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# Gassificazione del carbone in letto fluido di olivina alimentato da miscela H2O/O2: caratterizzazione del materiale granulare

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Report RdS/PAR2013/261

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Report Ricerca di Sistema Elettrico
Accordo di Programma Ministero dello Sviluppo Economico – ENEA
Piano Annuale di Realizzazione 2013
Area: Produzione di energia elettrica e protezione dell'ambiente
Progetto: Cattura e sequestro della CO2 prodotta da combustibili fossili
Parte A
Obiettivo a: "Tecnologie innovative per la cattura della CO2 in pre-combustione, con produzione di combustibili gassosi"
Task a.2 : Sperimentazione del ciclo di assorbimento sulla piattaforma ZECOMIX "
Responsabile del Progetto: Stefano Giammartini, ENEA

Sommario: L'unità di gassificazione della piattaforma ZECOMIX , contenente un reattore a letto fluido, è stata testata mediante gassificazione del carbone con miscela vapore acqueo/$O_2$. Un carbone antracitico sudamericano è gassificato a circa 850 ° C con rapporto unitario di vapore acqueo / $O_2$, mentre come materiale fluidizzante è stata scelta olivina naturale. Due prove sperimentali sono state condotte per valutare la ripetibilità dei risultati. Il flusso di gas all'uscita del reattore viene campionata attraverso una sonda di campionamento del gas riscaldato e filtrato prima di misurazioni gas cromatografiche in linea di $H_2$, CO, $CO_2$ e $CH_4$. La composizione media del syngas prodotto tra le due prove varia nell'intervallo di concentrazione 38-43 $H_2$, 38-39 CO, 19-22 $CO_2$, e 1-3 $CH_4$ vol.% su base secca, mentre la ripetibilità è entro il 15 vol.%. Il materiale rimanente nel letto del reattore è composto da agglomerati di ceneri e olivina e particelle di char residuo. Il particolato fine (dimensione inferiore a 250 micron), separata dal gas di scarico attraverso il ciclone, è principalmente composto di char non reagito.

I risultati della presente sperimentazione sono stati oggetto di una recente pubblicazione su rivista scientifica. Pertanto si riporta in allegato il suddetto articolo.

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# Steam-$O_2$ Coal Gasification in the Italian ZECOMIX Bubbling Fluidized Bed Gasifier Unit: Spent Bed Material Characterization

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**Abstract:**

Steam-$O_2$ coal gasification in bubbling fluidized bed gasifier of the Italian ZECOMIX platform has been tested. A South American anthracite coal is gasified around 850 C using steam/carbon ratio near unity and catalytic olivine as bed material. Two experimental runs are conducted to assess the repeatability of gathered results. The gas stream from the reactor exit is sampled through a heated and filtering gas sampling probe and dried before on-line gas chromatographic measurements of $H_2$, CO, $CO_2$, and $CH_4$ non-condensable gases. The product gas can be monitored stand alone during a very long-term. The mean composition of the producer syngas between two runs varies in the range 38-43 $H_2$, 38-39 CO, 19-22 $CO_2$, and 1-3 $CH_4$ vol.% on dry basis, whereas repeatability is within 15 vol.%. The solid matter remaining in bed reactor is composed by bottom-ashes, spent olivine with some agglomerates and coarse residual char particles. Fine particulates (size less than 250 µm) separated from flue gas through cyclone process, is mainly composed of unreacted char.

**Keywords:**

Bubbling Fluidised Bed; Olivine Agglomeration; Steam-oxygen Coal Gasification; Spent Bed Material Analysis; Zecomix Platform

## 1. INTRODUCTION

Gasification represents nowadays a sustainable and environmentally benign technology for the conversion of solid fuel to synthesis gas (syngas), because emissions of many pollutants and particulates can be noticeably reduced compared to conventional conversion process such as combustion. Although the gasification process is an old concept the application and commercialization of gasifiers in large-scale plant is still not feasible. Coal-derived syngas with low impurities content and high heating value (HHV) is advisable for the direct generation of electrical power [1]. In particular, steam coal gasification produces high calorific gaseous products. Steam coal gasification is an endothermic process that generates a gaseous mixture composed mainly of $H_2$, CO, $CO_2$, and $CH_4$ depending on coal type and operative conditions [2]. The heat needed for gasification process is provided by partial oxidation of coal with air or oxygen, the so-called "autothermal gasification". When using pure oxygen a product gas with higher $H_2$ content and HHV can be reached because the dilution by inert nitrogen is avoided. However, a cost-penalty is derived from the need of using the ASU unit (air spearation unit). The $N_2$-free syngas yield is further downstream enriched in $H_2$ via methane steam reforming (MSR) and water gas shift (WGS) reactions.

