IEA Bioenergy, Task 33
Thermal gasification of biomass

WORKSHOP

“Bed materials”

18. April 2012, Istanbul, Turkey

REPORT

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Abstract

This publication provides the summary and conclusions from the workshop **'Bed materials'**, held for the IEA Bioenergy Task 33, on the 18 April 2012 in Istanbul, Turkey.

All workshop presentations can be found at www.ieatask33.org

Table 1: Workshop presentations

Hüsnü Atakül, ITU, Turkey	"Hot gas clean-up with dolomite"
Friedrich Kirnbauer, Bioenergy 2020+, Austria	"Chemistry of olivine and its influence on biomass gasification"
H.J.M. (Rian) Visser, ECN, the Netherlands	"The requirements and main themes on bed materials"
Christian van der Meijden, ECN, the Netherlands	"Milena gasification and bed materials"
Bram van der Drift, ECN, the Netherlands	"Tar dew point"

Introduction

The synthesis gas from thermal biomass gasification process is an outstanding energy carrier. It can be used as a standalone fuel (heat and power applications) or it can be further treated and transformed into another energy source.

Nowadays, product gas is used not just for heat and power generation as in the last decades, but also for the transportation fuels production. That is why much more R&D work is performed and planned in this area.

The quality of the product gas from biomass gasification process plays an important role by the synthesis gas applications and it is influenced by many factors. One of the factors is the type and quality of bed material.

The most common bed materials used in commercial thermal biomass gasification facilities are silica sand, olivine and dolomite. Their influence on the quality of the product gas (especially tar content) was discussed during the workshop.

EERA

The workshop was organized with cooperation of EERA (European Energy Research Alliance).

EERA is an initiative by 10 (+5) leading European R&D institutes. The aim is to accelerate development of new energy technologies, expand and optimize research capabilities and harmonize national and EC programs.

Requirements on bed materials for fluidized bed systems

The requirements of bed materials for fluidized bed gasification are a good fluidization behavior of grains, attrition resistance, and relatively high melting temperature. Furthermore the bed material should be non-pollutant or hazardous and also cheap in use.

The choice of the right bed material can help to optimize the gas composition and avoid operational problems.

The problems with the agglomeration and the possible catalytic effect of bed materials were presented during the workshop.

There are two extreme mechanisms of agglomeration processes. Details can be seen in the following figure.

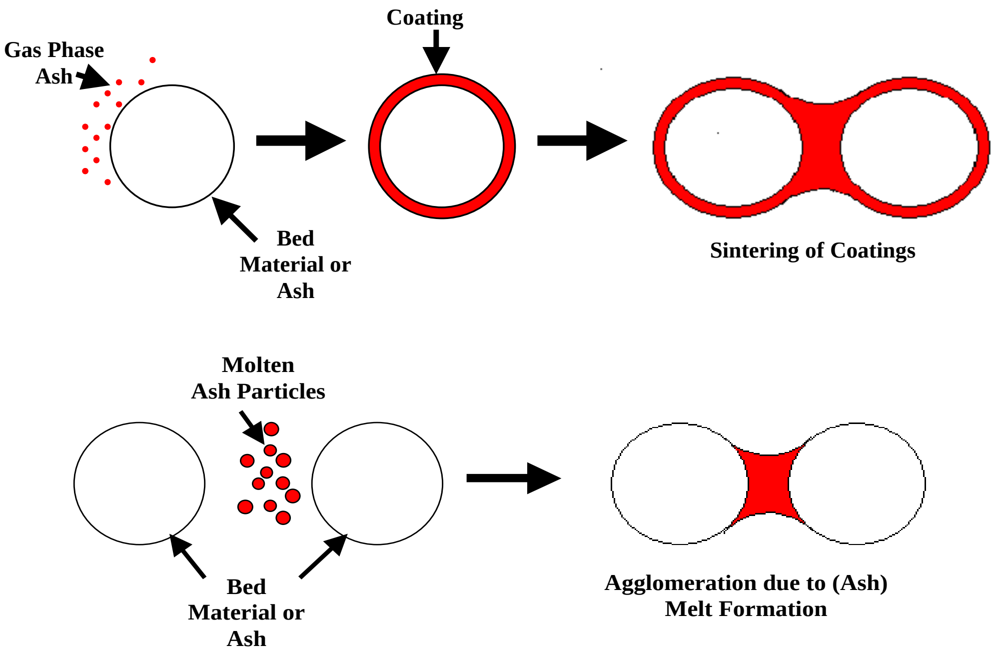

Figure 1: Agglomeration process

It should be considered, that based on the tests a porous coating of the bed material could have a positive effect on water gas shift reaction and gas composition.

The comparison of dolomite and olivine as a bed material for fluidized bed gasification was studied at ECN. The results can be seen in the table below.

