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Fe/olivine catalyst for biomass steam gasification: Preparation, characterization and testing at real process conditions

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ABSTRACT

Continuous steam gasification of biomass is carried out in a fluidized bed reactor with the utilization of 10 wt%Fe/olivine catalyst. The volume composition of the product gas is analyzed by means of IR, UV and TCD for online detection of CO, CO_2, CH_4, H_2, NH_3 and H_2S.

The results obtained have been evaluated with reference to a blank test (olivine bed inventory) performed with the same experimental rig: when 10 wt%Fe/olivine is utilized in the gasifier, the gas yield increases on average by 40% and the hydrogen yield by 88%. Correspondingly, the methane content in the syngas is reduced by 16% and tar production per kg of dry ash free (daf) biomass by 46%.

10 wt%Fe/olivine characterization after test shows that the catalyst is fairly stable.

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1. Introduction

Among different ways technically feasible for biomass energy conversion, gasification is considered a valid process option, to obtain a fuel gas composed of hydrogen and carbon monoxide usable for different applications. More than 70% by weight of biomass produces volatile compounds when it is pyrolysed, and this in fact makes convenient its thermal conversion in a valuable fuel gas that can generate electric power by means of internal combustion engines or fuel cells, with overall process efficiencies ranging from 25% to 40%, in addition to heat.

To increase the efficiency of the utilization of thermal and chemical energy of the produced gas, it is necessary to reform the high molecular weight hydrocarbons (tar), since the presence of tar means lower gas yields. Tar deposition could also block gas coolers, filter elements and engine suction channels, and interferes with catalysts performance [1]. In addition, tar separation is sometimes not as effective as it should be, and originates waste streams difficult to dispose or recycle properly.

The yield of these undesirable gas contaminants can be reduced by careful control of the operating conditions, appropriate reactor design and a suitable gas conditioning system [2].

A large number of investigations deals with biomass gasification in fluidized bed reactors utilizing dolomite ($(Ca, Mg)CO_3$) or olivine ($(Mg, Fe)_2SiO_4$) [3,4]. Olivine, a natural occurring mineral, demonstrates tar conversion activity similar to that of calcined dolomite, with the advantage of higher mechanical strength, and it has been applied as a primary catalyst to reduce the output tar levels form fluidized bed gasifiers [5,6].

The application of Ni/olivine catalysts in steam gasification has been largely investigated, as they are very effective in terms of tar conversion to hydrogen-rich gas [7–9]. The same synthesis methodology can be applied to other transition metals like cobalt, copper or iron.

It has been recently demonstrated that olivine activity, or more specifically olivine activation, depends on its iron oxides content [10]. In fact, depending on olivine temperature treatment, iron can be present in the olivine phase, or as iron oxides [11]. Thus, iron impregnation of natural olivine appears as a very interesting way to produce in-bed primary catalysts, for both economic and environmental reasons. Iron does not affect the catalyst cost due to its lower price in comparison to nickel. Moreover, the fines particles separated from the product gas, can be easily disposed due to the absence of carcinogenic metals such as nickel compounds. A Fe/olivine catalyst has been developed and its activity evaluated in comparison to olivine in steam reforming of toluene (as tar model compound) [12].

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In the present work, a Fe/olivine catalyst with relative high metal content (10 wt%) has been tested at real fluidized bed gasification conditions [12].

Tests with 10 wt%Fe/olivine in the gasifier bed inventory have been carried out to check the gas purity resulting from the effect of cleaning and conditioning the syngas. Comparison with blank tests allows the assessment of 10 wt%Fe/olivine performance against olivine. Instantaneous gas yield and composition, tar content, carbon conversion, etc., have been monitored to characterize each test. Mass balances have been utilized to verify the compatibility and reliability of measured data. The influence of operating parameters has been explored. 10 wt%Fe/olivine has been characterized before and after the gasification tests by X-ray Diffraction (XRD), Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO).

2. Materials and methods

2.1. Experimental apparatus and gasification method

Continuous catalytic steam gasification of biomass has been performed using a bubbling fluidized bed gasifier with an internal diameter of 0.10 m, in a temperature range of 800–830 °C.

A sketch of the laboratory gasification plant is reported in Fig. 1. Details concerning the plant configuration have been provided in a previous publication [13].

The gas quality is monitored in terms of gas yield and composition (H_2, CO, CO_2, CH_4, and H_2S) as functions of the operating time, and average tar content.

