

# Improved Gasifier availability with bed material and additives

A.J. Grootjes  
C.M. van der Meijden  
H.J.M. Visser  
A. van der Drift

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## IMPROVED GASIFIER AVAILABILITY WITH BED MATERIAL AND ADDITIVES

A.J. Grootjes<sup>1</sup>, C.M. van der Meijden<sup>2</sup>, H.J.M. Visser<sup>3</sup> & A. van der Drift<sup>4</sup>

<sup>1</sup> Corresponding author: Energy research Centre of the Netherlands (ECN), P.O. Box 1, 1755 ZG Petten, The Netherlands, Phone: +31 224-564983, Fax: +31 224-568487, E-mail: grootjes@ecn.nl

<sup>2</sup> ECN, Phone: +31 224-564582, Fax: +31 224-568487, E-mail: vandermeijden@ecn.nl

<sup>3</sup> ECN, Phone: +31 224-564557, Fax: +31 224-568487, E-mail: h.visser@ecn.nl

<sup>4</sup> ECN, Phone: +31 224-564515, Fax: +31 224-568487, E-mail: vanderdrift@ecn.nl

**ABSTRACT:** in order to valorize several feedstock, gasification is one of the technologies developed over the past decades. ECN developed the MILENA gasifier. In order for MILENA to become a commercial success, the gasifier needs to be feedstock flexible, robust and economically sound, operating with high availability. One of the characteristics of MILENA is high efficiency but with a higher tar content, compared to some other Dual Fluidized Bed (DFB) gasifiers. In order to reduce the issues that are associated with high tar levels in the product gas, the effect of a number of primary measures was studied. This paper presents results obtained in the last two years, focused on improving the gasifier availability by conducting experiments in a 25 kW<sub>th</sub> lab scale MILENA gasifier. Amongst others, gas composition, tar content and calorific value of the product gas were compared. Scanning Electron Microscope analysis were used to investigate bed material changes. Results show that Austrian olivine can be activated by Fuel B as well as by Additive A & B. The water-gas shift reaction is enhanced and the tar content is reduced significantly, especially the heavy tars that dominate the tar dew point. Activated olivine has a calcium-rich layer. The results show that with MILENA, we are able to lower and control the tar dew point, which will possibly increase the availability of a MILENA gasifier.

**KEYWORDS:** MILENA, OLGA, olivine, calcium, biomass gasification, bed material, tar reduction

### 1 INTRODUCTION

Over recent years there has been growing interest in the use of gasification technologies to treat solid biomass, high ash coal and waste. This idea is not new and gasification itself, first discovered by Belgian chemist Jan Baptista Van Helmont in 1609, has been used for about 200 years. Town gas for example was once in general use for lighting and heating [1].

In the past decade, gasification technology has matured and has proven to be an efficient, fuel flexible technology, able to thermochemically convert several feedstock into valuable products and energy. Approx. 10 years ago, Granatstein et al. [1] compared fluidized bed gasification and combustion plants using waste and biomass and concluded that gasification plants have a higher efficiency at comparable emissions. Gasifiers in Europe have evolved from cold flow models, kW<sub>th</sub> lab-scale set ups, MW<sub>th</sub> pilot scale installations to double digit MW<sub>th</sub> demonstration plants. At this moment, several of these plants are in operation, under construction or are being planned. For example [2]:

- GoBiGas, 32 MW<sub>th</sub>, Dual Fluidized Bed (DFB), wood, Gothenburg, Sweden
- 15 MW<sub>th</sub>, DFB, wood, Villach, Austria
- 15 MW<sub>th</sub>, DFB, wood, Ulm, Germany
- 21 MW<sub>th</sub>, DFB, wood, Großenhain, Germany
- Lahti Energy's Kymijärvi II, 40-90 MW<sub>th</sub>, SRF, Lahti, Finland
- GroenGas 2.0, DFB, 12 MW<sub>th</sub> waste wood, Alkmaar, Netherlands

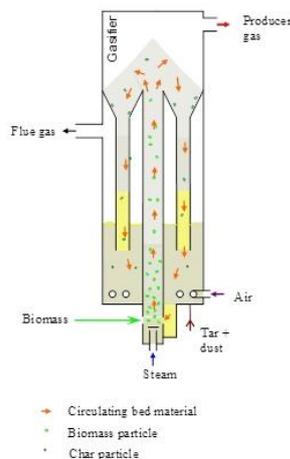
DFB (Dual Fluidized Bed) steam gasification, like ECNs MILENA is one of the various technologies for steam gasification of various feedstock [3]. MILENA is available at a 30 and 800 kW<sub>th</sub> scale at ECN for research

purposes.

