Biomass gasification with NiO/Olivine catalysts in fluidised bed gasifier.

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1. Introduction

Tar removal from biomass gasification gas is a crucial problem in applying syngas from biomass for its downstream applications. Catalytic biomass gasification has given promising results for tar cracking. A few research groups have investigated the use of olivine for tar cracking [2,3,4,7,8,9,10]. The presence of oxides of iron and magnesium in the mineral olivine give it the ability to crack higher hydrocarbons termed as tars. Olivine surely does have sustainable physical properties for the harsh conditions of a fluidised bed gasifier. Untreated olivine was previously compared by us with dolomite in cracking model tar compounds. Modifying the olivine by calcination at high temperatures showed very promising results towards tar cracking. Also tests related to attrition resistance showed that olivine is very capable of being the gasification catalyst as compared to dolomite. For the study of tar cracking and tar reforming nickel oxide is known to be effective. Therefore, the behaviour of a nickel oxide on olivine catalyst under reducing conditions with respect to tar cracking is studied.

2. Experimental setup

a. Biomass

The biomass used for the experiments are pine chips. The size of the biomass chips is approximately 2 – 3 mm. The analysis on biomass can be obtained from [1].

b. Fluidized bed gasifier

The experiments were performed using an atmospheric bubbling fluidized bed gasifier. The biomass gasifier is 1.078 m in length and has inner diameter of 0.107 m in the bed and 0.196 m in the freeboard. Fig. 1 shows the schematic of the bubbling fluidized bed biomass gasifier. The temperature in the gasifier can be measured at four different positions. The gas is analyzed by taking a sample of gas from just above the bed. An on-line gas chromatograph is used for analysing the gas sample.

The biomass is stored into a biomass hopper and approximately, 20 – 25 kg of biomass can be stored in the hopper. To avoid the biomass from sticking to the walls of the hopper and for proper mixing two motors are used. A two stage screw conveyor system is used for the feeding of the biomass into the gasifier. The first screw with motor M3 is the rate controlling screw. The biomass feed rate can be controlled from 0.5 – 2 kg/h. The second screw with motor M4 is the fast insertion screw conveyor.

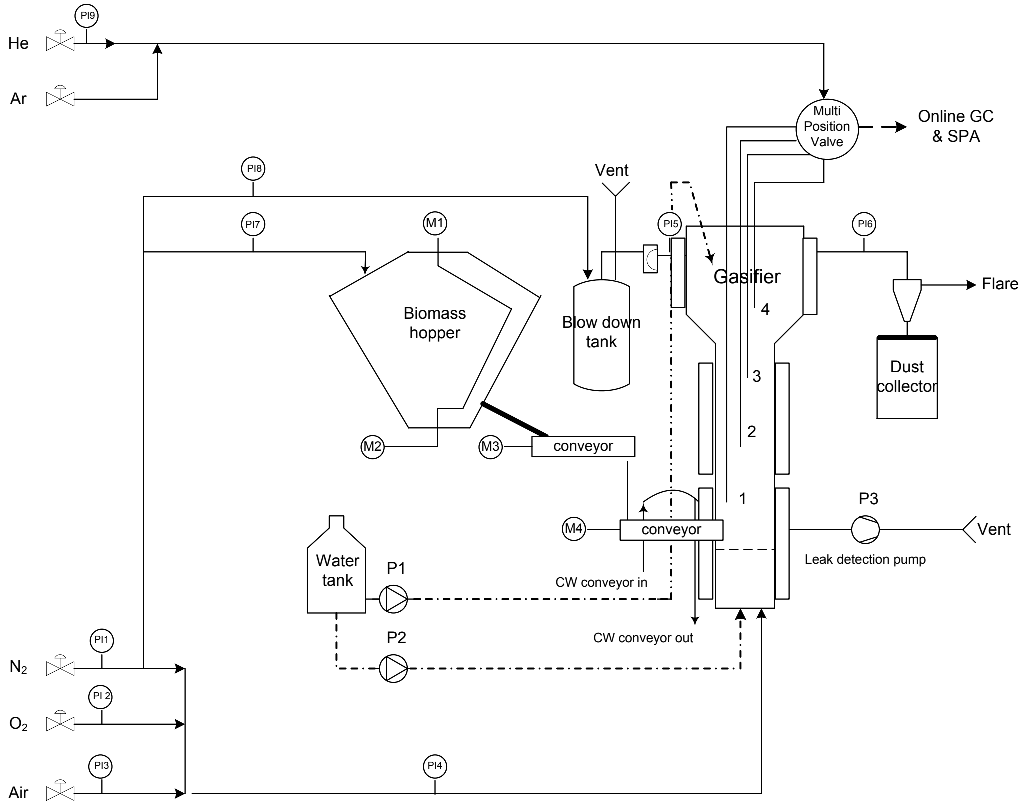

Fig. 1: Fluidized bed gasifier setup schematic.