Table 2: Comparison of olivine and dolomite for fluidized bed gasification

Olivine	Dolomite
Hardness OK	Too soft as FB bed material
Volume refreshment rate small	Refreshment rate high
Price rel. high (especially with pre- treatment)	Low price
Price/ton x volume/time determines the cost of use	
Chlorine/sulphur capture low	Cl and S capture high
Tar reduction depends on type of olivine and pre-treatment	Tar reduction high
No fines problem downstream/ no fouling of bed material	High quantity of fines downstream/fouling

Furthermore, three different types of olivine were tested; pretreated olivine from Austria and Canada and untreated olivine from Norway. As can be seen in the following table, not all the types of olivine have the same quality and properties.

Austrian olivine tested here was a porous material with partially segregated iron both internally and at the rim. Supplier has sintered material already at 1600°C for 4 hours and milled it to desired grain size.

Table 3: Characteristics of three different olivines

Characteristics	Norwegian olivine	Canadian olivine	Austrian olivine
Origin	Dunite (olivine) Mine, very pure	Residue from asbestos mining. Contains serpentines	Dunit (olivine) contains Forsterite rich olivine
Appearance	Solid grains, good hardness, light green	Brownish material, contains some porosity	Brownish material, contains some porosity
Pre-treatment	None	1260°C/2 hours	1600°C/4 hours
After oxidation /microscopy info	Some iron excluded and some Fe-minerals	Some iron excluded and some Fe-minerals	Some iron excluded and some Fe-minerals

In general, olivine as bed material reduces the amount of tar in the product gas better than silica sand. The main contribution is expected to be from iron segregated to the surface and on the different oxidation states the Fe can be in.

However, various “olivines” make difference to the extent of tar reduction. Noticeably, the higher the pretreatment temperature, the better the tar reduction capabilities are. Based on the tests, the worst performer was the untreated natural olivine.

The possible effects of tar reduction of olivine can be due to oxygen transport, active iron on the surface, or by forming a layer of CaO, which influences also the CO-shift reaction and catalytic methane reforming.

Table 4: Lab-scale experiments: summary results

	Sand	Olivine (Norway)	Olivine (Austria)	Olivine (Canada)	12% Dolomite in sand
Tar reduction	– –	o	+	o/+	+
WGS shift	–	o	o/+	o	+
O2 transport	–	o/+	+	+	–
Carbon/tar transport	–	–	–	–	+
Attrition res.	+	+	+	+	–
Price	++	o	–	–	+

Further tests, which are planned at ECN:

- sintered serpentine and pretreated olivine, which one is the better bed material?
- lab sale testing on elucidating which effects are occurring under which conditions in order to optimize further use
- do coatings have a positive contribution on tar reduction and is this the effect we see coming up after some 2 or 3 days of operation?
- feasibility to push the pCO2/pCO to the stability field of metallic Fe
- are the optimum conditions for tar reduction bed materials so different from the gasifier/combustor system that a separate reactor would be the wiser option

MILENA gasification bed materials

Milena is a gasification facility developed for high efficiency. In operation is since 2008, later in 2009 was connected to OLGA tar removal. Gasifier diameter is 0,2 m, combustor diameter 0,8 m. Total height 8 m.
The product gas has a medium calorific value, high CH_4 content and low N_2 content. Thus is well suitable for BioSNG production, for scale-up and pressurized operation.

Design details can be seen in the following figure.

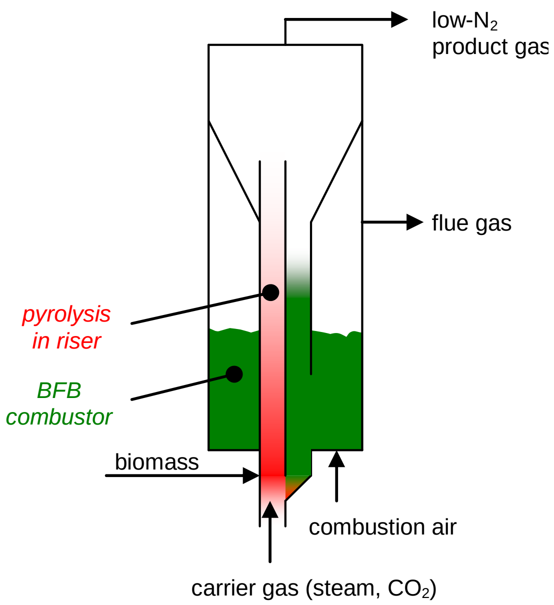

Figure 2: ECN Milena gasification unit

There were different fuels tested using MILENA 30 kW_{th} Lab-scale unit:

- Wood
- Sewage sludge
- Grass (not successful for the operation)
- Lignite

And different bed materials:

- Olivine (from Austria, Norway and Canada)
- Dolomite (calcinated and fresh)
- Silica sand (with additives)

Main goal of the bed material tests was to prevent fouling in cooler between gasifier and gas cleaning (OLGA) device. The results from the tests using dolomite can be seen in the following table and figure.