The biomass feedstock consisted of crushed and sieved almond shells with average particle size of 1054 μm. The elemental analysis of the biomass has been reported elsewhere [13]. The fluidized bed consisted of 3 kg of 10 wt%Fe/olivine catalyst, with an average diameter of 393 μm, and particle density of 2500 kg/m^3. The catalyst particle density has been measured by comparing the bulk densities of the olivine and catalyst particles, assuming the same bulk void fractions.

The overall gasification conditions are reported in Table 1. The fluidizing gas consists of a nitrogen/steam mixture. Nitrogen is supplied to help a smooth feeding of biomass particles and to stabilize the flow. In test IV, nitrogen is supplied at the minimum possible rate (compatible with that needed to assure a smooth biomass feeding rate), in order to obtain the greatest possible concentration of reactants in the gasifier bed.

The biomass feeding rate is kept constant during each test to avoid pressure fluctuations.

At the end of each test, the quantity of char produced by gasification is determined by the analysis of CO_2 and CO in the exit gas obtained by burning under air stream the whole carbonaceous residue trapped into the gasification rig.

2.2. Preparation and characterization of Fe/olivine catalyst

2.2.1. Catalyst synthesis

A sufficient quantity of 10 wt%Fe/olivine catalyst has been synthesized by using an optimized method of impregnation. Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), in an appropriate quantity to assure an iron content of 10 wt%, was dissolved in an optimized amount of water by heating. About 25 kg of olivine was added to the iron aqueous solution and the water excess was quickly evaporated under vacuum by heating at 90 °C. The sample was dried inside the tank, then overnight inside an extractor hood, before to be calcined at 1000 °C over 4 h (temperature heating rate of 3 °C/min).

In order to validate the synthesis method, characterizations have been performed on the catalyst prepared from large scale synthesis and the results compared to those obtained with the catalyst synthesized at laboratory scale (10 g) [14].

2.2.2. Methods of characterizations

X-ray Diffraction (XRD) patterns were acquired with a Brucker AXS-D8 advanced using Cu Kα radiation, the diffraction spectra have been indexed by comparison with the JCPDS (Joint Committee on Powder Diffraction Standards) files.

Temperature Programmed Reduction (TPR) allows the evaluation of catalyst reducibility by a flow of 3.85% of hydrogen in argon (total flow of 52 mL min^{-1}) on 50 mg of sample. The temperature was increased at a speed of 15 °C min^{-1} from room temperature to 900 °C. A thermal conductivity detector is used to analyze the effluent gas for a quantitative determination of hydrogen consumption.

The amount of carbon deposited on catalyst after reactivity tests can be determined by the quantification of the oxidation products (CO_2) observed during temperature programmed oxidation (TPO) by a Mass Spectrometer (Quadrupole Pfeifer Omnistar). This analysis was performed on 50 mg of sample. After desorption with helium until 900 °C with a slope of 15 °C.min^{-1} then cooling, an oxidizing gas mixture of 10% oxygen in helium (total flow of 50 mL min^{-1}) passed through the catalyst until 1000 °C with a slope of 15 °C min^{-1}.

2.3. Characterization and quantitative analysis of tars

At the end of each gasification run, a representative sample of the condensate fraction (tar + water) was filtered using a 0.45 μm pore sizes filter and diluted with high purity distilled water. The Total Organic Carbon (TOC) content was measured injecting the sample in a Shimadzu TOC-VCPN analyzer operating the complete catalytic oxidation at 680 °C. The tar content was then calculated using naphthalene as key component.

In addition, tars condensed in 2-propanol (HPLC grade) according to technical specification CEN/TS 15439 were characterized by means of HPLC technique. The system was equipped with an UV detector (Hitachi UV-detector L2400) set at 254 nm. The chromatographic column used was a reversed phase C18, 150 mm × 4.6 mm (Alltech "Apollo C18 5 μm"), protected with a guard column. Pure standard compounds were used to confirm the identification and also to quantify tars by external calibration. Standards of phenol (ph-OH), toluene (Tol), styrene (Sty), indene (Ind), naphthalene (Naph), byphenyl (Bph), diphenyl ether (DphE), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla) and pyrene (Pyr) were provided from Acros Organics (Geel, Belgium). Additional details of the method used are reported in a previous publication [15].