The fluidizing agent for the gasification can be chosen from air, steam and oxygen. The fluidizing agent is pre-heated before entering the gasifier. Provision for secondary agent is also present in the freeboard. The temperature of the gasifier is controlled by electrical ovens. The maximum allowable temperature is 1000 ºC.

The safety precautions for the process have been undertaken. A rupture disc with design pressure of 1 bar is used to avoid any pressure build up problem. Continuous monitoring of the air between the gasifier and the ovens is done by CO_2 and H_2 sensors. Fixed CO and H_2 sensors are also placed in the cabinet of the gasifier.

c. Catalyst

In this study the catalyst used for the biomass gasification is of prime importance. We have selected six different catalysts for gasification of biomass in a fluidised bed. Selection of *in-bed* additives was very much based on results from literature [2,3,4,7].

Therefore selection of olivine as *in-bed* additive was based on research done in our own group. Calcination of olivine at 1000 ºC in the presence of air resulted in calcined olivine. The calcined olivine does have very good tar cracking properties [2,3,4,7].

Nickel catalyst impregnated on olivine for methane reforming has been studied [5,6]. The concept of having olivine as a tar cracking catalyst and the presence of nickel for reforming reactions seemed very attractive. The catalyst preparation method can be obtained from [5,6]. Further we made modifications to this catalyst by impregnating the nickel nitrate on calcined olivine. We also calcined these new catalysts. Therefore six different catalysts as mentioned below were prepared for the experiments.

- Olivine
- Calcined Olivine
- NiO on Olivine (Cat 1)
- NiO on calcined olivine (Cat 2)
- Calcination of NiO on olivine (Cat 3)
- Calcination of NiO on calcined olivine (Cat 4)

d. Operating conditions

The current experiments are performed keeping constant the biomass feed rate, temperature in the gasifier, gasifying medium and the feeding rate of the gasifying medium. The amount of sand and catalyst in the gasifier bed is also kept constant. The various catalysts mentioned above are used for the gasification experiments. Table 1 gives an overview of the operating conditions in the gasifier.

Table 1. Biomass gasifier operating conditions

Parameter	Condition
Temperature	800 ºC
Biomass feed rate	1 kg/h
Air	1000 l/h
Sand	540 g
Catalyst	60 g

3. Characterization techniques

Characterization of the developed catalysts is necessary to identify the presence of various metal oxides. The developed catalysts are characterized with different techniques like X-ray Photon Spectroscopy (XPS), X-ray Diffraction (XRD), Temperature Programmed Reduction (TPR) and Scanning electron microscopy (SEM).

The surface characterization of the catalyst samples is investigated by means of XPS. XPS specifies the elements present at the surface of the catalyst sample with their relative atomic percentages. The characterization of the catalyst samples using XRD specifies the identity of the present metals in the catalyst and their structures. TPR using H_2 was done on the catalyst samples in order to determine the reduction temperature of the catalysts. SEM reveals information on the composition and internal structure of particles. Colour mapping of the cross section of the catalyst particle is performed.

4. Results and Discussion

a. <u>Catalyst characterization</u>

The results from TPR characterization study are promising. The TPR study was done till 1000 ºC. The identification of the peaks is done using literature references.

The characterization for cat 3 and cat 4 is shown in Fig.2 and Fig. 3. The result shows the presence of oxides of Fe and Ni.

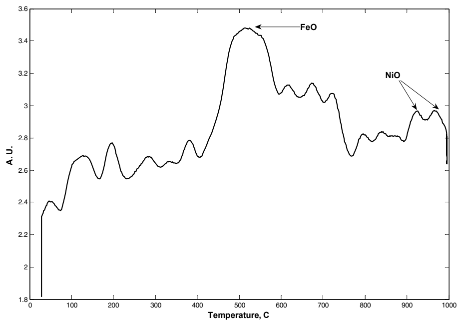

Fig. 2: TPR of Cat 3.

