

## Improvement of gas yield from biomass gasification by using Fe/olivine as gasifier bed inventory

Sergio Rapagnà<sup>1\*</sup>, Katia Gallucci<sup>2</sup>, Manuela Di Marcello<sup>1,3</sup>, Muriel Matt<sup>3</sup> and Pier Ugo Foscolo<sup>2</sup>

<sup>1</sup>Univ. of Teramo, Dep. Food Science, Via C. Lerici 1, 64023 Mosciano S. Angelo (TE), Italy; srapagna@unite.it

<sup>2</sup>Univ. of L'Aquila, Dep. Chemistry, Chemical Engineering and Materials, Via Campo di Pile Ex-Optimes, 67100 L'Aquila, Italy

<sup>3</sup>LCME – EA4164, University of Metz UFR SciFA, 1 Bd Arago, 57078 Metz cedex 3, France

In the present work, a bench-scale biomass gasification plant operating at atmospheric pressure is utilized in this work to check innovative, catalytic hot gas cleaning processes and plant arrangements. The cleaning step is realized by means of Fe/olivine, used as catalytic bed inventory for tar, methane and H<sub>2</sub>S reforming, or Fe/olivine coupled with a catalytically active filter candle. Natural olivine has been used in fluidized bed gasifier thanks to the catalytic activity and the mechanical strength. Iron (III) in his structure is responsible of the tar cracking reaction because of its efficiency in ring opening. Impregnation of iron leads to an improved catalytic efficiency. The aim of this work is to test the Fe/olivine in real gasification condition using a fluidized bed gasifier.

### 1. Introduction

To satisfy the energy requirements by preserving the environment, biomass sources appear as a good alternative to produce electricity, heat and fuel. Among different ways of biomass energy conversion, the gasification is considered a valid process option to obtain a fuel gas composed of hydrogen and carbon monoxide. The objective is to obtain a stoichiometric cleaned mixture of these gases for different applications. Nonetheless, these gases, called syngas, contain also by-products, in particular tars and methane. Removing of tar and methane can be well performed by the help of catalysts: either placed into the reactor (primary catalyst) and/or placed outside the reactor (secondary catalyst).

Many papers are reported in the literature concerning the use of catalysts placed into and outside the gasifier (Bangala et al. 1997; Devi et al. 2005; Toledo et al. 2006; Van Paasen and Kiel, 2004; Li and Suzuki, 2009).

Considering that biomass is a dilute energy source, the conversion plants should be distributed on the territory and therefore they are small compared to the plants that use coal or methane. Small plants involve the use of a compact design in order to decrease the heat loss and to simplify the overall process. Most of the catalysts reported in the

literature can not be utilized in a small gasification plant utilizing the fluidization technology, due to the fact that most of them are soft (high active surface means high porosity) and produce high amount of fines, and because they are also light (density  $\approx 1500 \text{ kg/m}^3$ ) they are easy elutriated from the gasifier. On the other hand, the use of catalysts outside the gasifier such as monolith structures involves a complication of the overall process and increases the heat loss, which for a small plant can be important. For these reasons, very few small size biomass conversion plants are in operation nowadays. Compact biomass gasification processes can be achieved by utilizing catalysts inside the gasifier: either in the bed inventory, and integrated in a ceramic candle placed in the freeboard of the gasifier itself. This process arrangement assures that the hot gas that leaves the reactor is free of solid particles and tar components and can be directly fed to SOFCs to produce electricity with high efficiency.

## 2. Experimental

### 2.1 Experimental plant

The experimental gasification plant utilized for these tests has been widely described in previous works (Rapagnà et al. 2009, Rapagnà et al. 2010a, Rapagnà et al. 2010b), and is mainly composed of a fluidized bed gasifier, ID 0.1 m, able to house in its freeboard a catalytic candle with an external diameter of 0.06 m, total length 0.4 m, delivered by Pall Schumacher GmbH.

The fluidized bed was made of 3 kg of Fe/olivine particles ( $d_{\text{average}} = 393 \mu\text{m}$ ,  $\rho_{\text{particle}} = 2500 \text{ kg/m}^3$ , measured by comparison with a bulk of olivine particles having the same volume, assuming similar bulk void fraction), delivered by ECPM-LMSPC - University of Strasbourg. Crushed and sieved almond shells with an average particle size of  $1054 \mu\text{m}$  were used as biomass feedstock. The biomass is introduced from the top of the bed by means of a continuous feeder unit. A cyclone and a ceramic filter are connected to the gasifier outlet to remove elutriated solid particles; although these units become redundant when gas filtration is achieved within the gasifier itself they were left in place to avoid unnecessary system modification. Three condensers in series are used to separate condensable components: the first, of stainless steel, is cooled with tap water and the remaining two, of glass, are cooled with refrigerated diethylene glycol.