3. Results and discussion

3.1. Characterization of Fe/olivine catalyst

Fig. 2 compares the X-ray diffraction patterns of 10 wt%Fe/olivine catalyst synthesized at laboratory scale (10 g) with three different 10 wt%Fe/olivine catalysts synthesized in large scale (25 kg). Olivine ($(Mg,Fe)_2SiO_4$) structure is the major crystalline phase for the iron catalysts. The presence of iron is indicated by the spinel phase rays (meaning Fe_3O_4 and $MgFe_2O_4$ at $2\theta = 30.19°$, 35.59° and 43.22°) and iron oxide phase Fe_2O_3 at $2\theta = 33.11°$ and 40.82°. These phases are already present in the olivine mineral (about 7 wt% of iron), and appear here amplified due to the addition of 10 wt% of iron and calcination at 1000 °C. Distinction between iron oxide phase Fe_2O_3 and $MgFe_2O_4$ has been performed by Mössbauer spectroscopy [16]. The presence of an enstatite phase ($MgSiO_3$) at $2\theta = 31.1°$ is due to the reaction of amorphous silica with MgO [11]. Those phases are observed for

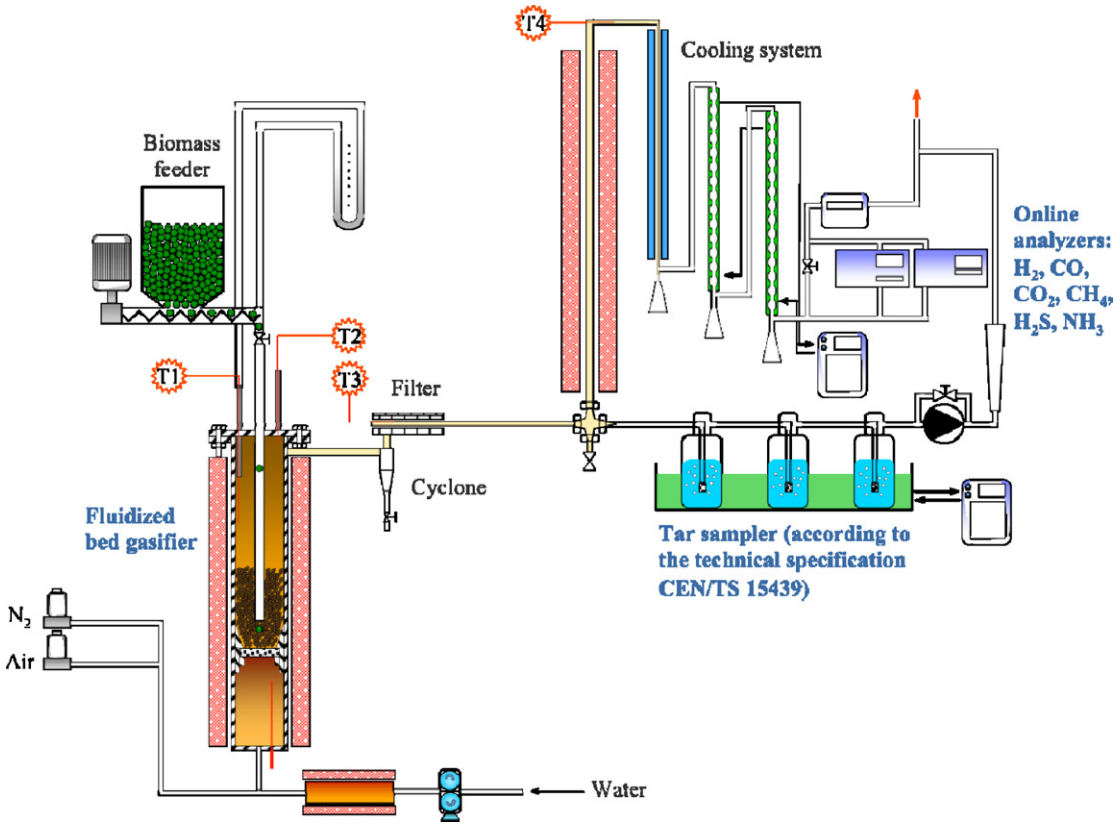

Fig. 1. Schematic view of the continuous biomass gasification test rig.

the three different samples of the large scale synthesis involving homogeneity in the catalyst preparation. The similar patterns of the large and laboratory scale catalysts involve repeatability of the synthesis.