MILENA is a compact designed fluidized bed gasifier. It consists of one reactor for pyrolysis/gasification and combustion respectively, see **Figure 1**. Heat is transported by circulating bed material from the combustion reactor to the gasification reactor. The fuel for the combustion is the solid residue from the gasification reactor, possibly with additional fuels such as the tar from the OLGA tar removal system.

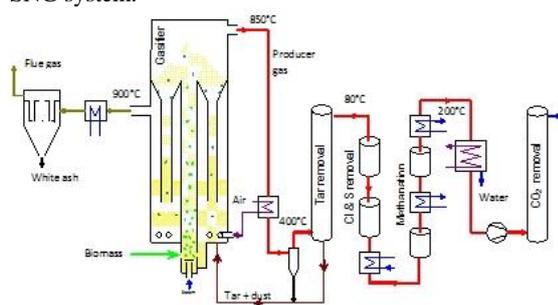
The main benefits of MILENA technology are:

- Complete conversion, no carbon-containing ash
- High efficiency
- Essentially N<sub>2</sub>-free producer gas, LHV ~ 15 MJ/Nm<sup>3</sup> (dry basis)
- No air separation unit (ASU) necessary
- Compact design
- Fuel flexible (tested with wood, demolition wood, lignite, grass, digestion residue, ...)



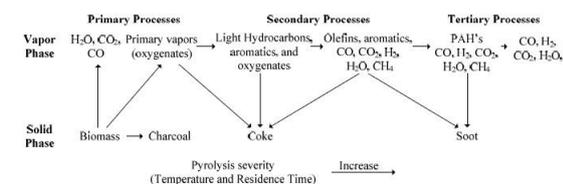
**Figure 1:** Schematic operation of the MILENA gasifier

MILENA is a patented gasification technology that is commercially available via our industrial partner Royal Dahlman, as well as the patented OLGA tar removal technology. OLGA is an advanced scrubbing technology for tar removal downstream gasification processes. See **Figure 2** for a schematic view of the MILENA-OLGA-SNG system.



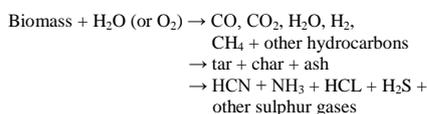
**Figure 2:** MILENA-OLGA-SNG system

In a very simple way, gasification of biomass can be seen as a two-step process: pyrolysis followed by further reactions promoted by e.g. the fluidizing agent (either  $H_2O$ ,  $O_2$  or some other reactant) and catalysts. Pyrolysis is a thermal process in which the biomass is heated in the absence of an oxidant. The biomass is converted into char, tars and gas. The proportions of the product yield depend on the process conditions like heating rate, temperature and gas residence time. The pyrolysis pathways are depicted in **Figure 3** [4, 5].

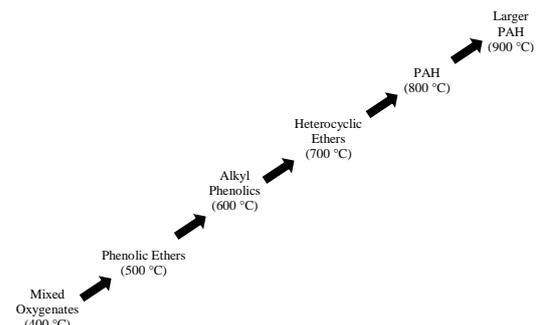


**Figure 3:** Pyrolysis pathways [4]

The reaction for biomass gasification in general is as follows [6]:



One of the products of the gasification reaction, tar, is an undesired by-products and is problematic in integrated biomass gasification systems for a number of reasons. Tars can condense in pipes and on particulate filters leading to blockages and clogged filters. Tars also have varied impacts on other downstream processes. Tars can clog fuel lines and injectors in internal combustion engines. Luminous combustion and erosion from soot formation can occur in pressurized combined-cycles where the product gas is burned in a gas turbine. When product gas needs to be compressed, tars can condense in the compressor or in the transfer lines as the product gas cools [6, 7].