Online gas analysers (IR, UV and TCD), for the volume composition measurement of  $\text{H}_2$ , CO,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$ , are fed at cold gas rates of 1.5 l/min and output to a PC in which the experimental data are stored as functions of time. Temperatures in various plant locations are measured by means of 5 thermocouples, and devices for the continuous monitoring of flow rates and pressures are also employed. Steam was generated from liquid distilled water fed, by means of a peristaltic pump, to a cylindrical, stainless steel evaporator encased in a 2.4 kW electric furnace. Weighting the feed tank before and after each test, the average water flow rate was also checked. The overall gas flow was measured with a volumetric gas meter.

### 2.2 Tar analysis

HPLC/UV technique has been chosen to follow the evolution of tars in the samples collected according to CEN/TS 15439.  $20 \mu\text{l}$  of each sample has been injected in a HPLC apparatus (Hitachi "Elite LaChrom" L-2130). The system was equipped with an

UV detector (Hitachi UV-detector L2400) set at 254 nm. The column for the chromatographic separation of the tar fraction was a RP-C18, 150 x 4.6 mm (Alltech “Apollo C18 5  $\mu\text{m}$ ”), protected with a guard column. A gradient elution was realized using methanol (Fisher Scientific, Loughborough, Leicestershire, UK) with water, at a flow rate of 1 ml/min (Rapagnà et al. 2010a). Twelve molecules have been identified and quantified using external calibration; the aromatic hydrocarbons used: phenol (Ph-OH), toluene (Tol), styrene (Sty), indene (Ind), naphthalene (Nap), biphenyl (Bph), diphenyl ether (DphE), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla) and pyrene (Pyr) were provided from Acros Organics (Geel, Belgium); the identified compounds are in qualitative agreement with the data found in the literature (Devi et al. 2005).

### 3. Results

#### 3.1 Catalytic fluidized bed steam gasification of biomass

Three tests have been performed in order to check the catalytic activity of the Fe/olivine particles, utilized as bed inventory. Results reported during this test campaign will be compared to those obtained with olivine bed inventory (test OL) previously published (Rapagnà et al. 2010b). The operating conditions are reported in Table 1.

*Table 1: Gasification operating conditions for test OL (olivine), tests I-II (Fe-olivine), and test III (Fe/olivine and catalytically active filter candle)*

Gasification test	OL	I	II	III
Duration of test (min)	60	154	80	120
Biomass flow rate (g/min)	8	5	5	5
Nitrogen flow rate (l/min)	11	11	11	11
Steam feeding rate (g/min)	8.5	6	6	6
Catalytic filter candle	No	No	No	Yes

The experimental results obtained during this test campaign are reported in Table 2.

*Table 2: Results of steam gasification tests under different operating conditions (see Table I)*

Gasification test	I	II	III
Bed temperature ( $^{\circ}\text{C}$ )	828	821	814
Steam/biomass dry	1.3	1.3	1.3
Water conversion %	20	19	29
Gas yield, $\text{Nm}^3_{\text{dry}}/\text{kg}_{\text{daf}}$	1.37	1.42	1.75
Tar content, $\text{g}/\text{Nm}^3_{\text{dry}}$	1.18	1.67	0.30
Char residue, $\text{g}/\text{kg}_{\text{daf}}$	125	101	126
$\text{H}_2$ (vol% dry gas, $\text{N}_2$ free)	53	53	56
$\text{CO}_2$ (vol% dry gas, $\text{N}_2$ free)	28	27	22
$\text{CO}$ (vol% dry gas, $\text{N}_2$ free)	13	15	17
$\text{CH}_4$ (vol% dry gas, $\text{N}_2$ free)	6	6	4

The routine total tar measurements reported in Table 2 have been obtained analyzing the condensate separated in the cooling system by means of a Shimadzu TOC V-CSN analyzer, with the assumption of naphthalene as the model tar compound.