Coal gasification in bubbling fluidized beds (BFBs) can be advantageous owing to good mixing of solids, rapid heat transfer between solids and gas stream, nearly isothermal conditions along the reactor and lower operating temperatures [3]. Moreover, bed materials can also play a role of catalyst for cracking of organic condensable by-product, the so-called "tar", thus the product gas purity can be noticeably improved [4]. However, the major obstacle encountered in the use of BFBs lies in bed grain agglomeration phenomenon, especially with feedstock containing alkali-rich ashes, which can cause shutting down the fluidized bed [5].

The formation mechanism of bed material agglomerates is supposed to occur through: i) molten ashes that are bonded to particles by necks and/or ii) fusion of ash-coated bed material particles [6]. Some operating conditions such as fluidization velocity, bed temperature, and fuel feeding rate can affect agglomeration of bed materials and provoke defluidization owing to the formation of large agglomerates within the bed [7]. Low-cost, naturally-occurring minerals such as dolomite, limestone, and olivine have been employed in catalytic conversion of solid fuel [8, 9]. Although dolomite is considered to be an active catalyst for tar removal, unfortunately it undergoes to attrition phenomenon, which generates a raw gas with high content of particulate. Iron-based olivine presents less attrition problems, whose behavior resembles that of conventional inert silica sand bed material [10]. The catalytic activity of olivine in tar-removal is considered to be connected to the iron part of mineral [11]. Olivine contributes in general to the conversion as solid that catalyzes the gas-gas reactions [12]. The olivine catalytic properties have been reflected in promoting WGS reaction. Specifically, calcined olivine has noticeably improved the CO shift reaction [13].

In the present paper the performance evaluation of the BFB gasifier unit operating within the Italian ZECOMIX (Zero Emission of CarbOn with MIXed Technologies) platform for $H_2$ production and electricity generation is described. The platform is conceived to operate each unit standalone. In our previous work on testing the performance of carbonator/calciner BFB reactor for absorption/desorption $CO_2$ chemical loop on solid absorber dolomite the analytical systems and sampling points and lines to obtain analytical results were presented [14]. The present paper relates on steam-$O_2$ coal gasification using a South American semi-anthracitic coal and mineral olivine as bed material in a BFB at a given set of conditions. The flue gas from the BFB reactor exit was monitored on-line by GC. Post-test analysis has been carried out on spent bed materials by several classical analytical techniques in order to establish agglomeration of olivine and the extent of remaining ungasified char.

## 2. EXPERIMENTAL

## 2.1 Samples and characterization

Raw coal. The coal used was anthracite coal from Venezuela country. The particle size distribution of coal varied between 1000 and 6000 µm.

Fresh bed material. The bed material for fluidizing medium consisted of olivine $(MgFe)_2SiO_4$ from quarry of Biella (Italy), a locality in the foothills of Alps. Olivine had a mean particle size of 500 µm with apparent density of 2300 kg ·m $^{3}$.

Used bed material. Spent olivine, residue chars, and ashes were separated by mechanical sieving. Particle size distribution (PSD) was carried out by mechanical sieving using ASTM sieves between 90 and 2800 µm. The amount of separated solid matter was given in a weight ratio (wt.%, db) to feedstock throughput.

Proximate analysis was carried out according to ASTM E1131 Test method by instrumental procedures.

Elemental analysis (C, H, N, S) was conducted by LECO TruSpec analyzer according to ASTM D 5373-08 and ASTM D 4239-08 Test method.

Thermogravimetry (TG). TGA/DSC 1 STARe System analyzer (Mettler-Toledo, Switzerland) was used to continuously monitor weight changes in different samples due to drying, pyrolysis, volatilization and combustion.

TG-FTIR. The raw coal was submitted to TG-FTIR analysis to check the degree of reactivity. The TG was coupled to the Fourier transform infrared spectrometer (FTIR Varian 640) through a heated stainless steel transfer line. FTIR measurements were recorded in the wavenumber range of 4000-400 cm $^{1}$ with a resolution and sensitivity of 4 cm $^{1}$ and 1.5, respectively. The dynamic evolution curves of the emitted gases were constructed as absorbance (integrated absorbance) versus time at a given characteristic band.