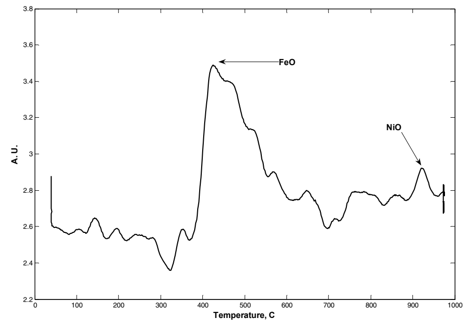

Fig. 3: TPR of Cat 4.

The characterization of the catalysts with the different techniques has revealed the presence of the metal oxides. Fig. 4 shows the presence of metal oxides on the surface of the impregnated catalysts by XPS. The XRD study shows the presence of the peaks of Fe and Ni oxides.

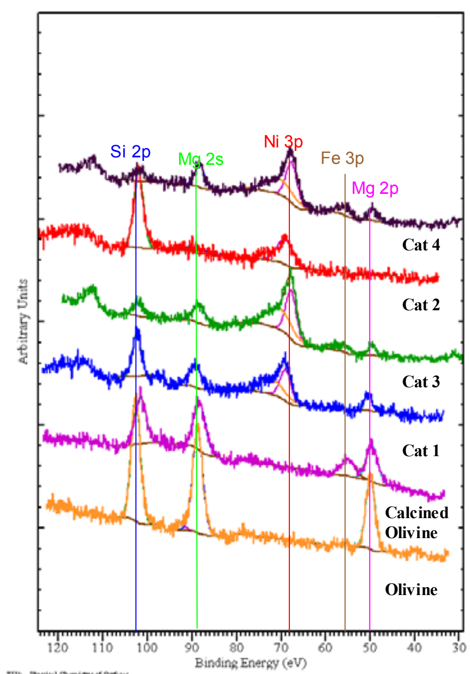

Fig. 4: XPS analysis of different catalysts.

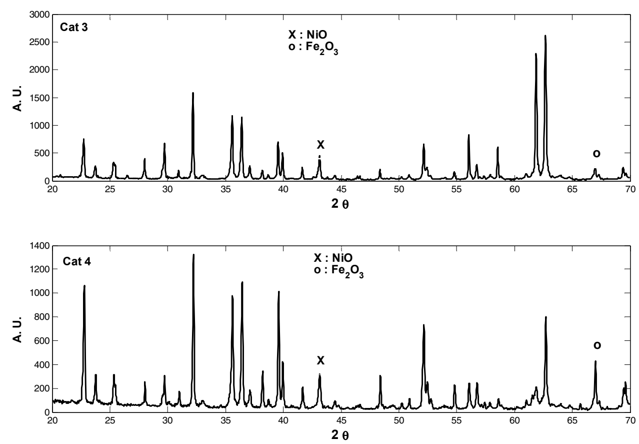

Fig. 5: XRD of Cat 3 and Cat 4.

Fig. 6 is the result from the SEM analysis for Cat 4. The result from the SEM shows the presence of the NiO which is only seen at the surface of the catalyst. The presence of iron, magnesium and silica is seen to be spread all over the catalyst particle as is expected with olivine as the support for the catalyst. It was expected that the NiO will be only on the surface of the catalyst and will not penetrate the olivine particle, since the olivine particle is non-porous.