Table 5: Dolomite experiments: lab scale (30 kWth)

	Sand	Dolomite	12% Dolomite/ sand	6% Dolomite/ sand	9% Cal. dolo./ sand
Tavg [°C]	860	854	857	845	~835
S/B [-]	0.5	0.37	0.34	0.33	0.34
H_2 [vol%]	20	38-50	33	23	25
CO [vol%]	39	20-21	28	25	35
CH_4 [vol%]	13	8-11	11	10	12
Tar class 5 [g/nm3 dr]	5	0.5	2.2	3	2.5
Total tar [g/nm3 dr]	32	2.1	21.8	27.3	26
Fines [gr/hr]	50	550	275	n.m.	45

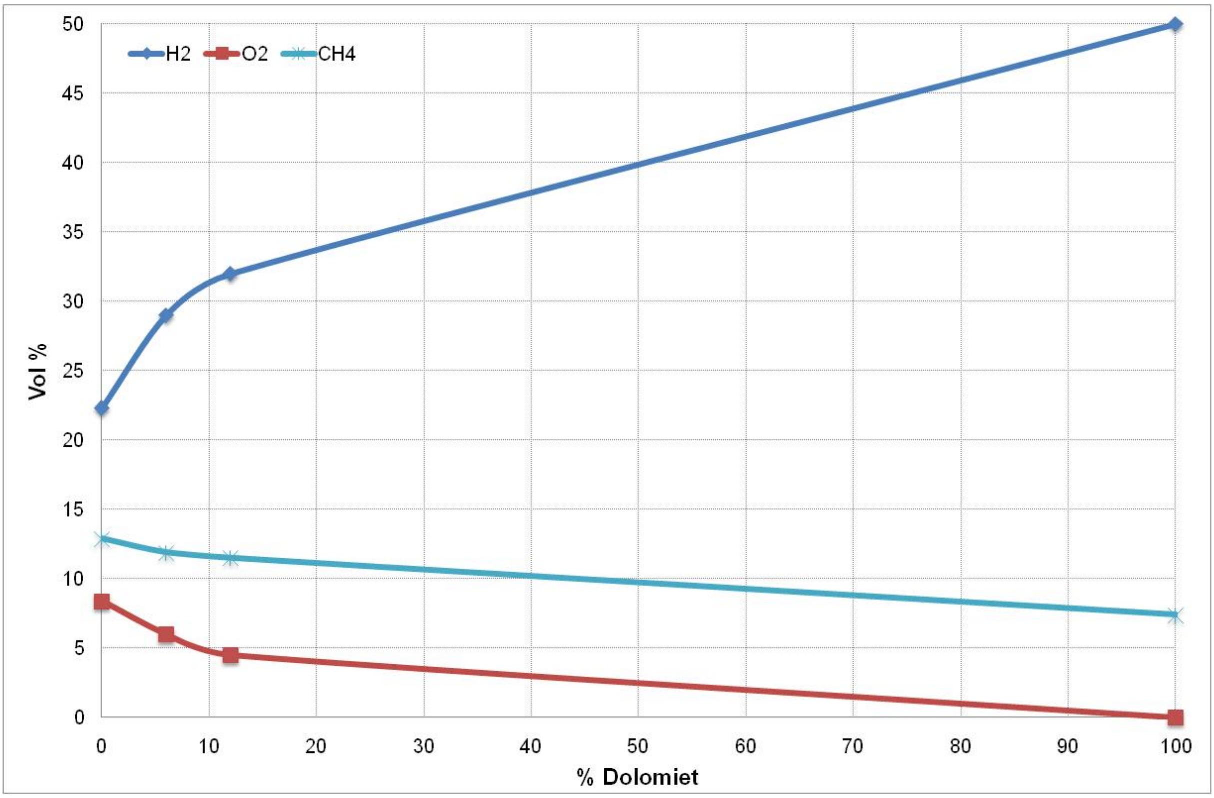

Figure 3: Hydrogen, oxygen and methane content in product gas using different dolomite content in bed material

Dolomite was flash calcinated when added to the hot bed. As the tests showed, using 100% dolomite it was too much tar/carbon transported to the combustor and increased the temperature. On the other hand 12% of dolomite in sand resulted controllable temperature and reduced tar content in product gas. Using calcinated dolomite there were no CO_2 peaks.

There were also 3 types of olivine tested:

- Pretreated olivine from Austria and Canada
- Untreated olivine from Norway

The results of olivine experiments can be seen in the following table.

