

Hydrogen-rich Gas Production with a Ni-catalyst in a Dual Fluidized Bed Biomass Gasifier

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ABSTRACT: To improve the gas quality (low tar content and high hydrogen volume fraction) of biomass steam gasification in a dual fluidized bed gasifier a nickel-based catalyst has been developed. This catalyst was tested as bed material in a 100 kW_{th} pilot plant. Gas composition and tar content were measured after the reactor and compared with data from gasification tests without a catalytic bed material. Tar and ammonia reduction, changes in the gas composition as well as water conversion, gas yield, chemical efficiencies and lower heating values are reported. The catalysts were characterized before and after the experiments. The catalyst shows strong metal-support interactions which of nickel on the surface which provide resistance against attrition. Furthermore the catalyst is highly resistant and stable for repeated high temperature processing in oxidizing and reducing atmosphere during circulation between the fluidized beds. The performance of the catalyst over 30 h showed no loss of reactivity for cracking tars and no deactivation by common catalyst poisons (sulfur, chlorine, and alkali metals). The presented data represent important results for the further development of catalytic gas cleaning in fluidized bed gasification processes.

INTRODUCTION

Biomass as energy source is required by climatic conventions and in the European Union White Paper. Electricity generation is possible in new applications via biomass gasification. This technology has a big potential due to its great flexibility and the high electrical as well as the overall efficiency. A dual fluidized bed steam gasifier has been developed during the last decade¹. The basic idea of this concept is to divide the reactor in two zones, a gasification zone fluidized with steam and a combustion zone fluidized with air. Between these two zones a circulation loop of the bed material is created but the flue gas remains separated from the product gas. This results in a nearly nitrogen-free, hydrogen-rich product gas. With the aid of a catalytic active bed material the hydrogen content can even be increased.

The key problem of gasification technologies is the tar removal from the product gas. The use of an active bed material as a primary catalyst is the best solution in contrast to more expensive use of secondary catalytic reactor downstream of the gasifier. The

choice of an appropriate in-bed catalyst is then crucial for the optimization of gasification technology.

Natural olivine (iron and magnesium orthosilicate) has been chosen as bed material because of its hardness and its higher catalytic activity compared to silica in biomass steam gasification². Ni-olivine catalyst has been developed^{3,4,5,6} to enhance olivine performances in steam biomass gasification by methane and tar reforming leading to hydrogen production and gas upgrading. The main advantage of this catalyst is its attrition resistance due to strong metal support interactions permitting its direct use in the fluidized bed.

The main limitation of nickel catalyst use for hot gas conditioning of biomass gasification product gases is its sensitivity to deactivation, which leads to limited catalyst lifetimes. Ni catalyst deactivation is caused by several reasons. Sulfur, chlorine, and alkali metals present in gasification product gases act as catalyst poisons. Coke formation on the catalyst surface can be substantial when tar levels in product gases are high. Loss of catalyst activity is apparently due to fouling by buildup of carbon which blocks access to the catalyst pores⁷. Coke can be removed by regenerating the catalyst; however, repeated high temperature processing of nickel catalysts can lead to sintering, phase transformations, and volatilization of nickel. Continued disposal of spent toxic Ni catalysts is not economical and poses an environmental hazard because of the toxicity of nickel. The catalyst can be regenerated by transporting the catalyst to the combustion zone and burning off the carbon.¹ A critical gap identified for catalytic tar reforming technology in biomass gasification processes is then the need for extended lifetime studies of promising commercial or novel catalysts⁸.

There is a need for understanding of catalyst evolution during gasification in real conditions in the dual fluidized bed steam gasifier. Therefore Ni-olivine catalyst as bed material was tested in the fluidized bed followed by the characterization of the used catalyst. Similarly gasification with olivine alone, followed by its characterization serves as a reference for the Ni-olivine catalyst.

The aim of the present work was a comparison of activity and selectivity of olivine and Ni-olivine catalysts and the evaluation of the catalyst stability. The effects of catalyst poisons like sulfur, chlorine, alkali metals and continued catalyst regeneration (circulation between gasification (850°C) and combustion zones (900°C)) in fluidized bed biomass gasification conditions during the extended-term test (30h) are especially studied.