*Table 2: Percentage variations with respect to test performed with only olivine particles*

Gasification test	Reference	Variations		
	OL	I	II	III
Gas yield, Nm <sup>3</sup> <sub>dry</sub> /kg <sub>daf</sub>	1.00	+37 %	+42 %	+75 %
Tar content, g/Nm <sup>3</sup> <sub>dry</sub>	3.67	-68 %	-54 %	-92 %
Tar content, g/kg biomass <sub>daf</sub>	3.67	-56 %	-37 %	-86 %
H <sub>2</sub> yield % per Nm <sup>3</sup> /kg biomass <sub>daf</sub>	39	+85 %	+91 %	+152 %
CH <sub>4</sub> yield % per Nm <sup>3</sup> /kg biomass <sub>daf</sub>	10	-25 %	-23 %	-30 %

Considering the data reported in Table 2 and 3, two positive results can be observed by using Fe/olivine particles: the higher gas and hydrogen yields, compared with those obtained by performing the biomass gasification test with plain olivine particles (Rapagnà et al. 2009, Rapagnà et al. 2010a, Rapagnà et al. 2010b). The high gas yield indicates that iron is a good catalyst to reform tars, as it has been extensively reported (Świerczyński et al. 2006), and the high hydrogen content is mainly due to the positive effect of Fe on the water gas shift reaction conversion.

The comparison of data obtained using Fe/olivine combined with the catalytic filter candle (test III) with the results of test I, without any gas cleaning element inserted in the gasifier, allows to notice a substantial improvement of all the representative gasification parameters. In particular, in the last test the gas yield has increased on average by 75%, the hydrogen yield by 152%. Correspondingly, methane and tar content in the gas is reduced by 30% and 92%, respectively, and tar production by 62% per kg<sub>daf</sub> biomass.

It is necessary to stress that the Fe-olivine particles are well fluidized with air during the heating up process, starting from room temperature up to the gasification temperature. It is then possible to consider that before performing test III, the Fe-olivine particles have been fluidized for more than 20 hours. This is a quite important indication that the active Fe sites are still present on the surface of the olivine particles, and they are not lost due to attrition phenomena.

As far as the ammonia concentration in the producer gas is concerned, tests I (and II) showed a strong evolution in the ammonia content in the range between 30 and 80 minute up to about 4000 ppmv; then, its value goes back down to the baseline level of 500 ppmv. When the catalytic candle is adopted (test III), the NH<sub>3</sub> baseline in the producer gas reduces from 500 ppmv in the test I to 100 ppmv: this is a further index of the activity of the Ni reforming catalyst, and the evolution on Fig. 1 (right) could be related to the opposite effect of Fe (NH<sub>3</sub> formation catalyst) and Ni (NH<sub>3</sub> decomposition catalyst); more experimental evidence is needed to confirm and to explain this phenomenon.

The presence of H<sub>2</sub>S in the product gas has been also monitored. In all experiments, with the biomass used as a feedstock, its concentration in the product gas remains below 10 ppmv.

### 3.2 Chemical characterization of tars

HPLC/UV method was used to study the tar composition. This technique has been extensively exploited for identification and quantitative determination of Polycyclic Aromatic Hydrocarbons (Ledesma et al. 2000; Zhang et al. 2007) and enables the aromatic composition of the tar to be quantified directly after sampling, without any pretreatment step.

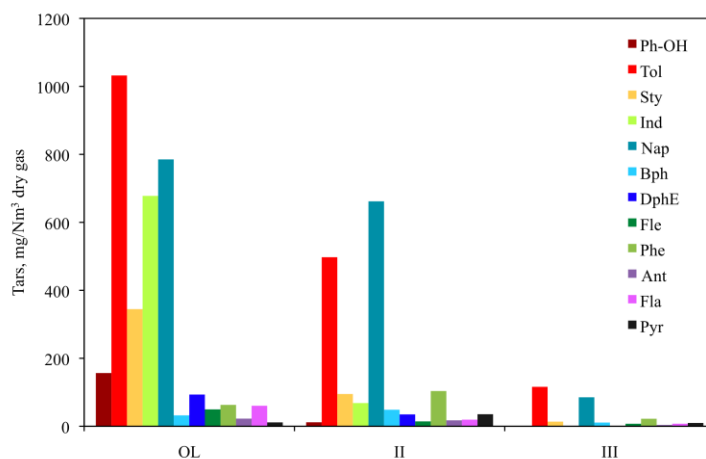


Figure 2: Characterization of tar molecules produced during test OL (olivine), test II (Fe-olivine) and test III (Fe-olivine + catalytically active filter candle)

The results obtained are reported in Fig.1, and they are compared with those reported in a previous test performed using plain olivine particles (test OL).