Table 6: Olivine experiments

	Sand	Olivine (No)	Olivine (At)	Olivine (Can)
Tavg [°]	860	865	860	856
S/B [-]	0.5	0.5	0.7	~0.35
H_2 [vol%]	20	26	21	22
CO [vol%]	39	33	31	30
CH_4 [vol%]	13	12	10	12
Sum O_2 + CO_2 [vol%]	18	17	14	15
Tar class 5 [g/nm3 dr]	5	3	3	3
Total tar [g/nm3 dr]	32	28	25	25

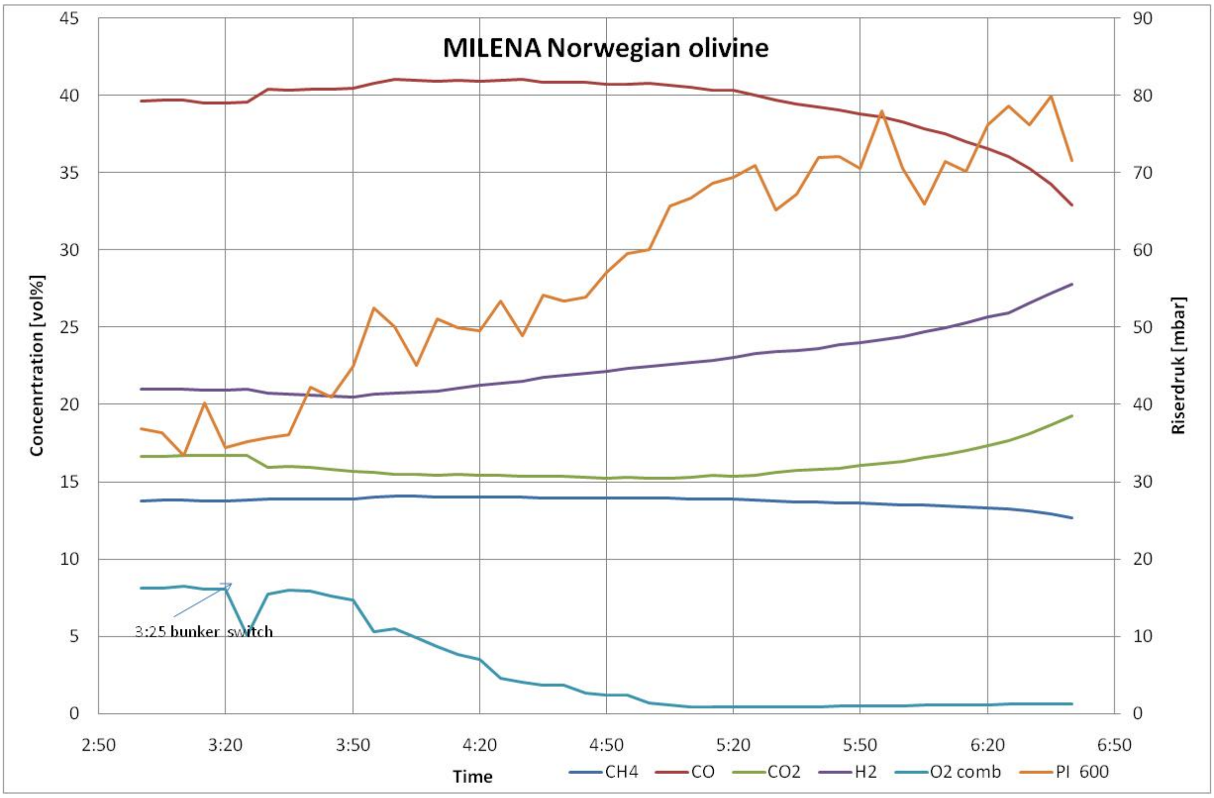

Figure 4: Olivine experiments, duration tests

Results from tests with olivine:

- Using the olivine as a bed material the tar reduction was limited
- Norwegian olivine was the worst option, but availability in right fraction was the best

- Pretreated olivine reduces tar concentration and transports O_2
- Untreated olivine, gets more active, over time during the reduction/oxidation cycles in MILENA
- Catalytic CO shift activity is influenced by air to fuel ratio in combustor
- Despite the bad performance was Norwegian olivine the standard in the lab and the pilot installation

Tar dew point

Tars are large hydrocarbons e.g. toluene, naphthalene, phenantrene, fluoranthene, coronene etc. Due to their undesirable effect on fouling problems, which occurs at surfaces with temperature of 300 and even above 400°C, tar removal from product gas is intensively studied since many years.

OLGA tar removal technology provides complete tar removal (heavy and light tars) from product gas. Furthermore it is responsible for particle removal and tar recycling.

During the gasification process tar content and composition is measured (SPA). This method is fast and easy, but limited to approx. 300 g/mol tar molecules (coronene). Tar Dew Point Analyzer (TDA), developed by ECN is a device, which is accurate and suitable up to 200°C.