## 2.2 Gas sampling points, sampling lines and analytical instrumentations

Gas chromatograph. Agilent 6850 gas chromatograph-TCD detector equipped with two columns connected in series, namely, Molesieve 5A for permanent gases ($H_2$, $N_2$, $O_2$, CO, and $CH_4$) and Hayesep Q for $CO_2$ was used. Quantification was made by GC Chemstation software (Agilent) according to the predefined method. Prochem software by S.R.A. Instruments (Milan, Italy) allowed to communicate with ABB Control and Data Acquisition Systems (SCADA), withdrawn gas sample from different sampling lines according to preset measurement sequence and compute reports created by Chemstation in final mole fraction. Remote control connection was made by VNC software. The GC was calibrated with reference gas (Air Liquid, France) supplied by high pressure cylinders before the start and after the end of gasification test. The ratio between sample peak area and the bracketing reference peaks was used to calculate gas volume %.

FTIR. Gasmet DX-4000 portable gas analyzer was used to monitor the exhaust gas produced from methane combustion.

Gas sampling probe and sampling lines. An Inconel sampling probe with filter was used to entrap solid particles from downstream gas. The sampling probe and connected lines were heated electrically up to 300 C to avoid condensation of organic matter. The filter was composed of quartz wool. Figure 2 shows the picture of filter after runs. It can be seen that the amount of dust entrapped by filter is very low.

Figure 1. Photograph of sampling probe in sampling point V2

## 2.3 Gasifier unit

A schematic diagram of gasifier unit of ZECOMIX platform is shown in Figure 3. The experimental gasification tests were conducted in a bubbling fluidized bed (BFB). The rectangular stainless steel reactor had a height of 3.5 m and two cross sectional surface area whose smaller base area was 0.38x0.36 m through which the fluidizing/gasification medium is injected. The oxygen contained in a cryogenic vessel is heated up via a electrical heat exchanger up to 150 C. The water steam is generated in a boiler by a heat exchanger using the combustion gases of methane. The analysis of combustion fumes were monitored on line through the sampling point V1 by FTIR analyzer. The bed material was heated up in the combustion zone. The coal is fed above the material bed by a screw-type feeding at a fed rate (revolution per minute RPM) controlled via a distributed control system. The produced fuel gas was depulverized in the cyclone and scrubbed in two spray water columns. Then the syngas is burnt in a flare. The coarser bed-ashes accumulated into bed are drained directly via a rotary valve from the bed when needed. The gas leaving the cyclone was intercept by a heated stainless steel tube connected to sampling probe (sampling point V2), which through a heated sampling line was connected to GC.

Figure 2. Photograph of filter of sampling probe after runs

## 2.4 Gasification test procedure

Two gasification tests were conducted at one week temporal distance and without discharge solid matter from the first run. In the second run only raw coal was fed into reactor. Therefore, the bed material was composed by spent olivine along with eventually unreacted char and bottom ashes. In a typical run approximately 200 kg of olivine was fed into reactor when the temperature was around 500 C. The fluidization medium was air at 120 kg h $^{1}$ flow rate. When the pressure drop through the solid bed material was fairly stable coal was introduced via the gravity feeding system at 8 kg h $^{1}$ flow rate. Then the auxiliary methane combustor was turned off and coal was combusted by the oxygen content of the fluidizing agent. When temperature in the bed reached about 700 C the air flow rate was slightly decreased and oxygen and steam were introduced at 25 kg h $^{1}$ flow rates (total mixture: 50 kg h $^{1}$). The temperature during the gasification test was approximately 850 C. The spent olivine, residue char and ashes generated during the two experimental tests were discharged from both the reactor and cyclone and then submitted to characterization in laboratory by common analytical methods.