As expected, light aromatics such as toluene, styrene, indene and naphthalene represent the more representative molecules of tar fraction. During test II, a considerable reduction of these molecules in the producer gas has been observed in comparison with test OL. Especially, toluene, styrene and indene decrease of 52%, 72% and 90% respectively. Thus, the iron impregnation of natural olivine results in a promotion of reforming activity, which leads to a decreased tar concentration.

In case of test III, the concomitant use of Fe/olivine and the catalytically active filter candle leads to a drastic abatement of tars in the producer gas. Light molecules as well as heavy compounds are reformed, resulting in an average tar reduction upper then 80% in comparison with test II.

## 4. Conclusions

Tests performed by using Fe/olivine particles as the reactor fluidized bed inventory, utilized to gasify biomass in presence of steam, have demonstrated that they are more active than olivine particles. It is also important to note that the Fe-olivine particles are still active even when they have been stressed for many hours under a vigorous fluidization state at high temperature.

The use of iron as the active catalytic element does not pose problems of environmental risk. The use of nickel grains contained into a ceramic candle assures almost complete

elimination of tar compounds in the product gas and prevents char particles to be elutriated from the gasifier, as a result of which, clean and high yield of gas is obtained.

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### References

- Bangala, D.N., Abatzoglou, N., Martin, J.P., Chornet, E., 1997, Catalytic gas conditioning: application to biomass and waste gasification, *Ind. Eng. Chem. Res.* 36, 4184–4192.
- Devi, L., Ptasiński, K.J., Janssen, F.J.J.G., van Paasen, S.V.B., Bergman, P.C.A., Kiel, J.H.A., 2005, Catalytic decomposition of biomass tars: use of dolomite and untreated olivine, *Renew. Energy*. 30, 565–587
- Ledesma, E.B., Kalish, M.A., Nelson, P.F., Wornat, M.J., Mackie, J.C., 2000, Formation and fate of PAH during the pyrolysis and fuel-rich combustion of coal primary tar, *Fuel*. 79, 1801 – 1814.
- Li, C., Suzuki, K., 2009, Tar property, analysis, reforming mechanism and model for biomass gasification – an overview, *Renew. Sust. Energy Rev.* 13, 594–604
- Rapagnà, S., Gallucci, K., Di Marcello, M., Foscolo, P.U., Nacken, M., Heidenreich, S., 2009, In situ catalytic ceramic candle filtration for tar reforming and particulate abatement in a fluidized-bed biomass gasifier, *Energy Fuels*. 23, 3804–3809.
- Rapagnà, S., Gallucci, K., Di Marcello, M., Matt, M., Foscolo, P.U., Heidenreich, S., Nacken, M., 2010a, Characterisation of tar produced in the gasification of biomass with in-situ catalytic reforming, *Int. J. Chem. Reactor Eng.* 8, A30
- Rapagnà, S., Gallucci, K., Di Marcello, M., Matt, M., Nacken, M., Heidenreich, S., Foscolo P.U., 2010b, Gas cleaning, gas conditioning and tar abatement by means of a catalytic filter candle in a biomass fluidized-bed gasifier, *Biores. Tech.* 101, 7134–7141
- Świerczyński, D., Courson, C., Bedel, L., Kiennemann, A., Vilminot S., 2006, Oxidation reduction behavior of Iron-Bearing Olivines ( $\text{Fe}_x\text{Mg}_{1-x}$ )<sub>2</sub>SiO<sub>4</sub> used as catalysts for biomass gasification, *Chem. Mater.* 18 (4), 897–905
- Toledo, J.M., Corella, J., Molina, G., 2006, Catalytic hot gas cleaning with monoliths in biomass gasification in fluidized beds. 4. Performance of an advanced, second-generation, two-layers-based monolithic reactor, *Ind. Eng. Chem. Res.* 45, 1389–1396.
- Van Paasen, S.V.B., Kiel, J.H.A., 2004, Tar formation in a fluidized bed gasifier: impact of fuel properties and operating conditions, Report ECN-C-04-013. 1–58.
- Zhang, C., Zhang X., Yang, J., Liu, Z. (2007) Analysis of polynuclear aromatic hydrocarbons in heavy products derived from coal and petroleum by high performance liquid chromatography. *J. Chromat. A.* 1167, 171–177