CATALYSTS

Natural olivine

Natural olivine originates from an Austrian mine and its composition (30.5 wt.% of Mg, 7.1 wt.% of Fe and 19.6 wt.% of Si), obtained by atomic adsorption, leads to the mean formula $(\text{Mg}_{0.95}\text{Fe}_{0.05})_2\text{SiO}_4 + 0.04 \text{Fe}_2\text{O}_3$. Iron excess in the form of free iron oxide corresponds to ~4 wt.%. The material already contains small amounts of nickel as well as Ca, Al and Cr (lower than 0.2 wt.% of each). The material was delivered after calcination at 1600°C during 4 hours, crushing and sieving to obtain the particle sizes between 400 and 600 µm. The specific surface area of olivine is very low (<1m²/g). Some interesting physical properties of olivine are given in Table 1.

Bulk density	1700-1900 kg/m ³
Material density	3025 kg/m ³
Hardness	6.5-7 Mohs scale
Melting point	approx. 1760 °C
pH	8.9-9.5
Particle size	400-600 µm
BET-surface area	<1 m ² /g

Table 1 Physical properties of olivine

Ni-olivine catalyst

Large amount of Ni-olivine (100 kg) was prepared by wet impregnation of natural olivine with an excess of nickel nitrate solution. A glass lined steel rotary dryer was used for the preparation. Nickel nitrate (Ni(NO₃)₂·6H₂O) was dissolved by addition of water and salt into the reactor. Natural olivine was added after the nitrate dissolution. The sample was mixed by the rotation of the reactor and then heated to 100°C. Then, the water excess was evaporated under vacuum. The sample was dried overnight in an oven at 120 °C and calcined at 1100 °C during four hours after a temperature increase slope of 3 °C.min⁻¹. Characterization of representative samples of the catalyst by elemental analysis, TPR and XRD showed good homogeneity of the large scale preparation. The nominal percentage of Ni was equal to 3.7 wt %.

The foreseen price for this Ni-olivine, when produced in large scale for the use at the demonstration plant in Güssing, is about twice of the price for olivine.

CHARACTERIZATION METHODS

The crystalline phases contained in the samples and the structural modifications occurring after gasification test were examined by powder X-ray diffraction (XRD) on a Siemens D500TT diffractometer using Cu K α radiation.

Scanning electron microscopy (SEM) was performed on a JEOL 6700 F microscope. The surface composition has been obtained by X-ray microanalysis. The values given are mean values from at least 4 analyses taken on different grains (with a window of 200 µm) and correspond to about 1 micron depth of the surface.

The active phase for hydrocarbon reforming is the metallic nickel. So, the reducibility of the catalysts under hydrogen gives valuable information. This has been followed by temperature programmed reduction (TPR) performed on 200 mg of catalyst placed in a U-shaped quartz tube (6.6mm ID). The reductive gas mixture (H₂ = 0.12 L.h⁻¹ and Ar = 3 L.h⁻¹) passed through the reactor heated from room temperature to 950°C with a slope of 15°C.min⁻¹ then maintained at 950°C until the end of H₂ consumption showed by the baseline return. A thermal conductivity detector (TCD) was used for quantitative determination of hydrogen consumption.

The ⁵⁷Fe Mössbauer spectra were recorded at liquid nitrogen temperature with ⁵⁷Co source dispersed in rhodium matrix. From the obtained spectra, the isomeric shifts were determined in comparison with metallic iron standard at room temperature. To

identify the different forms of iron present in the sample, the spectra were fitted with a computer program MossFit.

DESCRIPTION OF THE PILOT PLANT

Fig. 1 shows a simplified flow sheet of the 100 kW_{th} pilot plant used in this study. The system is a dual fluidized bed steam gasifier. The gasifier is divided into two zones, a gasification zone and a combustion zone. The gasification zone has at the bottom of the bed an inner diameter of 100 mm. The fluidised bed is expanded to a square with 285 mm side length and has a total height of about 1 m. The gasification zone is a bubbling fluidised bed whereas the fluidisation velocity about five times higher than the minimum fluidisation velocity. Biomass is fed into the gasification zone and gasified with steam. The gas produced in this zone is therefore nearly free of nitrogen and has a high hydrogen content. The bed material, together with some charcoal and ungasified biomass, circulates to the combustion zone. This zone is fluidized with air and the charcoal is burned. Light fuel oil as additional fuel is used to raise the temperature of the bed material leaving the combustion zone to the desired temperature. In this way the gasification temperature is controlled. The exothermic reaction in the combustion zone provides the energy needed for the endothermic gasification with steam. The flue gas is removed from the bed material without coming in contact with the product gas. To accomplish this, the gasification zone is separated from the combustion zone by the use of two siphons which are fluidized with steam too (Fig. 1).