**Figure 4:** “Tar” maturation scheme [4]

Tars can be defined as the collective term for higher, mainly aromatic hydrocarbons [8, 9]. The formation of tars is depending on the temperature and the state of pyrolysis or gasification, as was described by Milne et al [4]. The formation or specific groups of tars depends on the gasification temperature as shown in **Figure 4**. Tars can be classified into 5 groups, according to Rabou et al [10], based on the number of rings of the aromatic compound, see **Table I**.

**Table I:** Tar classification

Tar class	Class name	Properties
1	GC undetectable	7- and higher ring compounds
2	Heterocyclic	Cyclic hydrocarbons with heteroatoms, (highly) water soluble
3	Light aromatic	Compounds that usually do not pose problems regarding condensation or water solubility
4	Light polyaromatic	2- and 3-ring compounds that condensate at intermediate temperatures at relatively high concentrations
5	Heavy polyaromatic	4 – 6-ring compounds that condense at high temperature at low concentrations

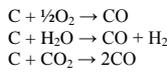
According to Figure 4, Poly Aromatic Hydrocarbons (PAH), amongst other tar species, are formed in the MILENA gasifier since the gasification temperature is often above 800 degrees Celsius. These multi ring PAH tar species, like coronene, with a molecular weight (MW) of 300 g/mol have a large influence on the overall tar dew point. The overall tar dew point is defined as the temperature at which first tar condensation takes place, mostly based on molecular size or vapor pressure. However, sometimes it can be a concentration effect. The effect of the quantity of (multi ring) PAH tar species on the overall tar dew point is shown in **Table II**. Heavy tars dominate the tar dew point, even at 1/10<sup>th</sup> of the concentration [11].

**Table II:** Dew point of tars

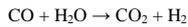
Fluoranthene (202 g/mol)	Benzo(a)pyrene (252 g/mol)	Coronene (300 g/mol)	Dew point (calculated)
-	-	100 mg/Nm <sup>3</sup>	236 °C
-	1000 mg/Nm <sup>3</sup>	100 mg/Nm <sup>3</sup>	237 °C
10000 mg/Nm <sup>3</sup>	1000 mg/Nm <sup>3</sup>	100 mg/Nm <sup>3</sup>	239 °C

It can be concluded that when the tar dew point is above the surface temperature of the pipes and filters and other product gas handling equipment, condensation of tars occurs, with potentially problematic effects like blocking and clogging.

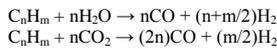
The char yield in gasification can be optimized to maximize carbon conversion or the char can be thermally oxidized to provide heat for the process. In the MILENA the remaining char after gasification is oxidized in the combustor to provide heat for the gasification reactions. Char is partially oxidized or gasified according to the following reactions [4]:



The gasification product gas composition, particularly the H<sub>2</sub>:CO ratio, can be further adjusted by reforming and shift chemistry. Additional hydrogen is formed when CO reacts with excess water vapor according to the water-gas shift reaction [4]:



Reforming light hydrocarbons and tars formed by gasification also produces hydrogen. Steam reforming and dry reforming occur according to the following reactions [4]:



Both the water-gas shift reaction as well as the reforming reactions can be promoted by the use of catalysts, such as active bed materials [4].

Since tars are undesired products of gasification several measures can be taken to reduce the quantity of tars in the product gas. The approaches for reduction of tar formation and for tar removal from the product gas can be divided in two categories [6, 9]: treatment inside the gasifier (primary measures) and gas cleaning after the gasifier (secondary measures). Secondary measures include cyclones, filters, scrubbers, catalytic tar cracking reactors and OLGA. Primary measures consist of a selection of operating parameters (e.g. temperature, fluidization velocity, bed height), use of active bed material, catalysts, additives and specific gasifier design modifications. It is likely that an adequate combination of different primary and secondary measures may optimize the gasifier performance and allow for production of a product gas with low tar concentrations [9]. The availability of the gasifier, as defined by **Equation 1**, may also be improved when primary and secondary measures are used, resulting in a reduced frequency for maintenance/equipment cleaning. Agglomeration behavior can also be influenced by primary and secondary measures but was left outside the scope of this study.