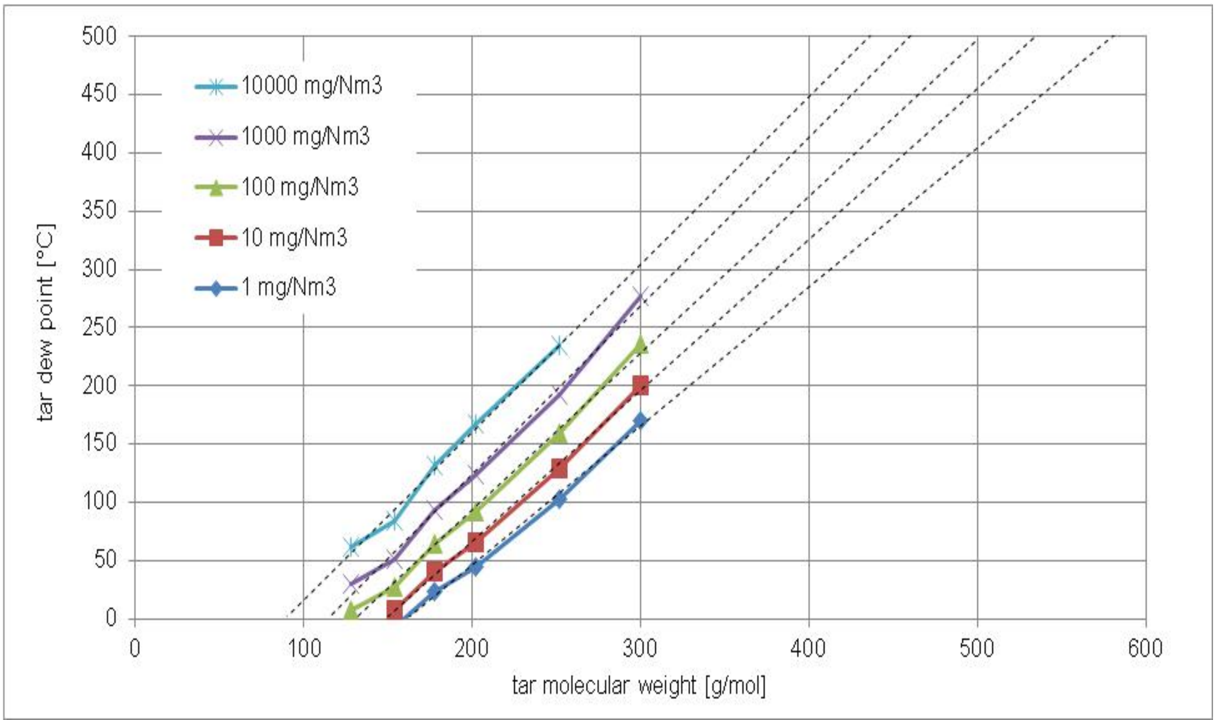

Figure 5: Tar dew point of larger tars

Table 7: Concentration of larger tars

	CFB/air - sand	MILENA - sand
<300 g/mol	9 000	33 000
300-350 g/mol	80	650
350-400 g/mol	28	295
400-450 g/mol	10	130
450-500 g/mol	3	59
500-550 g/mol	1	27
550-600 g/mol	0.4	12
% >300	1%	4%

A test showed that tar condensation is possible even at temperature of 400-500 ° C. OLGA is able to remove all tars, but the problem is upstream. Extrapolation leads to conclusion that fixed Tar Dew Point does not exist. Now a more practical approach is needed.

Chemistry of olivine and its influence on biomass gasification

Olivine is a natural mineral $(Mg, Fe)_2SiO_4$ with a high abrasion resistance and positive catalytic effects on tar reduction. Thus olivine is more suitable for thermal biomass gasification in DFB than silica sand. Calcination of olivine improves further its catalytic activity.

Tests at Bioenergy 2020+ showed that there are some differences between fresh and used olivine in DFB gasification. Used olivine is covered with inner and outer layer which is formed with CaO, SiO_2 and MgO (only in outer layer observed)