The biomass is fed into the gasification zone by two screws. The first one is equipped with a frequency converter to control the amount of fuel. To keep the biomass in close contact with the hot bed material, the biomass is brought in by the second screw directly into the fluidized bed. This is important especially in the case of catalytically active bed materials.

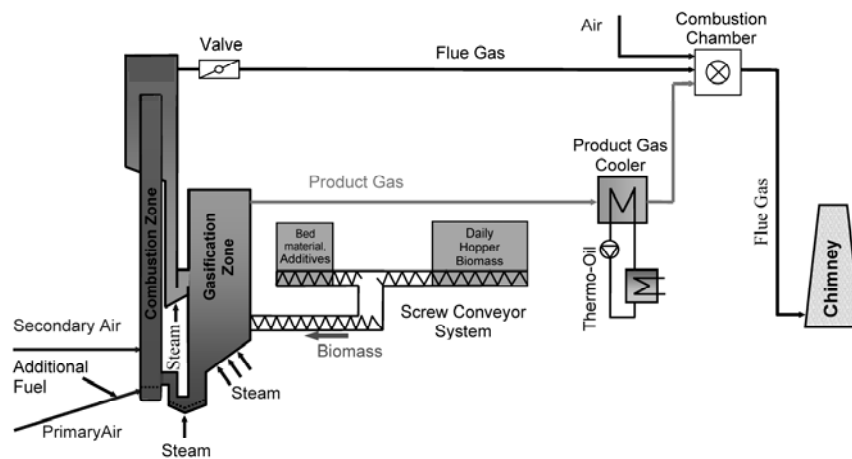


Fig. 1 Simplified flow sheet of the pilot plant

parameter	value	units
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C	49	mass% wf
H	6.52	mass% wf
N	0.12	mass% wf
S	< 0.05	mass% wf
O	44.31	mass% wf
Ash	0.26	mass% wf
LHV	17120	kJ/kg
HHV	18620	kJ/kg

Table 2 Results of the fuel analysis

Wood pellets with a mass flow of 25 kg_{wet}/h were used as feedstock for all experiments. The water content of the wood pellets was 9 wt%. The water-free (wf) composition of the fuel is reported in Table 2.

Tar Sampling and Analysis

The dust and tar contents as well as the gas composition are measured after the product gas heat exchanger. The tar measurement is carried out similarly to the tar protocol “gravimetric tars”⁹. A small amount of product gas is sampled isokinetically for a certain period of time. Dust and heavy tars ($T_B > 200$ °C) are deposited in a filter cartridge filled with glass wool. Low-boiling tars ($T_B < 200$ °C) are washed out with toluene using washing flasks, which are operated at -20 °C. The tars in the filter cartridge are washed out with isopropanol using a soxhlet extractor and the tars are added to the amount of tars of the toluene phase. Samples of the toluene from the washing flasks as well as of the isopropanol are taken for the characterization of the tars using a gas-phase chromatograph coupled with a mass spectrometer (GC-MS). Along with the tar content, the particle, coke and moisture contents in the product gas are measured. A gas meter and a thermocouple are used to determine the dry product gas stream.

The gas composition of the product gas is analyzed with an offline gas-phase chromatograph as well as with an online gas-phase chromatograph both coupled with a thermal conductivity detector (TCD) to get reliable figures.

The experiments were carried out at 850 °C (100 % Olivine) and at 838 °C (100 % Ni-olivine) and a steam-to-fuel ratio of 0.63. Both tests were carried out for about 30 hours under gasification conditions. The gasification temperature is defined as the temperature of the fluidized bed at the height of the biomass feeding point and the steam-to-fuel ratio is defined as the total mass flow of water in the gasifier (fluidization agent and biomass moisture) divided by the dry biomass mass flow.

EXPERIMENTAL RESULTS

RESULTS FROM THE PILOT PLANT EXPERIMENTS

Chemical engineering results

The usage of Ni-catalysts in combination with biomass gasification processes decreases the tar content of the product gas and increases the hydrogen volumetric content^{10,11}. The methane content decreases because of steam reforming which is a

heavily endothermic reaction¹². For this reason the gasification temperature could not be raised without changing the settings for the operation of the pilot plant.