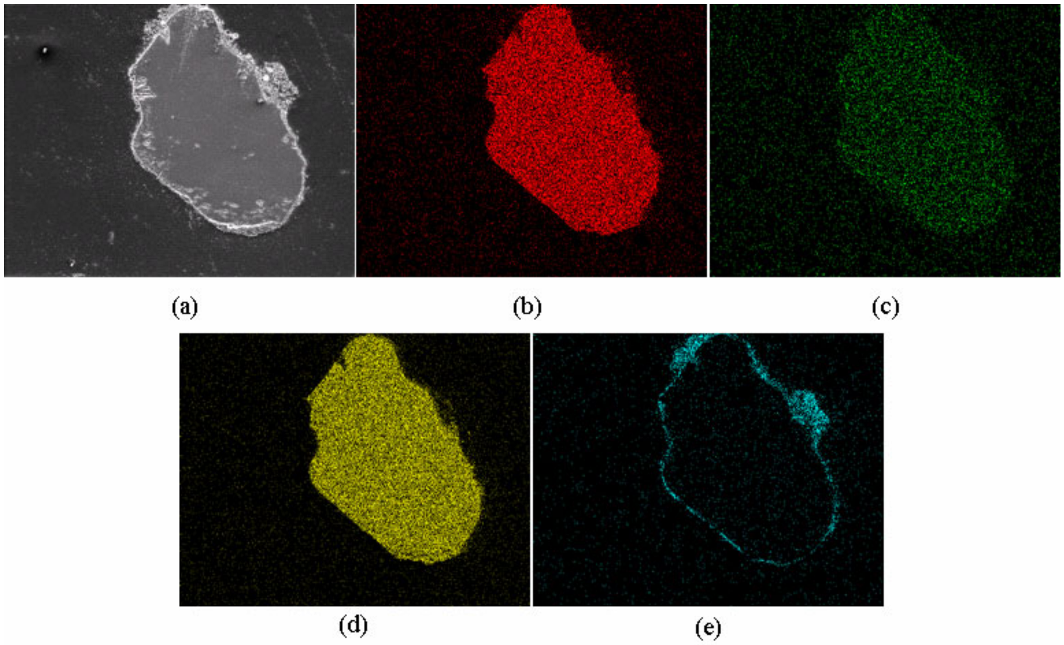

Fig 6: SEM images of calcined olivine impregnated with nickel nitrate and recalcined. (a) Photograph of olivine (b) silica (c) magnesium (d) iron (e) nickel

b. <u>Tar reduction</u>

The gasification of biomass is done using the different catalysts. The operating conditions are as mentioned in Table 1. For each experiment we use fresh catalyst and sand. Results from experiments with different catalysts are discussed below.

<u>Olivine</u>

The temperature profile during the experiment is seen to be very stable at the operating conditions. Olivine has shown promising results for model tar decomposition [2,3,4,7]. With 10% olivine in the fluidized bed, there was reduction in the tar concentration. The total tar concentration reduces from 51.18 g/m^3 after 1h of experiment to 17.52 g/m^3 after 4h of time on stream. Fig. 7 shows the total tar concentration in the gasifier gas on the y-axis whereas; the x-axis shows the time on stream.

Table 2. gives an overview of all the catalysts used for the gasification of biomass.

No.	In-Bed	Time (h)	Char (g)	Ash (g)	Conversion (%)	H_2/CO	Total tar(g/m3)
1	Olivine	4	16	50	98.35	1.12	51.18-17.5
2	C. Olivine	4	6	30	98.2	2.35	6.39-4.55
3	Cat 1	4	92	50	96.45	2.7	3.93-2.17
4	Cat 2	4	40	50	97.8	3.16	2.23-1.3
5	Cat 3	2	20	20	98	3.24	2.26-1.4

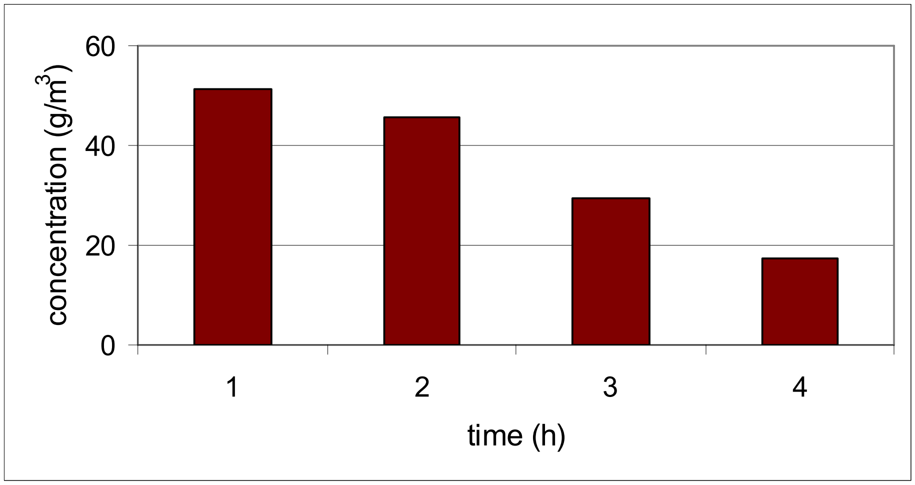

Fig. 7: Total tar concentration using olivine in the gasifier bed.