**Equation 1:** Availability = (1 – gasifier downtime / theoretical amount of gasifier operating hours) x 100%

One of the characteristics of the MILENA gasifier is that it can produce more tar compared to other DFB gasifiers, which is due to the fact that gasification takes place in the riser instead of the bubbling fluidized bed (BFB). Typical for steam gasification in the MILENA riser are: short residence time of the biomass, short contact time between bed material and tars and a lower steam to biomass ratio, resulting in high concentrations of tars. For these reasons, it was thought that the MILENA gasifier was less effective in tar reduction by primary measures, such as catalytically active bed material. The use of less steam results in a high overall efficiency, which was one of the reasons for choosing this gasifier configuration.

One of the potential tar problem areas is a gas cooler that usually is installed between the gasifier and the gas clean-up section. This cooler reduces the product gas temperature to the gas clean-up inlet temperature. The overall tar dew point in the gas dictates the minimum temperature that can be used in the gas cooler without the risk of problematic tar condensation. When the tar dew point is high, this may result in the use of expensive materials and cooler designs, affecting the CAPEX negatively. ECN aims to reduce the concentration of heavy tars (class 5), because they are responsible for cooler fouling when the cooler wall temperature is too low.

Furthermore, in order for MILENA to become a commercial success, the gasifier system needs to be feedstock flexible, robust and economically sound, operating with high availability.

For these reasons, the aim of the study was to investigate if tar levels in the product gas could be lowered and controlled despite the characteristics of the MILENA gasifier. The focus was on reducing tars in-situ, in the reactor, by means of active bed materials, the effect of a different fuel and additives. This paper presents results obtained in the last two years focused on improving the gasifiers availability by conducting experiments in the 25 kW<sub>th</sub> lab scale MILENA gasifier.

## 2 EXPERIMENTAL

### 2.1 Description of lab MILENA

ECN realized a 25 kW<sub>th</sub> lab-scale MILENA gasifier in 2004, capable of producing approximately 7 Nm<sup>3</sup>/h methane-rich medium calorific gas with high efficiency. The installation consumes approximately 5 kg/h of biomass. In general dry beech wood particles between 0.75 and 3 mm are used as fuel, but also pine chips, sewage sludge, high ash coal, soy residue and grass were tested. The internal diameter of the riser (gasifier) is 36 mm. The internal diameter of the combustor is 250 mm. The lab-scale installation is made of stainless steel. Heat loss from the process is compensated by high temperature electrical trace heating and external insulation. Methane is added to the combustor to simulate the recycle of tars collected by the OLGA tar removal system. The riser is fluidized with steam. The amount of fluidization steam varies between 0.1 and 2 kg/h. The amount of steam required to fluidize the riser is low (0.1 kg/h), but additional steam is used to increase the water content of

the producer gas, because the biomass used for lab-scale experiments is relatively dry (10 wt% moisture), the fuel foreseen for commercial applications contains more moisture (25 wt%). Bed material circulation rate rate is  $\pm 40 \times$  biomass input  $\approx 200$  kg/h. BFB bed material inventory is approximately 40 kg. Average residence time of bed material in the BFB combustor is  $\pm 12$  minutes. Residence time in the riser is in the order of 5 seconds.

## 2.2 Gas analysis of process gas with micro-GC's and online gas monitors

The sampled gas is cooled to a dew point of 5 degrees Celsius by a peltier gas cooler. The formed condensate is constantly removed by a peristaltic pump. After the cooler, the gas is filtered by an aerosol filter and pumped to the continuous flow analysers or micro GC's.

The continuous flow analysers used at ECN are NDIR's (Nondispersive Infrared Analysers) for CO, CO<sub>2</sub>, CH<sub>4</sub>, SO<sub>2</sub>, N<sub>2</sub>O, Thermoconductivity analysers for H<sub>2</sub>, and paramagnetic analysers for O<sub>2</sub>. The sample gas coming from the pre-sample system is flowing through the analysers with a continuous flow of 30-80 L/h regulated by a rotameter. The concentrations are constantly monitored and registered by a PC, but can also be seen on the display placed on the monitors. The monitors are calibrated with zero gas (pure N<sub>2</sub>) and span gas (a certified gas mixture with about the same component concentrations as the process gas to be measured).