The main results of the experiments are shown in Table 3. Previous publications describe different mixtures of olivine and Ni-olivine^{13, 14} whereas the matter in hand shows a comparison of only olivine resp. Ni-olivine. Because of some changes in the gasifier design the experiments with different olivine-catalyst mixtures are not comparable with those described here.

	olivine	Ni-olivine
bed temperature, °C	850	838
steam-to-fuel ratio, kg _{H2O} /kg _{dry fuel}	0.63	0.63
dry gas composition, vol%		
H ₂	38.9	43.9
CO	29.1	27.2
CO ₂	17.5	18.8
CH ₄	11.4	8.3
C ₂ H ₄	2.0	1.3
lower heating value of the product gas, MJ/Nm ³	13.8	12.4
gas production, Nm ³ /kg*	0.95	0.99
water conversion, %	4.4	7.2
* Volume of dry gas per kg dry wood		

Table 3 Results with olivine and with nickel catalyst

The water conversion is the difference of the total mass flow of water in and the total mass flow of water out divided by the dry biomass mass flow. The water conversion is an important value used to estimate the efficiency of steam gasification systems. As expected, the water conversion increases when using a bed material with a higher catalytic potential. But as can be seen in Table 3 the water conversion is quite low (4.4 resp. 7.2 %) which means that the main part of the steam leaves the gasifier unreacted. Nevertheless the conversion rates are increased parallel with the excess of water found in previous work^{13, 14}. An optimum has to be found between the wanted gas quality and the heat loss due to unreacted steam. From results of previous work a steam-to-fuel ratio of about 0.6 represents a procedural optimum.

An important parameter for gasification processes is the chemical efficiency which is defined according the following equation:

$$\eta_{chem} = \frac{LHV_{pg} * \dot{V}_{pg}}{LHV_{fuel} * \dot{m}_{fuel} + LHV_{add_fuel} * \dot{m}_{add_fuel}} \quad [\%]$$

The chemical efficiency varies not significant comparing olivine and Ni-olivine as bed material and lies in the same range (about 70%) as resulted at the demonstration plant in Güssing¹⁵. The chemical efficiency is heavily dependent on the moisture of the biomass feed and the heat loss over the reactor.

Fig. 2 shows the gas composition using Ni-olivine as bed material over the experimental time of about 30 hours. It can be observed that the catalyst has initially a

high reactivity. The methane volumetric content could be lowered from 11.4 compared to natural olivine to 7.2 vol%. After reaching the so called steady state reactivity the methane fraction increased up to 8.3 vol% (see Table 3). The catalyst reached the steady state reactivity after about 20 hours under gasification conditions. The decrease of reactivity at the beginning is mainly due to attrition of nickel loosely deposited on the olivine surface. This point is discussed in details in the characterization chapter.

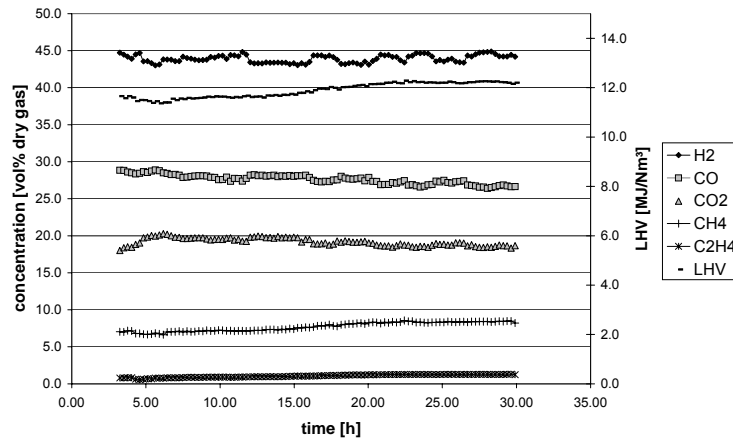


Fig. 2 Product gas composition over time (gasification temperature: 838 °C, steam-to fuel ratio: 0.63, Ni-olivine)

Fig. 3 shows the difference in the molar flow rate (in [moles/kg_{dry biomass}]) for the main gaseous components in the product gas at steady state conditions compared to natural olivine. To close the mass and energy balances the mass flow of ungasified carbon to the combustion zone has to be increased. This flow is not displayed in Fig. 3.