# 3. RESULTS AND DISCUSSION

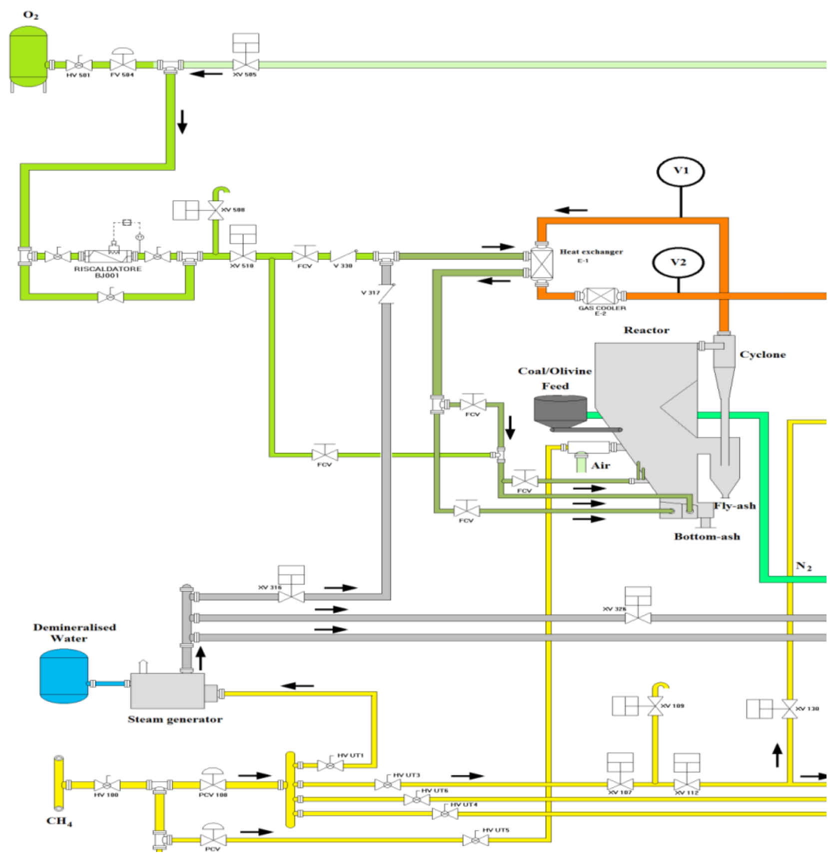


Figure 3. Schematic drawing of gasifier unit of ZECOMIX plant

Table 1. Main chemical reactions in reactor gasifier

| No | | Chemical reaction | $DH_{298K}$ / kJmol$^{1}$ |
|---|---|---|---|
| 1 | Partial combustion | $C+1/2O_2=CO$ | +123 |
| 2 | Combustion | $C+O_2=CO_2$ | +409 |
| 3 | Pyrolysis | Coal+heat=$(H_2+CO+CO_2+H_2O+CH_4+C_nH_m)_{(g)}+tar_{(l)}$ | |
| 4 | Boudouard | $C+CO_2=2CO$ | -173 |
| 5 | Water gas (primary) | $C+H_2O=H_2+CO$ | -131 |
| 6 | Water gas (secondary) | $C+2H_2O=2H_2+CO$ | -76 |
| 7 | Water gas shift | $CO+H_2O=H_2+CO_2$ | -42 |
| 8 | Methanation | $C+2H_2=CH_4$ | +75 |

## 3.1 Steam-$O_2$ coal gasification

The main chemical reactions taking place in the reactor during steam-$O_2$ coal gasification are reported in Table 1. The necessary heat for steam gasification is provided by oxidation reactions (1) and (2). It can be supposed that the complete combustion occurs very rapidly in limited zone of gasifier. The coal injected in the feeding gasifier zone entered in contact with preheated fluidized olivine bed and instantaneously is pyrolysed according to the reaction (3). The primary and secondary pyrolysis by-product could be neglected as an anthracite coal with a very low volatile matter content is used in order to avoid influence