To quantify the amount of reducible iron and identify the strength of interactions between iron and olivine, the hydrogen consumption of the samples has been determined by TPR. A similar profile for both 10 wt%Fe/olivine catalysts, prepared in large and laboratory scale respectively, is observed: a broad peak between 550 °C and 850 °C (Fig. 3). This peak is attributed to the reduction of iron oxides present inside the 10 wt%Fe/olivine grain. The hydrogen diffusion through the grain is more difficult, hence the reduction occurs at higher temperature.

At the same reduction conditions, it is observed for olivine a large hydrogen consumption between 550 °C and 790 °C attributed to the reduction of the free iron oxide (α-Fe_2O_3) and $MgFe_2O_4$ together with the iron (II) of the olivine structure [11,16]. The weak shift of hydrogen consumption peaks toward higher temperatures for iron olivine catalysts indicates higher diffusion of added iron through olivine support which is improved by the calcination temperature at 1000 °C.

The percentage of metallic iron available after reduction has been calculated from the hydrogen consumption given by the TPR profiles. The amount of iron reduced, available for tar steam reforming, is equivalent for both catalyst syntheses (around 12.5 wt%, against 3.5 wt% for olivine).

Table 1
Operating conditions and results of biomass steam gasification tests.

Gasification test	I	II	III	IV
Bed inventory	Olivine	Fe/olivine	Fe/olivine	Fe/olivine
Duration of test (min)	60	154	80	120
Biomass flow rate (g/min)	8	5	5	5.7
Nitrogen flow rate (l/min)	11	11	11	6
Steam feeding rate (g/min)	8.50	6	6	6
Gasifier bed temperature (°C)	808	828	821	820
Steam/biomass dry	1.15	1.3	1.3	1.14
Water conversion %	16	20	19	25
Gas yield, Nm^3 dry/kg daf (N_2 free)	1.00	1.37	1.42	1.41
Tar content, g/Nm^3 dry (N_2 free basis)	3.67	1.18	1.67	n.a.
Char residue (g/kg daf)	94	125	101	115
Carbon conversion (%)	80	74	79	77
H_2 (vol% dry gas, N_2 free)	39	53	53	52
CO_2 (vol% dry gas, N_2 free)	26	28	27	26
CO (vol% dry gas, N_2 free)	24	13	15	16
CH_4 (vol% dry gas, N2 free)	10	6	6	6

n.a. = tar samples for these tests are not available.

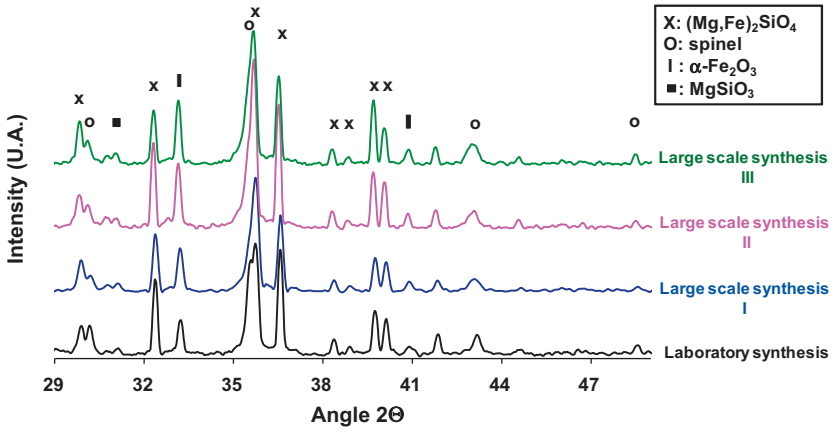

Fig. 2. XRD diffractograms of 10 wt%Fe/olivine samples prepared by large scale synthesis, and synthesized in laboratory, respectively.

This validates the reproducibility of the catalyst synthesis and the scale up of the catalyst preparation.

3.2. Results of the laboratory scale tests

The catalyst has been used in previous studies at laboratory scale, concerning 10 wt%Fe/olivine activity in toluene and 1-methylnaphtalene steam reforming. The effect of hydrogen concentration has been studied in toluene steam reforming at 825 °C by varying the molar ratio of hydrogen/water between 1/1 and 2/1. The H_2/H_2O ratio equal to 1.5/1 has been determined to be the optimized ratio that leads to 90% of toluene conversion and to 60% of hydrogen yield [12]. The XRD diffractogram indicated an unchanged olivine structure after test; however the disappearance of the phase Fe_2O_3 rays and the presence of metallic iron Fe^0 and spinel phase rays are observed. Mössbauer spectroscopy performed after test revealed iron reintegration in the olivine structure (25% of Fe^{2+}), metallic iron Fe0 (49%) and Fe_3O_4 (29%) which is well known to be active in water gas shift reaction [17].