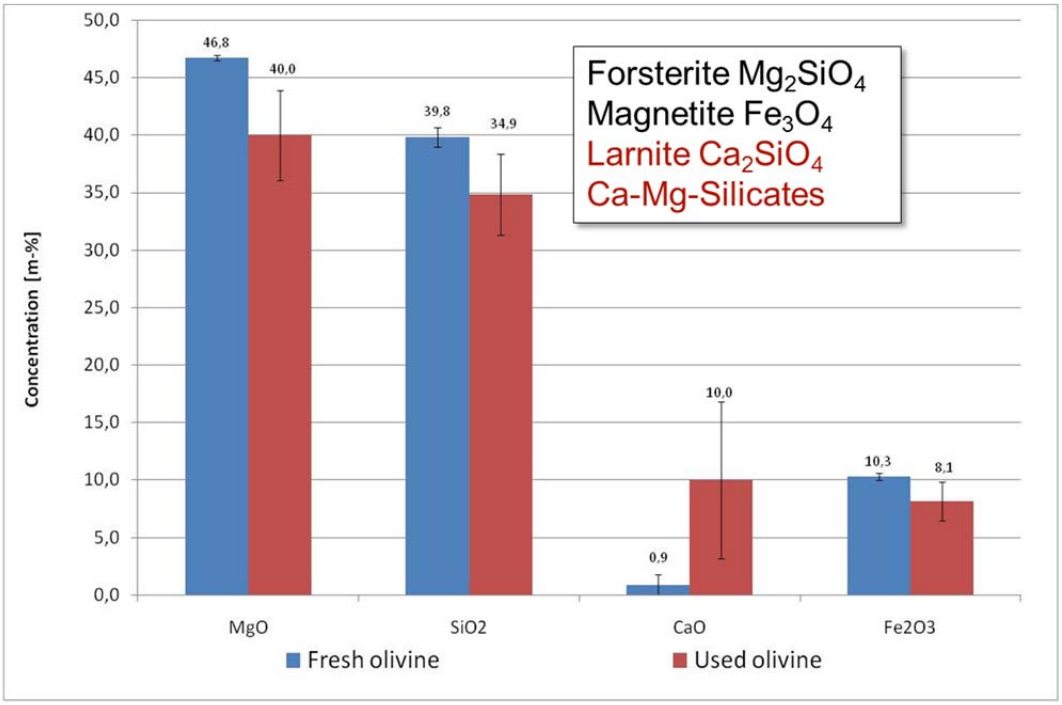

Figure 6: Analyses fresh and used bed material – main elements

Furthermore, the calcium content in bed material vs. CO content in product gas was tested in pilot plant and commercial plant in Güssing. Tests showed that with higher CaO content in bed material the concentration of CO in product gas decreases.

Product gas composition was studied also, using pilot gasification plant with fresh and used olivine. The product gas composition from commercial gasification plant in Güssing was compared with the results. As it can be seen in the following figure the water-gas shift reaction plays an important role in a product gas formation and is enhanced by the layer. Using used olivine, higher content of H_2 and lower content of CO was observed in product gas in comparison with fresh olivine. The influence of used olivine on tar reduction, about 60-80% was also proved. The main responsibility on the tar reduction has a calcium rich layer on olivine, which is probably formed during the DFB gasification process. The results of the 100 kW plant were in accordance with commercial scale plant in Güssing.

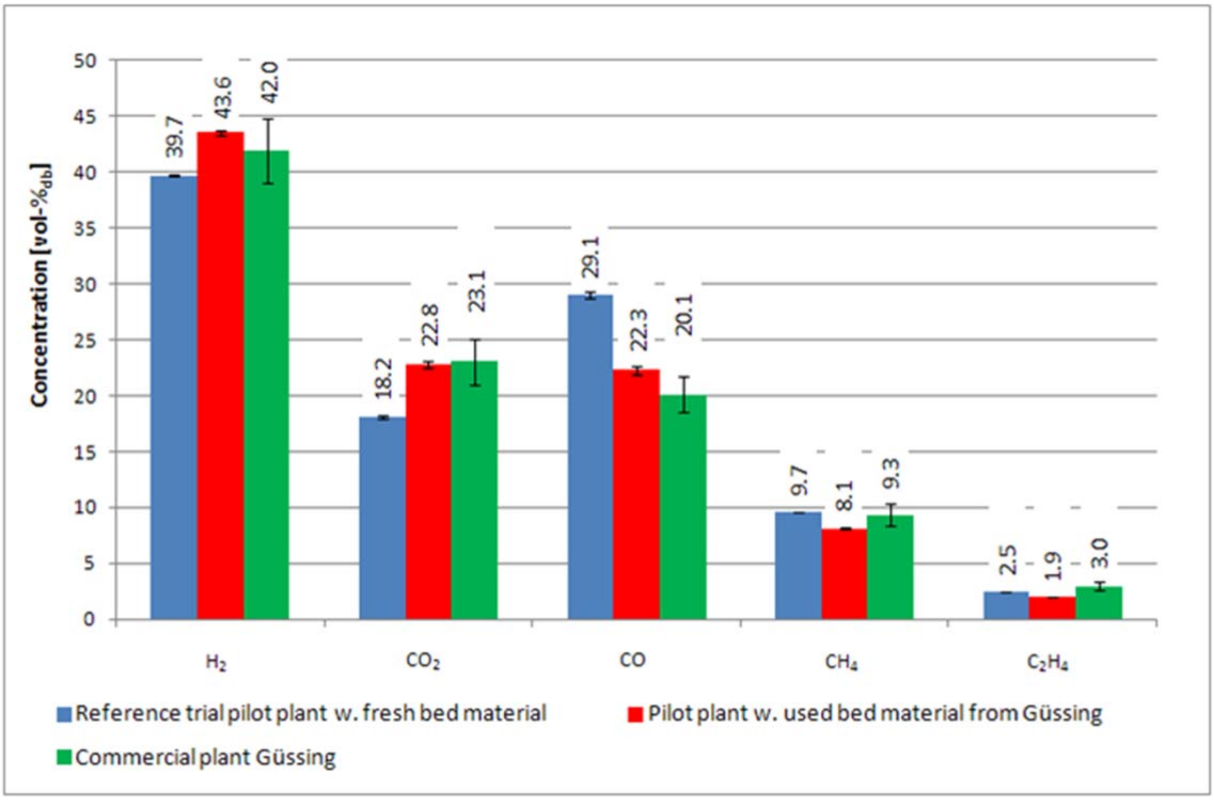

Figure 7: Comparison of influence of fresh – used olivine on product gas composition