Micro-GC's (Varian 4900) can perform fast and accurate gas measurements in various process gases. The analysis time is about 60 seconds. At ECN the following gases can be measured with micro-GC's: H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>S, COS, Benzene and Toluene. The GC's are calibrated with certified gas mixtures.

## 2.3 Tar sampling and analysis

ECN often uses the Solid-Phase Adsorption (SPA) method for the tar analysis, since it is more convenient than the tar guideline. The SPA method is useful for compounds from phenol to coronene. It works as follows: collection of (mainly) Poly Aromatic Hydrocarbons on Solid Phase Adsorber column (LC RP18-amino), after which the tars are desorbed with Di-Chloro Methane (DCM), followed by analysis on a GC-MS system. At ECN, the contributions of about 35 compounds are evaluated from the GC spectrum. Contributions of unidentified compounds are estimated by comparison to those from identified compounds and are reported as 'unknowns'. Because the SPA result for toluene is unreliable, we exclude toluene from tar class 3. Instead, we measure the toluene concentration by gas chromatography (GC) and treat toluene as one of the gaseous compounds in the product gas. The reproducibility of the SPA method is within 10%.

## 2.4 Used materials

The standard fuel for the MILENA lab scale gasifier is Rettenmaier Räucher Gold HBK 750/2000. This fuel is the reference fuel and has a constant quality and particle size distribution. Bed material usually has a particle size in the range of 0.1 to 0.4 mm. The base case bed material

is quartz sand, which is a robust, attrition resistant material without catalytic activity. 2 types of olivine were used, Norwegian olivine and Austrian olivine. Austrian olivine was heat treated by the manufacturer. In earlier studies, formation of tar reducing, calcium-rich layers around olivine particles was demonstrated [7, 8, 12, 13]. The formation of this layer by use of additive A and B was part of the experiments in order to investigate if this process could be managed as a primary measure. Additive A is added to the BFB directly and is rich in inorganics. Additive B was mixed with the fuel and is rich in inorganics as well, but with another composition. Apart from the standard beech wood fuel, a fuel (Fuel B) was used to study the effect of these inorganics on the tar content, using different bed materials.

## 2.5 Experimental set-up

**Table III** shows the main operational parameters of MILENA for the experiments. The biomass feed rate to bed material inventory ratio is 1 : 8 (5 kg/h to 40 kg). This ratio, along with the mineral content of the fuel and/or additives, determines the minimal duration of an experiment where possible build-up of minerals in the bed material is required. In practice, most of the experiments had a duration of 24 to 200 hours to build up a quantitative level of inorganics.

The gasification temperature was around 850°C which is based on the temperature of an industrial sized MILENA gasifier. In the lab-scale MILENA the ashes collected by external cyclones were not recycled to increase the inorganic content of the bed material. For all experiments, the steam to carbon ratio is typically low, at around 0.6 [kg/kg], compared to the Austrian DFB, where it can be around 1 – 2 [kg/kg] [7].

Experiments were conducted with sand, Austrian olivine (A. olivine), Norwegian olivine (N. olivine) using the standard fuel, as well as Fuel B. Furthermore with Austrian olivine, activated by 200 hour of gasification, using the standard fuel. And finally Austrian olivine with additives A and B.

**Table III: Main parameters of experiments**

	T gasification [°C]	T combustion [°C]	Fuel [kg/h]	Steam to C [kg/kg]
Sand	810	849	4.5	0.65
N. olivine	853	890	5.0	0.60
A. olivine (fresh)	876	912	4.5	0.68
Sand + Fuel B	855	898	4.6	0.68
N. olivine + Fuel B	853	914	5.0	0.58
A. olivine + Fuel B	846	921	4.5	0.65
A. olivine (200 h)	870	924	4.5	0.65
A. olivine + Additive A	867	902	4.5	0.65
A. olivine + Additive A + B	855	868	4.5	0.65

## 3 RESULTS AND DISCUSSION

Several experiments were conducted to measure the effect of primary measures on the tar content of the product gas. **Table IV** shows the main gas compositions. When comparing the inert sand to olivines, it reveals that

the olivines can enhance the water-gas shift reaction, resulting in higher H<sub>2</sub> and higher CO<sub>2</sub> contents, while the CO content decreases. A higher hydrogen concentration dilutes the gas, by lowering the gas density, lowering the methane concentration. This has an effect on the heating value of the product gas, lowering it up to 15 %. A lower heating value of the product gas may influence the application in gas-to-power applications. A high concentration of methane might be beneficial for the efficiency of Substitute Natural Gas (SNG) production.