In addition, the 10 wt%Fe/olivine catalyst has been tested in 1-methylnaphthalene steam reforming in the optimized conditions H_2/H_2O 1.5/1. The low conversion in permanent gases (10% at 850 °C) and hydrogen yield (24% at 850 °C) showed that, in these conditions, the catalyst is not as efficient as in toluene steam reforming. The XRD analysis performed after test, confirmed that the olivine structure was maintained and indicated the disappearance of the hematite oxide phase Fe_2O_3 rays and the presence of spinel phase rays. This was confirmed by Mössbauer spectroscopy, revealing as well iron reintegration in olivine structure and the presence of Fe_3O_4 and FeO.

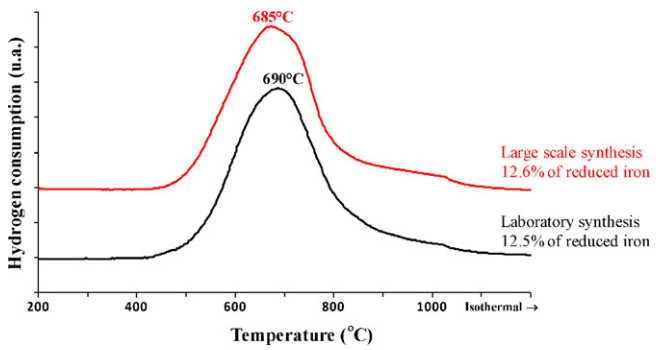

Fig. 3. TPR profiles of 10 wt%Fe/olivine obtained from (red) large scale and (dark) laboratory scale syntheses. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.3. Continuous biomass gasification tests

The significant results of all gasification runs, such as, gas yield, water conversion, tar content in the syngas, char residue, carbon conversion, composition of the syngas, are all shown in Table 1.

In Fig. 4, the product gas composition, expressed as the percentage by volume of H_2, CO, CO_2 and CH_4 in dry, nitrogen free gas, is reported as a function of gasification time, for test I with a olivine particle bed (Fig. 4A), and when 10 wt%Fe/olivine is used (Fig. 4B) instead of olivine. Comparing data obtained using the 10 wt%Fe/olivine particle bed, with the results of test I, allows to notice a significant improvement of all representative gasification

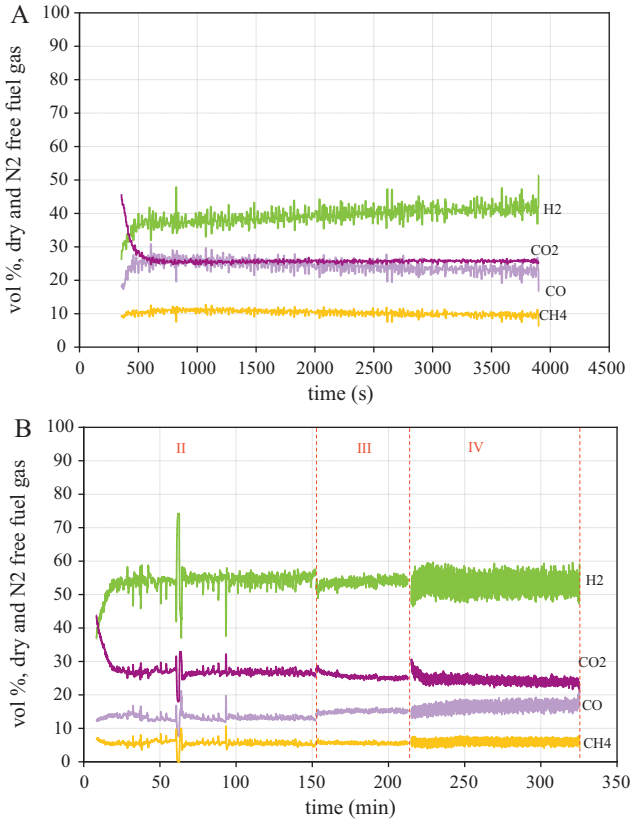

Fig. 4. Product gas composition in % by volume (dry, N_2 free gas) as a function of gasification time, when the fluidized bed in the gasifier is made of olivine particles (A – test I), or of 10 wt%Fe/olivine particles (B – tests II–IV).