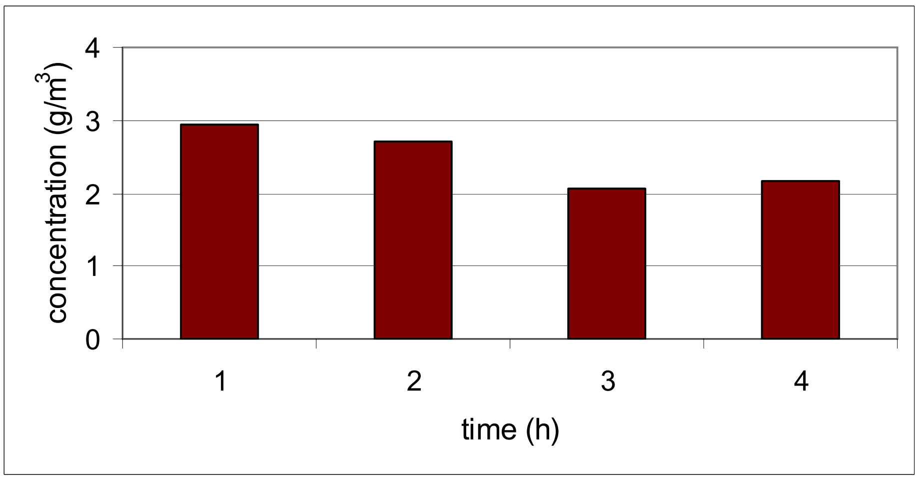

Fig. 8: Total tar concentration using NiO on olivine in the gasifier bed.

Calcined Olivine

The use of calcined olivine during gasification produces more hydrogen than mineral olivine. The total tar concentration using calcined olivine reduces considerably. After 1h of experiment the total tar was 6.39 g/m^3, which further reduced to 4.55 g/m^3 after 4 h of experiment.

Cat 1

Impregnation of NiO on the mineral olivine enhanced the catalytic activities for production of hydrogen. Fig. 8 shows the total concentration with respect to experimental time. The total tar concentration using this catalyst was reduced from 2.93 g/m^3 to 2.17 g/m^3 after 4h of experiment. This indicates that with the use of NiO on the catalyst there is considerable decrease in the amount of tar in the gas along with increase in the hydrogen amount.

Cat 2

Impregnation of NiO on calcined olivine was seen to perform as expected with the presence of NiO and FeO on the surface of the catalyst. The H_2/CO ratio was quite high at 3.16. Also the total tar concentration after 4h on stream is 1.3 g/m^3.

Cat 3

For this catalyst the experiment performed was only till 2h. The catalyst is calcined after impregnation of NiO on the mineral olivine. The amount of total tar concentration is seen to be reducing with the two analyses we performed. The amount of hydrogen is seen to be very high.

Cat 4

The experiment is not yet performed with this catalyst for biomass gasification. But in future we expect to use this catalyst and expect better results from the catalysts discussed above.

5. Conclusions

The characterization study of the catalyst samples has revealed presence of Ni_{3p} on the catalyst along with Fe_{2p}. The difference in the catalyst and the calcined catalyst is noticeable in all the different characterization techniques. The performance of these catalysts was tested in the bubbling fluidized bed gasifier to get an insight into the catalyst activity. The comparison of these catalysts is based on the results that we got from the analysis by GC. The use of these catalysts was effective in tar reduction. The catalysts are not only active in tar reduction but also enhance the production of hydrogen. The Fig 9 below shows the comparison between the different catalysts with respect to total tar removal. The total tar removal is defined with respect to tar formed using sand in the fluidized bed.

% tar removal = (Conc. of tar using sand – Conc. of tar using catalyst) * 100/ Conc. of tar using sand

Fig. 9 concludes that tar removal is increased at these experimental conditions using these catalysts.