Adding additive A during the experiment using the standard wood fuel and Austrian olivine delivered a product gas composition with some enhanced water-gas shift activity, as can be seen by the moderately lowered CO content, compared to activated Austrian olivine. Additionally, the H<sub>2</sub> and CO<sub>2</sub> contents are slightly higher than in the case of fresh Austrian olivine. Adding both additive A and B resulted in a product gas composition that is comparable to the case of activated Austrian olivine. This seems to support that the interaction of Austrian olivine with inorganics may increase the water-gas shift activity.

**Table IV:** Summary of average product gas compositions

	CO [Vol % <sub>gas</sub> ]	H <sub>2</sub> [Vol % <sub>gas</sub> ]	CO <sub>2</sub> [Vol % <sub>gas</sub> ]	CH <sub>4</sub> [Vol % <sub>gas</sub> ]
Sand	45	18	15	14
N. olivine	29	26	25	13
A. olivine (fresh)	35	21	24	12
Sand + Fuel B	31	24	21	14
N. olivine + Fuel B	25	30	24	10
A. olivine + Fuel B	21	29	32	10
A. olivine (200 h)	22	28	33	11
A. olivine + Additive A	28	27	27	11
A. olivine + Additive A + B	23	27	30	12

Apart from enhancing the water-gas shift reaction, active bed materials, additives and mineral rich fuel may promote in-situ tar reduction. **Table V** shows the SPA tar measurement results, divided in the tar classification system of ECN. The experiments with sand, using the standard fuel as well as Fuel B, give an indication of the tar content when using inactive bed materials. When comparing the results of sand to Norwegian olivine and fresh Austrian olivine, and focusing mainly on the class 5 tars, it can be concluded that these bed materials are not very active towards tar reduction. Using Norwegian olivine, somewhat less tars are produced and this can not be explained by the operational parameters of the experiment or by anything else, other than that the olivine was from another batch than the Norwegian olivine that was used with Fuel B. Another observation is that sand + Fuel B produces more tar, compared to the standard beech wood fuel.

The experiments with Austrian olivine with Fuel B and when Austrian olivine was used for 200 hours with the standard fuel, show that this bed material can be activated to reduce tars significantly. Especially the high dew point, class 5 tars, are reduced up to 86%, resulting in less than 1 g/Nm<sup>3</sup>.

The estimated dew point of tars in the product gas, using inactive materials, is estimated to be around 400°C. This results in applying wall temperatures for the cooler of 450 °C for the MILENA system. In practice this means that steam coolers can not be used. The activation of Austrian olivine has an immediate effect on the overall tar dew point which was calculated to be less than 200°C. This makes application of low cost steam coolers possible.

The time to achieve significant activation of Austrian olivine by the standard fuel and fuel B was approximately 200 hours and 24 hours respectively. It is thought that during the oxidation step the migration of iron from the bulk of the olivine grain to the surface and subsequently oxidation state may contribute to tar reduction and promotion of the water-gas shift reaction [14, 15]. In the MILENA gasifier, the Austrian olivine bed material is exposed to an oxidative atmosphere in the BFB for about 10 minutes, which presumably is long enough to transport iron to the surface and oxidize it to hematite (Fe<sub>2</sub>O<sub>3</sub>) as well as to a certain extent to magnetite (Fe<sub>3</sub>O<sub>4</sub>) and MgFe<sub>2</sub>O<sub>4</sub> [15]. The bed material residence time in the riser, under 'mildly reducing' conditions, is in the order of seconds and we believe that this will reduce the iron oxides at the surface to a certain extent, likely to magnetite (Fe<sub>3</sub>O<sub>4</sub>) and possibly FeO and FeC<sub>x</sub>, as described by Lancee et al. and Frederiksson et al. [14, 15], but probably not to a significant extent further to e.g. metallic iron. This characteristic of the MILENA, where the bed material continuously cycles between an oxidative and reducing atmosphere is thought to drive and keep the iron available at the surface of olivine particles. This is assumed because the residence time under oxidation is relatively long followed by the riser conditions that are not strongly reducing, due to the water and CO<sub>2</sub> content of the gas, as well as short termed, in the order of seconds.