Table 2
Percentage variations of the main gasification parameters, with respect to the blank test I.

Gasification test number	II	III	IV
Gas yield, %	+37	+42	+41
Tar content in the produced gas, %	−68	−54	–
Tar content per kg biomass daf, %	−56	−35	–
H_2 yield, %	+85	+91	+87
CH_4 yield, %	−25	−23	−16
H_2 yield, mol/kg daf	+32	+33	+33

parameters. Slightly different operating conditions (II, III, and IV) do not show significant changes in the results.

It is worth mentioning here that the values reported in the table are the average results of the whole tests. Difference in the bed temperature can explain the slight increase of tar content in the product gas for test III compared with test II.

Clearly, an increased gas yield (Table 1) and hydrogen content is noticeable as a result of the utilization of 10 wt%Fe/olivine instead of olivine. As shown in Fig. 4B, H_2 concentration keeps an almost constant value in tests II–IV, equal to about 53% by volume (dry, N_2 free gas), resulting in an average enhancement in molar concentration of 36% in comparison to test I (Fig. 4A). No noticeable improvements have been achieved in test IV, performed at higher concentration of reactants.

In Table 2 the main gasification parameters have been reported as percentage variation with respect to the blank test (olivine fluidized bed).

The ammonia concentration in the produced gas is of the same order of magnitude: 500 ppmv in the blank test (test I), 1000 ppmv in the 10 wt%Fe/olivine tests (II–III–IV). The presence of H_2S in the product gas has been also monitored: with the type of biomass used as a feedstock in these experiments, its concentration remains below 30 ppmv; some activity studies on Ni-catalysts for biomass gas reforming, indicate that, below the threshold limit of 100 ppmv, H_2S deactivation resulting from poisoning the catalytic layer only occurs to a negligible extent [18].

After test IV, a particle bed sample has been recovered from the gasifier bed, for "post-gasification" characterization of 10 wt%Fe/olivine.

3.4. Characterizations after tests in the pilot plant

3.4.1. Tar characterization by HPLC/UV

The HPLC/UV method was used to study tar composition. This technique has been extensively exploited for identification and quantitative determination of Polycyclic Aromatic Hydrocarbons and enables to characterize tars directly after sampling, without any pretreatment step.

Fig. 5 shows the cumulative data of tar composition related to test with olivine (test I – reference) and the average value of the two tests with 10 wt%Fe/olivine (test II and III). In all experiments, the main compounds turn out to be hydrocarbons such as toluene, styrene, indene and naphthalene which are composed by one or two aromatic rings.

With tests performed with a 10 wt%Fe/olivine particle bed in the gasifier, the content of tar is well below that measured in the reference test. In this case, naphthalene and toluene, which are considered quite refractory to cracking/reforming reactions, decrease by 48% and 59% on average, respectively. The experimental evidence confirms that the iron impregnation of natural olivine leads to a promotion of reforming activity and a coherent decrease of tar concentration.

It is also to stress that HPLC/UV analyses of samples obtained from 10 wt%Fe/olivine gasification tests show a content of higher molecular weight hydrocarbons (A3, A3+) generally very low when

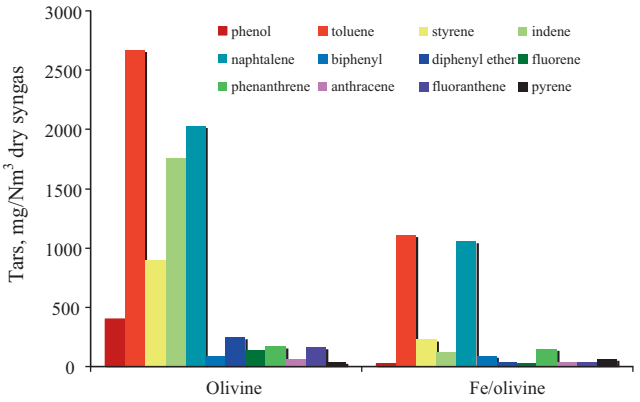

Fig. 5. Characterization of tar samples obtained from biomass gasification with olivine (I – reference test) and with 10 wt%Fe/olivine tests.

compared to the test with plain olivine (Fig. 5): their concentration decreases by 37%. These compounds have a great influence on the tar dew point: heavy tars condense out as the gas temperature drops and cause major fouling, efficiency loss and unscheduled plant stops. So, the reduction in tar dew point is a beneficial factor.