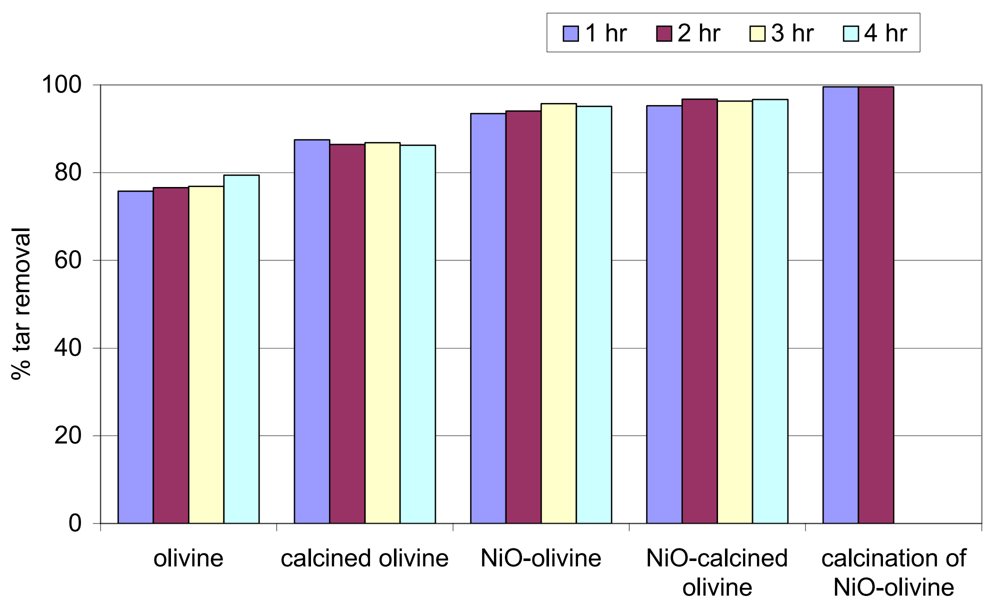

Fig. 9: Total tar removal using different catalysts.

6. Acknowledgement

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7. References

[1] Energy Research Centre of the Netherlands. Phyllis, database for biomass and waste. http://www.ecn.nl/phyllis

[2] L. Devi, K. J. Ptasinski, and F. J. J. G. Janssen. A review of the primary measures for tar elimination in biomass gasification processes. Biomass and Bioenergy, 24(2) (2003) 125-140.

[3] L. Devi, K. J. Ptasinski, F. J. J. G. Janssen, S. V. B. van Paasen, P. C. A. Bergman, J. H. A. Kiel. Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. Renewable Energy 30 (4) (2005) 565-587.

[4] L. Devi, K. J. Ptasinski, F. J. J. G. Janssen. Pretreated olivine as tar removal catalyst for biomass gasifiers: investigation using naphthalene as model biomass tar. 86 (6) (2005) 707-730.

[5] C. Courson, E. Makaga, C. Petit, A. Kiennemann. Development of Ni catalysts for gas production from biomass gasification. Reactivity in steam and dry-reforming. Catalysis Today 63 (2000) 427-437.

[6] C. Courson, L. Udron, D. Świerczyński, C. Petit, A. Kiennemann. Hydrogen production from biomass gasification on nickel catalysts Tests for dry reforming of methane. Catalysis Today 76 (2002) 75-86.

[7] L. Devi, M. Craje, P. Thűne, K. J. Ptasinski, F. J. J. G. Janssen. Olivine as tar removal catalyst for biomass gasifiers: catalyst characterization. Applied Catalysis A: General, 294 (1) (2005) 68-79.

[8] Z. Y. Abu El-Rub, E. A. Bramer, G. Brem. Tar removal in an entrained flow cracker (EFC) with application to biomass gasification. Proceedings of Expert meeting on Pyrolysis and Gasification of Biomass and Waste, Strasbourg, France. (2002). 337-346.

[9] S. Rapagnà, N. Jand, P. U. Foscolo. Utilisation of suitable catalyst for the gasification of biomasses. Proceedings from the 10th European Conference and Technology Exhibition on Biomass for Energy and Industry, Wuerzburg, Germany. (1998). 1720-1723.

[10] S. Rapagnà, N. Jand, A. Kiennemann, P. U. Foscolo. Steam-gasification of biomass in a fluidized-bed of olivine particles. Biomass and Bioenergy. 19 (2000). 187-197.