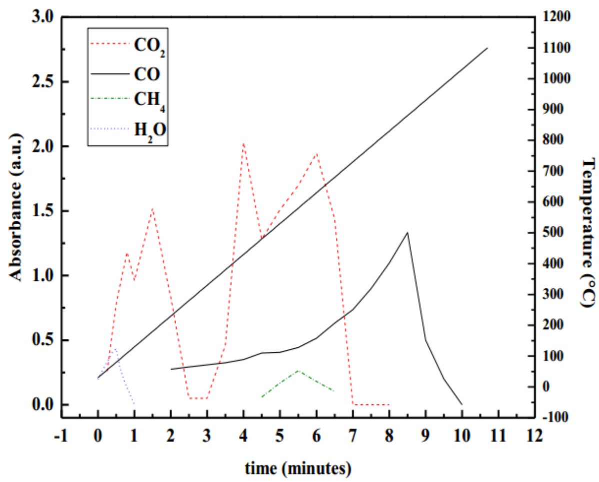


Figure 4. Evolved gases during $N_2$-pyrolysis of Venezuelan coal from TG-FTIR

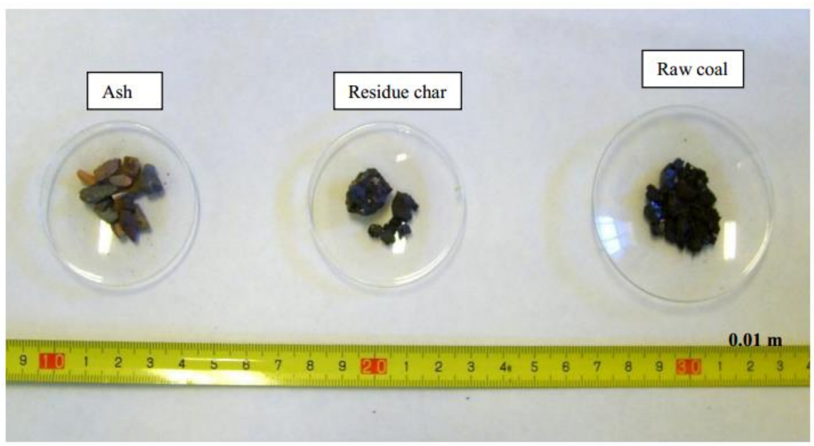


Figure 5. Photographs of raw coal, residue char and ash from bottom reactor

of tar formation in the gas stream product. Moreover, steam and oxygen can have a positive effect in destroying tar [15]. The solid char product from (3) (for the sake of simplicity containing only C) is subjected to participate to several heterogeneous and homogeneous chemical reactions through (4)-(8). The gasification processes have had duration of approximately 150 minutes. The mean composition of syngas of two runs varies in the range 38-43 $H_2$, 38-39 CO, 9-22 $CO_2$, and 1-3 $CH_4$ vol.% on dry basis, whereas repeatability is within 15 vol.%. Under steam-$O_2$ gasification conditions the synthesis gas product has a high $H_2$ content owing to the $N_2$-free producer gas. Moreover, this high $H_2$ concentration in the product gas could be a consequence of instauration of WGS reaction (7), which is favored by olivine. The high value of CO could also come from reaction (4) [16]. The reactivity of fresh char versus $CO_2$ gas has been evidenced during $N_2$-pyrolysis of Venezuelan coal studied by TG-FTIR. The absorbance/time profiles of evolved gases are showed in Figure 4. From this results it is evident that with the raising of temperature CO emissions continuously increased and reached the maximum intensity around 800 C, which can be due to in situ gasification (Boudouard's reaction) of the nascent char exposed to freshly formed $CO_2$.

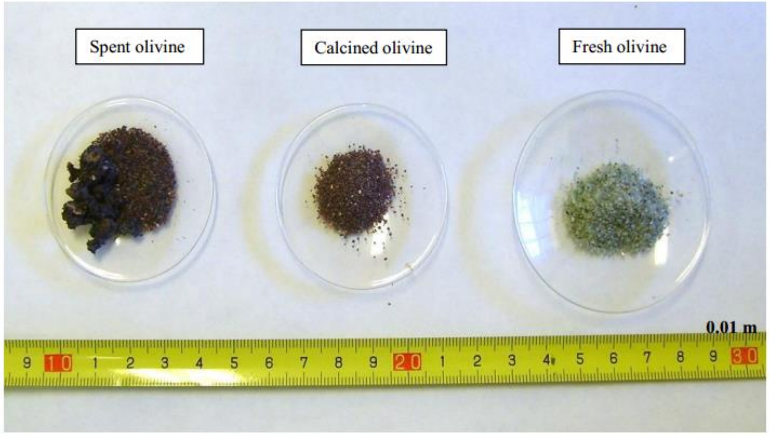


Figure 6. Photographs of raw olivine, calcined olivine and spent olivine from bottom reactor