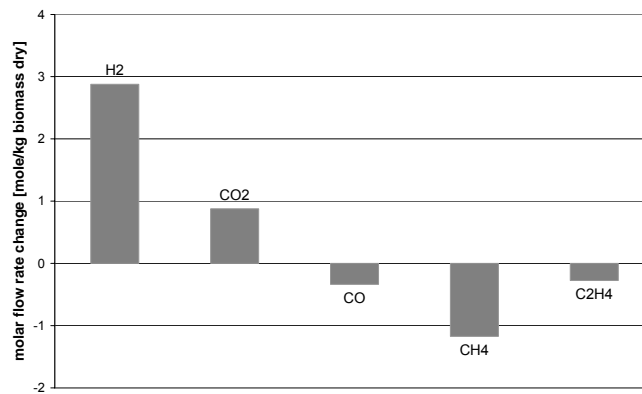


Fig. 3 Difference in the molar flow rate; catalyst – olivine

Generally, it can be stated that the catalyst showed no further deactivation after reaching steady state condition. This performance is also known from literature.⁷ Attrition is an important value for in-bed catalysts especially in circulating fluidized bed processes. A comparison of the attrition of pure olivine and the catalyst showed no

significant difference. The attrition rates were about 0.025 kg/kg of fuel (dry). The attrition rate could be lowered by sieving the entrained fines and bringing back the larger fractions to the process. Investigations at the demonstration plant in Güssing showed that the recirculation of the sieved bed material could lower the loss of bed material down to 5 %¹⁶. Nevertheless frequent disposal of spent nickel catalyst becomes an economic problem as well as an environmental burden. At present the ash from the demonstration plant in Güssing has to be deposited anyway because the particle size is too low to bring the ash out on the fields. But from the environmental point of view this problem must be solved. Thus investigations about this topic are in process.

Two tar analysis methods were performed – a gravimetric analysis and a gc-ms. The total values of these two methods are different. The reason for this is that one of the steps to determine the gravimetric tars is the evaporation of the toluene from the sample. During this intermediate step the main part of the lighter hydrocarbons (e.g. indene, naphthalene) disappears which is the reason for the gap between the gravimetric tars and the so called gc-ms tars (Fig. 4 and Fig. 5).

The conversion is calculated with both the gravimetric tars and the tar amount calculated from the results of the GC-MS measurements. The tar reduction was always more than 90 % (Fig. 4).

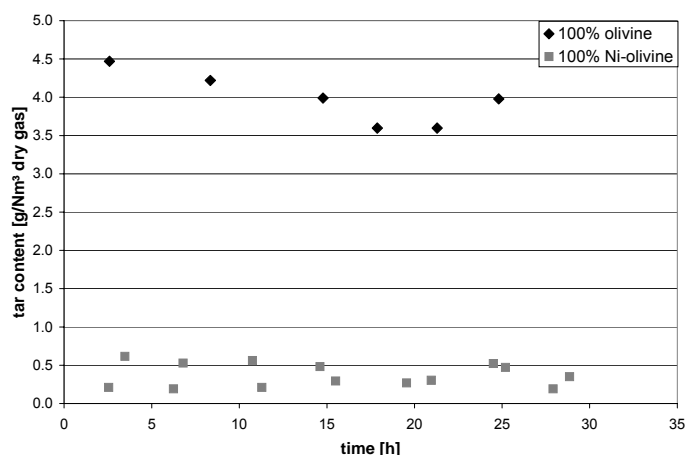


Fig. 4 Gravimetric tars over gasification time

What can be clearly seen in Fig. 5 is that the catalyst is more able to crack naphthalene than indene. Secondary indene and naphthalene are intermediate products from the cracking reactions of the heavy tars. The catalyst showed no loss of activity in reforming the tars which can be seen in the amount of gravimetric tars (Fig. 4) as well as on the tar composition over the gasification time (Fig. 6).