Hot gas clean-up with dolomite

Turkish lignite in a mixture with biomass was used to prove the influence of dolomite on hot gas clean up during the thermal gasification process. This lignite has a high ash (21,5wt%) and sulphur content (1,85wt%-7wt%), which complicates the gasification process. Nearly 50% of sulphur presented in the coal leaves the gasification system in the gas phase and thus 5000-10000 ppmv of sulphur can be expected in the outlet stream of gasifier.

The sulphur removal is necessary not just for process reason, but also because of health risk. Higher concentrations of sulfur can cause also corrosion of pipelines. Furthermore, there are sulfur limits for catalytic systems such as FT process, methanol production etc.

In conventional treatment, H_2S or other sulfur components are removed via low temperature amine scrubbers. Wastewater containing chemicals from the scrubbing process must be treated accordingly to prevent the contamination of drinking water. Using scrubbers required lowering the temperature of the synthesis gas from 850°C to 50°C.

Furthermore, tar condensation can cause plugging and fouling of the condenser and is also a loss of hydrocarbon and leads to decrease in carbon utilization ratio.

Nowadays, there are different strategies to remove the tar from the product gas. One of them can be physical strategies (scrubber and filter) which are not really attractive because of their costs, large amount of waste water requiring treatment. On the other hand catalytic strategies are more efficient, improves the carbon efficiency, but the catalysts may be easy polluted with NH_3 or H_2S components.

In the project concerning the hot gas clean-up "TRIJEN Liquid Fuel Production from Biomass and Coal Blends" the influence of dolomite on cleaning of product gas was investigated. The experimental-set up can be seen in the following flow sheet.

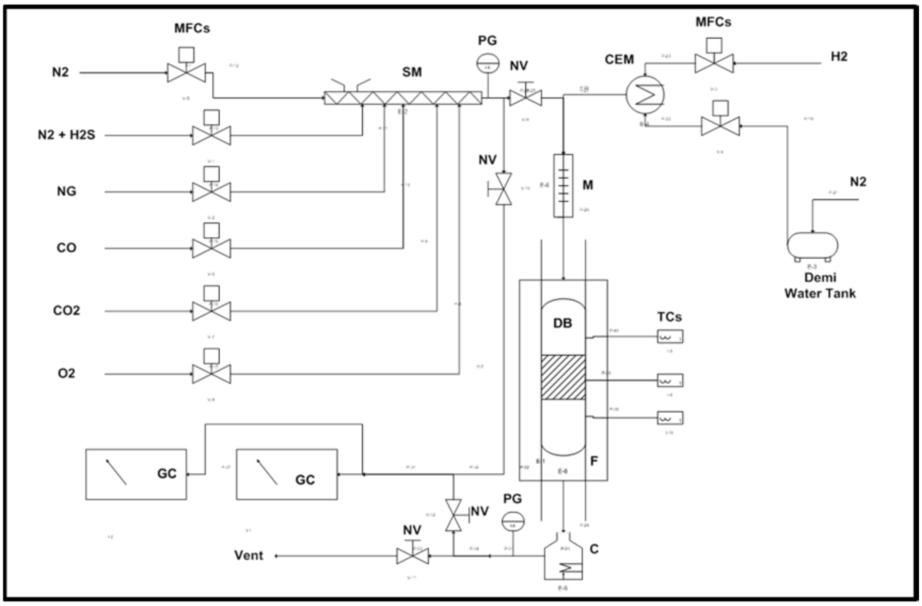

Figure 8: Flow sheet of the experimental set up

F: furnace, DB: dolomite fixed bed, GC: gas chromatograph, CEM: controlled evaporator and mixer, M: mixing manifold, NV: needle valve, SM: static mixer, PG: pressure gauge, TC: thermocouple, C: condenser

H_2S removal in N_2 atmosphere

At 700 K, the H_2S concentration in the reactor effluent gas was reduced to below 100 ppmw. The degree of H_2S chemisorption on dolomite reached to a maximum level at around 773 K. The H_2S levels of the effluent gases below 1 ppmw were observed between 773 and 1073 K. the H_2S concentration in the equilibrium at 750K is around 0,16 ppmw.