As mentioned above, tar content in the produced gas has been measured by TOC of the condensate fraction, and tar composition by HPLC/UV of the samples obtained according to UNI CEN/TS 15439. The evolution of tar concentration obtained by both analytical methods follows the same trend with a fairly good agreement, specifically when the comparison in tar content decrease among different types of test is considered. Nevertheless, a variation in the results is to be expected, considering the sweeping difference between these two analytical techniques, and also in the nature of the analyzed samples.

3.4.2. Characterizations of 10 wt%Fe/olivine catalyst after test

The XRD analysis has been performed on 10 wt%Fe/olivine catalyst samples taken from the bed inventory of gasifier after test IV. The results indicate that the olivine structure and solid phases are preserved after gasification. It is observed a small ray of α-Fe_2O_3 at $2\theta = 33.11^\circ$ and 40.82° and spinel phase ($MgFe_2O_4$, Fe_3O_4) at $2\theta = 30.19^\circ$, 35.59° and 43.22° for the catalyst recovered at the end of gasification tests. No metallic iron (Fe^0) has been observed due to the operating conditions for char analyses.

TPO was performed on catalyst after gasification tests. No carbon deposition has been quantified indicating that the oxidative step could easily and totally oxidizes the surface carbon.

The TPR curve of the catalyst after gasification (Fig. 6) indicates a peak of hydrogen consumption between 500 °C and 700 °C which corresponds to the reduction of iron oxide in strong interaction

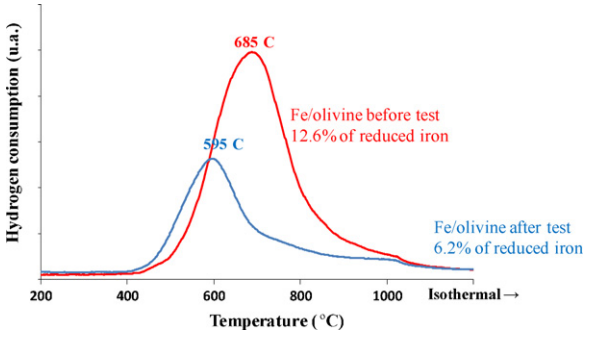

Fig. 6. TPR profiles of 10 wt%Fe/olivine: (red) before test; (blue) after biomass gasification. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

with olivine structure. However, compared to the TPR curve of the 10 wt%Fe/olivine catalyst before test, a decrease in the hydrogen consumption is observed (after gasification, the hydrogen consumption allowed to reduce about 6.2 wt% of iron, instead of 12.6 wt% of iron before test). This can be explained partly by the presence of iron in an oxidation state less than that prevailing initially (Fe_3O_4 ($Fe^{2.5+}$) instead of Fe_2O_3 (Fe^{3+}) before test) which needs less hydrogen to be reduced to metallic iron (Fe^0). However, a loss of iron added on olivine (about 5 wt% of total iron) during fluidization because of particle attrition phenomena, could mainly explain the decrease of hydrogen consumption.

4. Conclusions

The 10 wt%Fe/olivine catalyst has been chosen for reactivity, due to its strong metal-support interactions and significant amount of metallic iron available after reduction.

This catalyst remains stable despite of a decrease in the reducible iron available for tar removal. No carbon deposition has been observed, and this prevents catalyst deactivation.

Although higher ammonia production and lower carbon conversion have been observed during biomass steam gasification in presence of 10 wt%Fe/olivine in the reactor fluidized bed, the performance of the catalyst is not compromised: the tar reforming extent obtained by means of 10 wt%Fe/olivine catalyst is on average equal to 61%; methane content is also decreased (24%); as a result, an increase is obtained in the gas yield (about 40%) and the hydrogen concentration in the dry gas (N_2 free basis) raises to 53%.

As far as tar content and composition are concerned, the evolution of tar concentration obtained by both analytical methods (HPLC/UV and TOC) follows the same trend with a fairly good agreement. Regarding tar characterization, naphthalene and toluene, which are considered quite refractory to cracking/reforming reactions, decrease by 48% and 59%, respectively, when 10 wt%Fe/olivine is used instead of olivine. The iron impregnation of natural olivine leads to a promotion of reforming activity.

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