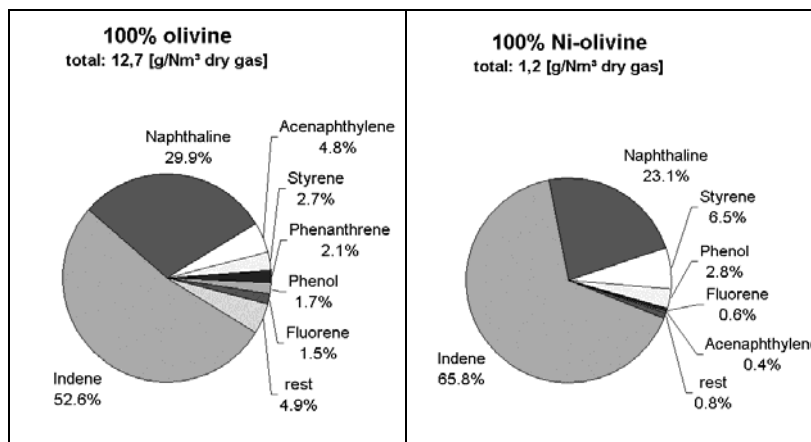


Fig. 5 Comparison of the tar composition

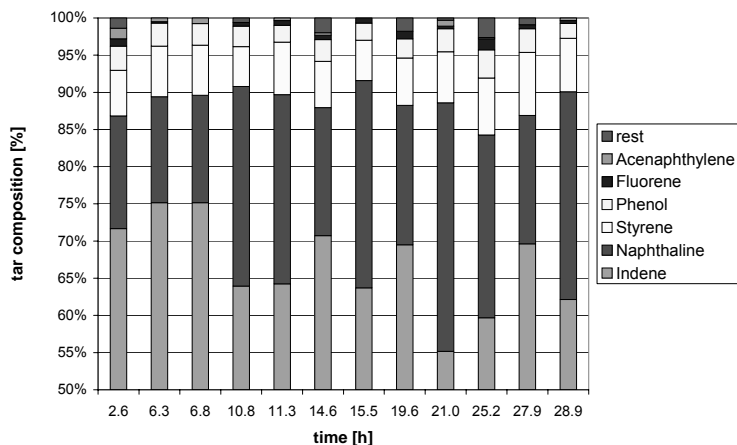


Fig. 6 Tar composition using Ni-olivine over gasification time

The catalyst is also able to reduce the ammonia content in the product gas from 820 ppm down to about 500 ppm that stands for a conversion of ammonia of more than 40 %.

Characterization of catalyst before and after test

X-Ray diffraction was performed on the samples to verify stability of the structure and to follow the evolution of crystalline phases present in the catalyst during the test. The diffractograms for the olivine and Ni-olivine samples before and after test are shown in Fig. 7.

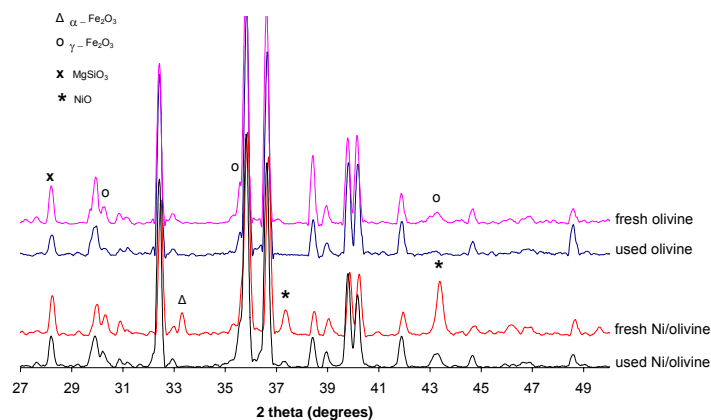


Fig. 7 XRD of olivine and Ni-olivine before and after test in FICFB gasifier

XRD of fresh olivine shows that the main lines are close to those of the Mg_2SiO_4 forsterite (34-0189 JCPDS file). The secondary crystalline phases observed are the MgSiO_3 phase (19-0606 JCPDS file) visualized by its 100-intensity line at $28.2 (2\theta)$ and $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$. The presence of those secondary phases is due to a modification (oxidation) of the $(\text{Mg},\text{Fe})_2\text{SiO}_4$ phase at high temperature during initial calcination of olivine. After gasification test crystalline phase of olivine is preserved but the intensities of the strongest lines of the secondary phases MgSiO_3 and Fe_2O_3 decrease.

Similar trends can be also observed for Ni-olivine catalyst. The main lines of natural olivine close to those of the Mg_2SiO_4 forsterite are maintained indicating that the support structure is not changed. Small decrease of the MgSiO_3 peak can be seen and $\alpha\text{-Fe}_2\text{O}_3$ disappears after the test. The two lines characteristic for the cubic NiO phase (1-1239 JCPDS file), observed for the fresh catalyst indicate the presence of large size aggregates. They diminish significantly after gasification test. This indicates a loss of nickel containing particles by attrition in fluidized bed or nickel insertion into the olivine structure.