H_2S removal from binary gas mixtures (nitrogen + hydrogen) using dolomite

All H_2S was captured by dolomite, hydrogen behaved like an inert gas and consequently the results obtained were similar to that obtained in pure nitrogen.

H_2S removal from tertiary gas mixtures (nitrogen + hydrogen + CO_2)

H_2S removal efficiency was lower than that obtained with the binary gas mixtures. This might be attributed to the existence of CO_2 in the reactants and the water vapor produced as result of WGS reaction. The water vapor reduces the activity of dolomite toward H_2S. This tertiary gas seemed to promote the formation of COS to a larger extend in comparison to the binary mixture with similar CO.

H_2S removal from simulated gasifier outlet gas mixtures

H_2S removal was obviously low, efficiency about 30%. Thermodynamic calculations with this inlet gas composition dictated a maximum achievable equilibrium H_2S of ~120 ppm. Hence a 140 ppmv in the reactor off gas seems to be reasonable. The changes in the outlet gas stream with increased H_2 and decreased CO, indicated that the WGS reaction also took place to some extent. The carbonyl sulfur formed likely due to the reaction between H_2S and CO/CO_2.

The results of these studies showed that:

- H_2S removal by dolomite is limited to around 150-200 ppmv.
- Due to thermodynamical constraints, the H_2S removal efficiencies with calcium containing materials are only on the order of 90 % under typical gasification conditions, resulting in residual H_2S levels of 100 ppmv or greater.
- This may suggest that dolomite could be used for strictly bulk H_2S removal requiring an additional bed to further polish the gas for the applications with more stringent sulfur cleanup.

Further the tar removal with dolomite and commercial catalyst was investigated.

Dolomite showed a low degree of tar removal activity during the tests. Xylene and toluene concentrations decreased whereas benzene concentration increased in the outlet stream. At 750°C thermally/catalytically broken methyl groups in toluene producing benzene and methane. With the same mechanism, xylene was dealkylated into toluene and benzene, consecutively in the presence of excess hydrogen. The increase in methane percentage from 3.2% to 4.0% supported this suggestion.

Using a commercial catalyst, Xylene was converted into benzene and toluene. Gases such as CO, CO2, H_2, CH4 were detected at 563°C. This proces can be attributed to steam dealkylation reactions. At 775°C: tar reduced from 61gC/Nm^3 to 6.6 gC/Nm^3.

Table 8: Experimental conditions using dolomite by tar removal

Exper. conditions	Feed gas comp., %V (db)	Outlet gas comp., %V(db)	Contaminants, inlet	Contaminants, outlet
T_r=750°C Steam/C=0.21 Steam/tar=4.9	% 28.5 CO, % 25.0 CO_2, % 31.4 H_2, % 3.2 CH_4, % 11.9 N_2	% 35 CO, % 22.0 CO_2, % 25 H_2, % 4.0 CH_4, % 14.0 N_2	240 ppmv H_2S 8.67 gC/Nm^3 2.63 g C/Nm^3 Benzene 2.60 g C/Nm^3 Toluene 3.44 g C/Nm^3 Xylene	216 ppmv H_2S with trace COS 7.28 gC/Nm^3 4.62 g C/Nm^3 Benzene 2.28 g C/Nm^3 Toluene 0.38 g C/Nm^3 Xylene

Conclusions

- H2S removal performance of dolomite is strongli depening on operating temperature. Operating temperature need to be higher than 700K.
- Removal degree of H_2S from hot gases by dolomite dictated by thermodynamic limitations
- During H2S removal process, in addition to H_2S chemisorption, the WGS and RWGS reactions may occur depending on gas composition.
- The Boudouard reaction was another concern to be taken into account.
- Deactivation of CaO likely occurred at high CO_2 concentrations in the atmosphere, namely higher than 10 % by volume at ~ 1023 K.
- COS formed during the H_2S removal by dolomite, possibly due to the presence of CO. Higher H_2S levels in the gas stream could likely improve the kinetics of reactions between CO/CO_2 and H_2S which produce COS.
- Preliminary results showed that dolomite has some activity toward Tar (benzene, toluene and xylene as surrogated compounds).
- The comercil precious metal based catalyst catalyst catalyzes dealkylation reaction tar components such as xylene

Conclusions

The influence of the bed materials on the product gas quality during the thermal biomass gasification was confirmed in different projects and scientific studies. The most used bed materials are dolomite, calcite and olivine, because their catalytic activity is much higher than of silica sand. The most important factor, why to use the bed material with a catalytic activity is the tar reduction. Tars are higher hydrocarbons, which are formed during the thermal gasification and can cause serious technical problems during the process such as fouling and plugging.

During the workshop very informative contributions to this topic were presented. Furthermore, the EERA (European Energy Research Alliance) was introduced. The aim of EERA is to accelerate development of new energy technologies, expand and optimize research capabilities and harmonize national and EC programs.