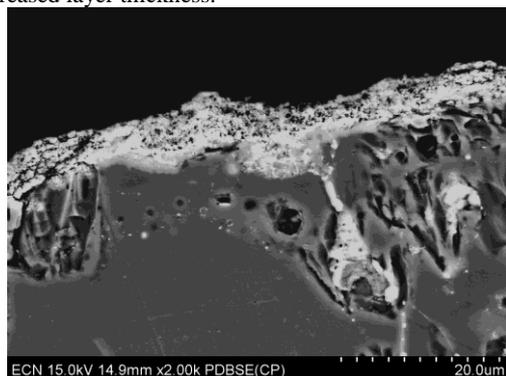
Furthermore, an active calcium-rich layer, formed around the olivine grains, as was described by Kirnbauer et al [7].

The experiments with additives A and B show a reduction of tars, of up to 50%, compared to fresh Austrian olivine. The duration of these experiments was about 30 hours and we believe that by increasing the alkali build-up in the bed, an increased level of tar reduction is possible. One of the objectives is to have tools at hand that can control the tar dew point during operation of a gasifier, especially when the fuel composition can vary, e.g. in the case of waste gasification. We believe that additives might be suitable for this task. The product gas composition might be suitable for indicating the amount of additive necessary in real time.

**Table V: Summary of SPA tar analysis**

	Class 2 [g/Nm <sup>3</sup> ]	Class 3 [g/Nm <sup>3</sup> ]	Class 4 [g/Nm <sup>3</sup> ]	Class 5 [g/Nm <sup>3</sup> ]	Unknowns [g/Nm <sup>3</sup> ]	Total [g/Nm <sup>3</sup> ]
Sand	1.3	0.7	27.5	6.6	12.9	49.1
N. olivine	2.2	0.6	15.7	3.2	5.2	26.9
A. olivine (fresh)	0.7	0.5	23.1	5.6	8.9	38.8
Sand + Fuel B	1.2	0.9	27.6	6.5	13.7	49.9
N. olivine + Fuel B	0.4	0.9	23.6	5.7	8.6	39.2
A. olivine + Fuel B	0.1	0.4	8.0	0.6	1.9	11.0
A. olivine (200 h)	0.1	0.4	7.9	0.8	1.5	10.5
A. olivine + Additive A	0.4	0.4	14.8	2.8	4.8	23.1
A. olivine + Additive A + B	0.2	0.5	13.9	2.1	3.1	19.7

**Figure 5** shows activated Austrian olivine with a porous layer of around 5 to 10  $\mu\text{m}$  thickness build up around the grain. This layer was build up during a 30 hours experiment. It is believed that a longer duration might have resulted in a thicker layer around the particle, however attrition may reduce the layer thickness until an equilibrium is reached. A thicker layer may be more active towards tar reduction since the active surface area and amount of catalytically active sites increases with an increased layer thickness.

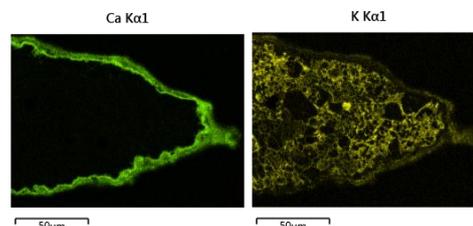
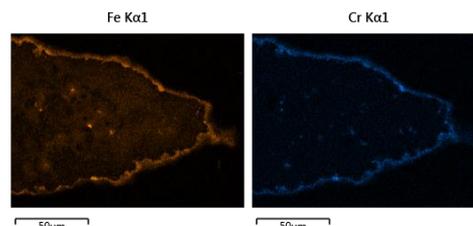
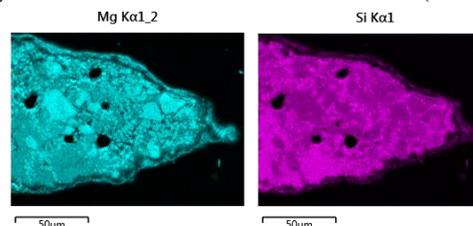
**Figure 5:** SEM image of activated Austrian olivine