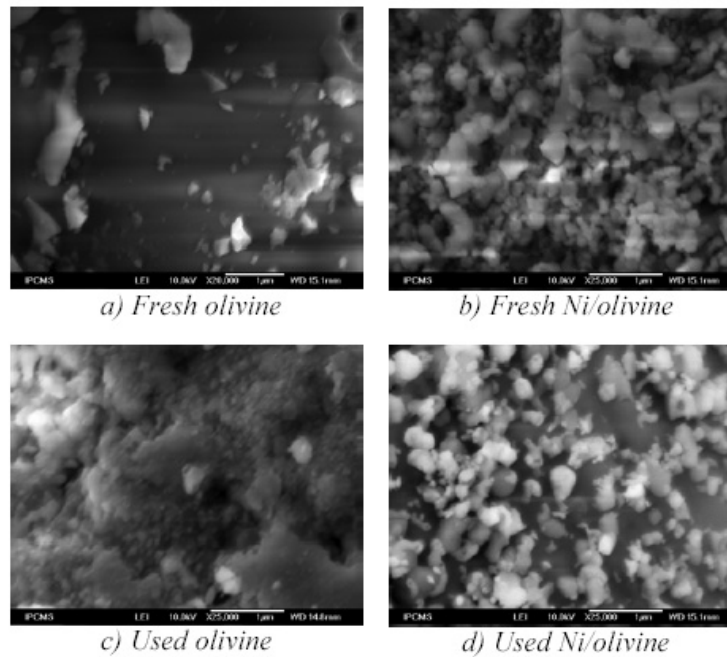


Fig. 8. SEM of olivine and Ni-olivine before and after tests in the gasifier.

The scanning electron micrographs of Fig. 8 show the changes in the surface of olivine and Ni-olivine after the test in the pilot plant. The surface of the fresh olivine support is shown in Fig. 8a. Smooth grain surface can be observed (probably due to prior calcination at 1600°C) with few iron oxide and olivine phase particles present on the surface. The surface of used olivine presented in Fig. 8c is changed and seems to be covered with a kind of deposit. Those changes of surface morphology can be related to the changes of the surface composition obtained by X-ray microanalysis shown in Table 4. Principal elements present on the surface of fresh olivine are Mg (26%), Si (13.5%), O (54.5%) and Fe (4.9%) coming from the olivine structure. In the sample of used olivine lower percentages of Mg (17.3%) and Si (7.9%) and higher Fe (6.9%) contributions can be found. The diminishing of Mg and Si contribution can be explained by the apparition additionally of 7% of calcium and small contributions of P (1%), K (0.4%) and Na (0.2%), elements present in biomass.

For fresh Ni-olivine shown in Fig. 8b the deposit of NiO grains cover homogeneously nearly all surface of olivine. The NiO deposit can be also observed in the used Ni-olivine sample but only a part of the surface is covered in this case.

	<i>Atomic %</i>								
	Mg	Si	O	Fe	Ni	Ca	P	K	Na
<i>fresh olivine</i>	26,2	13,5	54,5	4,9	0,7	0,1	0,0	0,0	0,0
<i>used olivine</i>	17,3	7,9	58,8	6,9	0,0	7,4	1,0	0,4	0,2
<i>fresh Ni/olivine</i>	9,4	1,9	50,8	3,6	34,1	0,1	0,0	0,1	0,0
<i>used Ni/olivine</i>	15,6	5,8	53,6	8,8	10,3	5,2	0,5	0,2	0,0

Table 4. Surface composition of the olivine and Ni-olivine before and after tests in the gasifier. (Determined by X-ray microanalysis coupled with SEM)

X-ray microanalysis of fresh Ni-olivine shows lower surface concentrations of Mg, Si and Fe due to the fact that the surface of olivine is covered with NiO deposit (34% of Ni) observed in Fig. 8b. Comparison with the used Ni-olivine shows that Ni content is about 3 times lower (10%) than in the fresh sample. These results could explain the partial loss of nickel loosely deposited on the olivine surface and are in agreement with XRD results. Very low concentration of P and alkaline metals (K and Na) as well as no presence of S nor Cl on the surface of used Ni-olivine were observed.

In both olivine and Ni-olivine used in the biomass gasification we can observe the apparition of Ca on the surface in a concentration comparable with this of Fe (7 and 5 % respectively). Without any further investigations it is difficult to evaluate the real influence of this element. However calcium oxide has been already proven to be an active catalyst for biomass gasification and it has been reported in the literature as an additive having beneficial effect for enhancement of carbon gasification and increasing coke deposition resistance.¹⁷

Different parts of the catalyst were also tested under reductive conditions (Fig. 9). Reduction profile for fresh olivine shows only one reduction peak with a maximum at 660°C. This broad peak is attributed to the reduction of the free iron oxide associated to the olivine structure and formed by oxidation of Fe²⁺ present in olivine structure during the initial calcination. The quantity of reducible iron oxide diminishes in the used olivine sample. The decrease of the iron quantity is not in accordance with the results of surface analysis obtained by X-ray microanalysis where the contrary effect is observed. However, the difference could be due to the fact that TPR refers to reduction of larger surface of the sample including pore surface and total reducible iron oxide distribution can be different than in the external surface layer of 1 micron analyzed by X-ray microanalysis.

