to promote reaction of tar reforming and cracking. On a N_2-free basis, the data in Table 11 also revealed a slightly reduction in the CH_4 content.

Finally, in accordance with the known higher brittleness of the calcined dolomite compared to the olivine, the experimental measurements on the entrained particulate content have provided a dust content about double when using the olivine/calcined-dolomite mix bed inventory (i.e. about 0.5 vs 1 g/Nm^3_{dry}) compared to only olivine.

4.2.2.2 Efficiency in contaminant removal

The evaluation of the removal efficiency of the several type of contaminant are summarized in Table 12. The data are compared with the values related to the gasification of olive pomace carried out using only olivine as reactor bed material.

Table 12. Overview of the removal efficiency of the Na_2CO_3, K_2CO_3 and calcined-dolomite towards the organic and inorganic contaminant species.

Gas Contaminant	OLV	Removal eff. (%)		
		OLV + K_2CO_3	OLV + Na_2CO_3	OLV + DLM
HCl (mg/Nm^3_{dry})	390	~ 40	~ 45	--
H_2S (mg/Nm^3_{dry})	280	~ 35	--	> 90
NH_3 (mg/Nm^3_{dry})	4100	--	--	> 10
Tot Tar - Chromatographic (g/Nm^3_{dry})	23.0	--	--	~ 40
Tot Tar - Gravimetric (g/Nm^3_{dry})	11.0	--	--	> 25

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K_2CO_3 and Na_2CO_3 are known in the literature as elective sorbents for HCl mainly, although a certain effectiveness is also recognized towards H_2S [4, 3]. The data in Table 12 give confirmation on that direction indicating a better efficacy of the Na_2CO_3 compared to the K_2CO_3. Nonetheless, a very significant removal efficiency towards H_2S (>90 %) was shown by the calcined dolomite.

A certain effectiveness of dolomite was also found against the NH_3, though in this case the reduction appeared relatively low (around 10 %).

As far as the gas contamination due to the production of tar molecules is concerned, the effectiveness of the use of dolomite was evidenced, and quantified in order of magnitude, by the chromatographic and gravimetric values. In particular, the chromatographic identification and quantification of single molecules, revealed benzene and toluene as the most abundant aromatic compounds, together accounting up to 50 %-wt of the total value. Among the compounds with more than one ring, indene and naphthalene were found to be the most abundant, representing about 25-27 % of the total. By the use of calcined-dolomite the amounts of benzene and naphthalene turned out to be about 20% lower, while for toluene and indene the percentages of reduction exceeded 40 % and 70 %, respectively.

Via GCMS analysis, some N- and and S- containing compounds were also considered (i.e. pyridine, quinoline, benzothiophene and dibenzothiophene). The N-aromatic compounds accounted for about 150 mg/Nm^3_{dry}, while the S-aromatics for about 20 mg/Nm^3_{dry}. By using calcined-dolomite their contents were reduced by more than 50 %.

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5 CONCLUSIONS

Overall, the experimental activity carried out in relation to the use of additives (i.e. calcined-dolomite and alkali carbonates) for in-bed applications in reducing the contaminant load in the producer gas has given significant responses. The achieved results indicated their usefulness and provided confirmation about the opportunity to their implementation at the pilot scale stage, together with the downstream solutions focused in Tasks 2.4, 2.5 and 2.6, in order to meet the level of contaminant contents in the produced gas low enough to ensure a long lasting operation of the SOFC unit.

At the same time, the experimental results indicated that, to some extent, the global process performances are related to the nature of the specific feedstock to be gasified. This suggested the need of a certain adjustment of the process conditions based on the feedstock, in order to achieve an in-bed conditioning as effective as possible.

Specifically, under the experimental conditions adopted in the first and second gasification campaigns, the tests carried out with and without calcined-dolomite confirmed a general beneficial effect on the overall gasification performances in terms of improvement of conversion of the feedstocks into gas products, although to the detriment of a gas with a higher dust content.

By the use of calcined-dolomite, in combination with olivine (30:70 %-wt), the most relevant and positive results were achieved towards the reduction of the contaminants, both organic and inorganic, in the producer gas. Regarding the inorganic compounds, the experimentation indicated that to achieve a more effective in-bed gas cleaning action, and thus address to the downstream sections of refining a producer gas as clean as possible, the feedstock gasification should be carried out also in the presence of alkaline carbonates (i.e. Na_2CO_3, K_2CO_3), being these salts able to give an important contribution in reducing HCl and H_2S.

As far as the tar content is concerned, the experimental results suggested that the ultimate achievement is not only influenced by the process conditions adopted, but to a certain extent also by the specific feedstock processed, as indicated by the reductions achieved (on a weight basis) in the case of the low-grade corn grit and olive pomace.

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