**Table VI** shows the EDX results of unused Austrian olivine and activated Austrian olivine. For the activated olivine, the elemental analysis is given for the inside of the particle as well as for the build up layer. The porous layer has a high level of calcium, which is thought to be catalytically active towards tar reduction [6, 13, 16]. Apart from calcium, other elements like iron, magnesium, potassium, phosphorous, silica and chrome are present in the layer. Most elements, except iron are thought to originate from the fuel. Iron and chrome seem to have migrated to the surface of the grain. The analysis of the inside of an activated Austrian olivine particle shows the presence of potassium. It seems that potassium has a preference to diffuse more to the inside of the particle than to the outside layer itself. This may be explained by the fact that at the surface of the olivine particle, calcium blocks sites for potassium to deposit.

**Table VI: Summary of EDX analysis**

	Inside fresh A. olivine	Inside activated A. olivine	Outside activated A. olivine	Unit
O	46.6	44.8	41.3	[wt%]
Mg	29.9	26.1	9.3	[wt%]
Si	17.1	15.1	8.5	[wt%]
Fe	6.3	4.2	10.0	[wt%]
C	n.a.	8.5	3.9	[wt%]
K		1.2	0.8	[wt%]
Ca			20.0	[wt%]
P			3.4	[wt%]
Cr			2.5	[wt%]

Apart from EDX measurements, EDS analysis has been performed, as shown in **Figures 6 to 11**. The element scans clearly show a calcium rich layer around the olivine particle and give a good impression of the diffusion of potassium inside the particle. The potassium and silicon concentrations in the outside layer is somewhat lower. Additionally, it seems there is a thin inner layer with a slightly higher calcium concentration, between the particle itself and the outer layer, as has been described by Kirnbauer et al [12]. The EDS also shows an increased concentration of iron and chrome at the outside of the particle. Overall, the presence of calcium, magnesium and iron at the surface of the bed material and in the porous outside layer may be considered as the components contributing to the catalytic activity of this activated olivine.

**Figure 6 & 7:** EDS activated Austrian olivine (Ca & K)**Figure 8 & 9:** EDS activated Austrian olivine (Fe & Cr)**Figure 10 & 11:** EDS activated Austrian olivine (Mg & Si)

Agglomeration of bed material has been associated with formation of layers around the bed particles and can cause operational problems for the plant and may reduce the effective operating hours of the plant. Bed agglomeration can be caused by the coating induced agglomeration mechanism, as described by H.J.M. Visser

et al. [18], e.g. by ‘sticky’ potassium silicates. Agglomeration depends on many factors such as temperature, fluidization velocities and layer composition [17, 18, 19]. No agglomeration occurred in the experiments. It is thought that the diffusion of potassium into the olivine particles instead of deposition on the outside of the particles, reduced the possibility to form potassium silicates at the surface. Even in the case of Austrian olivine and the inorganics-rich fuel B, as well as during the experiment with additives A and B, no agglomeration occurred.

#### 4 CONCLUSIONS

Several bed materials, fuels and additives in the lab-scale MILENA gasifier were studied. These studies showed that, despite or perhaps, because of the characteristics of the MILENA gasifier, it is possible to reduce the tar content of the product gas by applying primary measures. These primary measures, being activation of Austrian olivine and subsequently its tar reforming properties, resulted in a significantly lower tar dew point. This however, requires careful selection of bed material.

The discovery of the tar reducing options of MILENA technology will certainly increase the availability of MILENA-based plants. Less tar related problems, like fouling and clogging of downstream equipment, will occur.

In 2013, a number of these primary measures will be tested in the pilot scale (800 kW<sub>th</sub>) MILENA, in order to verify the effect when scaling up from lab to pilot scale.

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**ECN**

Westerduinweg 3  
1755 LE Petten  
The Netherlands

P.O. Box 1  
1755 LG Petten  
The Netherlands

T +31 88 515 4949  
F +31 88 515 8338  
info@ecn.nl  
www.ecn.nl