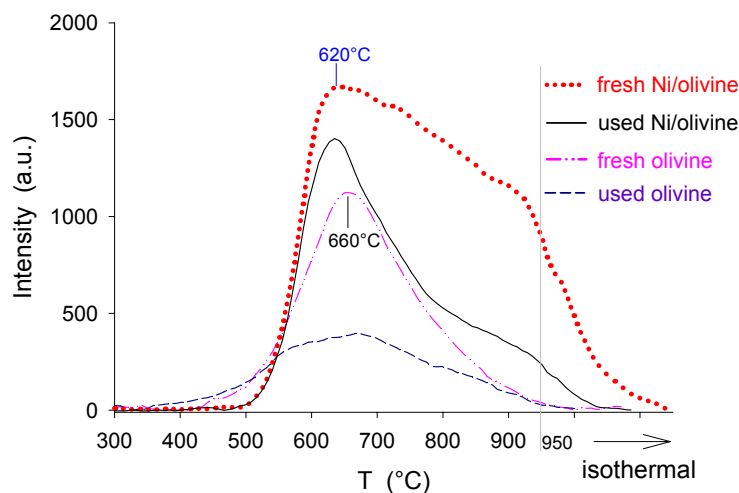


Fig. 9. TPR for olivine and Ni-olivine before and after test in FICFB gasifier

For fresh Ni-olivine the wide reduction profile includes a free iron oxide reduction peak (max. at 620°C) followed by reduction of nickel species in different degree of interactions with the support (reduction between 700 and 900°C) and linked nickel oxide reduction peak (max. at 910°C). As it was shown previously⁶ after calcination at 1100°C, nickel oxide forms grafts with the support and these strong nickel–olivine interactions were confirmed by high reduction temperature (910°C). In this case, linked nickel oxide reduction is compatible with gasification temperature.

TPR of used Ni-olivine shows a small decrease of the iron oxide reduction peak and an important decrease of the high temperature shoulder (700-900°C) attributed to the reduction of different Ni species. The diminishing of the nickel species reduction peak for the used catalyst confirms the results observed by XRD and X-ray surface analysis and can be attributed to the loss of Ni due to attrition.

The particle size distribution was found nearly the same for the fresh and used Ni-olivine catalyst with a mean particle size 574 and 578 μm respectively, confirming the attrition resistance (which could be related with the olivine hardness) of catalyst particles.

It seems that the only cause of catalyst deactivation could be the loss of the active phase by attrition of nickel loosely deposited on the olivine surface. This could explain the initial drop of activity. The followed stable performance indicates that grafted Ni is resistant for attrition in the fluidized bed.

CONCLUSIONS

Ni-olivine preparation has been successfully scaled up from laboratory scale to industrial scale (100kg). Large amount of NiO/olivine catalyst was prepared with high homogeneity. The results of catalyst characterization were in good agreement with those obtained for catalysts prepared previously in small amount (20g), confirming the presence of strong Ni-olivine interactions guarantying efficient performance of the catalyst in biomass gasification in the pilot plant.

This work has proven that Ni-olivine catalyst fulfils all the criteria for the use in fluidized bed biomass gasification process. It is highly effective in the removal of tars and methane, increases the hydrogen content and decreases ammonia content. The strong metal support interactions (Ni in the form of grafts on the olivine surface) prevent attrition, sintering and volatilization of the nickel. Ni-olivine catalyst proved high stability and resistance for repeated high temperature processing in oxidizing and reducing atmosphere during circulation between the gasification (850°C) and combustion zone (900°C). This provides constant regeneration of the catalyst excluding any deactivation as a result of carbon fouling. No deactivation by catalyst poisons like sulfur, chlorine, and alkali metals was observed during the 30h of catalyst testing.

Using of Ni-olivine as an inexpensive (compared to commercial catalysts) primary catalyst in the fluidized bed is a good solution to enhance the efficiency of the process, to simplify the gas cleaning line without an expensive secondary catalytic reactor and to decrease the operating costs.

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