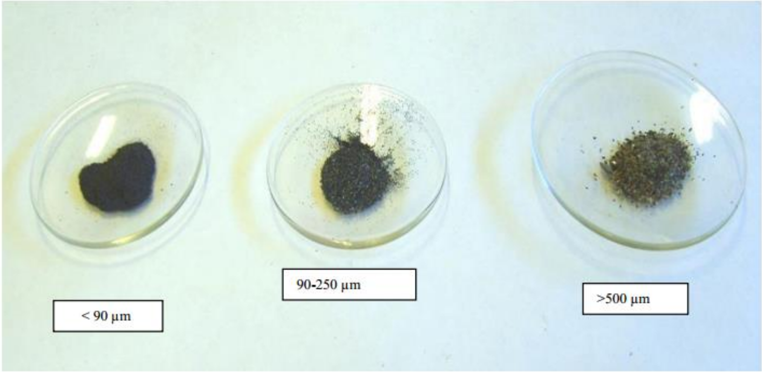


Figure 7. Photographs of sieved fine unreacted chars from cyclone

## 3.2 Post-test analysis of spent bed materials

The proximate and elemental analysis results of different samples are listed in Table 2, whereas the PSD of sampled matter from bottom reactor and cyclone are listed in Table 3. Residue char is an undesirable by-product of gasification process, which could indicate low carbon conversions. The photographs of collected matter discharge at bottom of reactor and separated by mechanical sieving are shown in Figures 5- 6. Product char pieces (particle size >2800 µm) and bottom-ashes have been distinctly separated from spent olivine along with its aggregates. For comparison purpose raw coal, fresh olivine and olivine, which has been calcined in an oven at 900 C for two hours in static air, are also showed. The used olivine as bed material in BFB reactor was clearly indicated by the change in color from green-grey to brown-reddish color, which is note to occur in air-calcined olivine [17]. Apart from residue char and bottom-ash the sieved bed material sampled from reactor is composed of spent olivine, which has particle sizes ranging between 90 and 500 µm and mass fractions between 1.5 and 54 wt.%. Compared to fresh olivine the mass fraction remains essentially unchanged: only a small fraction between 250 and 90 µm (1.5 wt.%) and below 90 µm (0.5 wt.%) are found, which are assumed to result from solid attrition during about 300 h gasification operation. This result is in accordance with the general consensus that olivine is a material highly resistant to attrition. A few olivine agglomerates with grain sizes around 2000 µm are found.

Table 2. Proximate analysis and elemental analysis of raw coal and residue chars from bottom reactor and cyclone

| Proximate, wt.% | Moisture | | Volatile matter | Fixed carbon | Ash |
|---|---|---|---|---|---|
| Raw coal | 2 | | 4 | 86 | 8 |
| Reactor Coarse | 1 | | - | 18 | 81 |
| (>2800 µm) Cyclone | | | | | |
| >500 µm | - | | - | 2 | 98 |
| 250-90 µm | 3 | | 3 | 67 | 27 |
| <90 µm | 1 | | 3 | 47 | 49 |
| Elemental wt.% d.b. | C | H | N | S | O* |
| Raw coal | 85 | 2.0 | 0.6 | 0.4 | 4 |

* Oxygen content calculated by difference method. [O] = 100- C- H- N- S- ash.

Table 3. Bed material inventory (mass fraction, wt.%)

| Particle Size Range (µm) | Fresh olivine | Reactor | | Cyclone |
|---|---|---|---|---|
| | | Residue char | Spent olivine | |
| >2800 | - | 1 | - | - |
| >500 | 66 | - | 54 | 26 |
| 250-500 | 33 | - | 43 | 3 |
| 250-90 | 1 | - | 1.5 | 27 |
| <90 | | - | 0.5 | 44 |

The presence of iron oxides, magnesium oxides, and silicates in the bed material leads to high melting point compounds with alkali metal of ashes, thus avoiding the formation of viscous salts responsible of agglomeration feature [18]. However, the agglomeration effect of bed material is heavily dependent on the operating temperature within the bed [5].

The fines captured by cyclone have a particle size typically <500 µm for more than 70 wt.% mass fraction (Table 3). Figure 7 shows photographs of different mechanically sieved fine particles. These solid matters are basically composed of unreacted char as it is showed by the results of proximate analysis (Table 2). The mass fraction with particle size above 500 µm is composed by fly-ash deposit. By plotting the fixed carbon content versus the ash content a linear relationship is found with correlation coefficient R2 better than 0.999. Owing to the low content of volatiles the inner pressure of particles during coal devolatilization is low, therefore formation of fine particulate entrained by the yielded flow gas could be derived from attrition with solids.

## 4. CONCLUSION

Two runs in the Italian ZECOMIX BFB gasifier unit were conducted for the steam-oxygen coal gasification. The fluidizing medium has been naturally occurring olivine with mean particle size of 500 µm. The gasification process was monitored on-line by GC. The mean composition of the producer syngas between two runs varies in the range 38-43 $H_2$, 38-39 CO, 19-22 $CO_2$, 1-3 $CH_4$ vol.% on dry basis, whereas repeatability is within 15 vol.%. Post-test analysis of solid matter from bottom reactor and cyclone indicated that olivine was prone to non significantly attrition effect and grain aggregation of bed material was at low level. Fine unreacted char from cyclone was indicative of coal particle attrition between solids.

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