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INVESTIGATION OF REFORMING
ACTIVITY AND OXYGEN
TRANSFER OF OLIVINE IN A DUAL
CIRCULATING FLUIDISED BED
SYSTEM WITH REGARD TO
BIOMASS GASIFICATION

Stefan Koppatz*

Tobias Pröll, Christoph Pfeifer†

Hermann Hofbauer‡

*Vienna University of Technology, stefan.koppatz@tuwien.ac.at

†Vienna University of Technology

‡Vienna University of Technology

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Investigation of reforming activity and oxygen transfer of olivine in a dual circulating fluidised bed system with regard to biomass gasification

Stefan Koppatz, Tobias Pröll, Christoph Pfeifer, Hermann Hofbauer
Vienna University of Technology, Institute of Chemical Engineering
Getreidemarkt 9/166, 1060 Vienna, Austria

T: 00 43 1 58801 15951; F: 00 43 1 58801 15999; E: stefan.koppatz@tuwien.ac.at

ABSTRACT

Natural olivine ($\text{Mg,Fe}_2\text{SiO}_4$) is examined in a dual circulating fluidised bed (DCFB) reactor system of 120 kW_{th} with regard to its reforming activity. Further, the oxygen transport capacity due to redox-cycling of the iron containing part of the olivine is considered. Based on a syngas composition derived from biomass gasification, the olivine is exposed to a surrogate gas mixture of H₂, CO, CO₂, CH₄ and a tar compound (1-methylnaphthalene) at 850 °C. The results show the tar conversion at different tar loads. The investigations reveal that a low content of oxygen is transported by the olivine due to the redox-cycling in the reactor system.

INTRODUCTION

Biomass derived syngas is widely expected to establish the local energy supply. Beside the conventional utilisation for heat and power supply, the syngas is considered as source for conversion processes into synthetic natural gas, liquid fuels or chemicals.

The quality of the syngas is defined by its composition of desired components (H₂, CO, CO₂, CH₄) and furthermore by undesired gaseous impurities. Tars and lower hydrocarbons are gaseous impurities, which are effected by the gasification process, whose condensation causes clogging or blockage in downstream process units (e.g. heat exchanger), due to low boiling points (< 300 °C).

The present paper concentrates on biomass steam gasification for syngas generation by fluidised bed processing. The focus is addressed on the bed material applied in the fluidised bed processing, since the properties influence the tar conversion and consequently the tar reduction capability.

Olivine is commonly used as bed material for such processes, since this abundant natural mineral is available at low costs. Moreover, with regard to the gasification process, olivine has available characteristics which enhance the tar conversion and

tar reforming, respectively. Olivine has been identified as a catalyst for tar reforming by several authors.

Reviews on olivine as well as on further materials (e. g. dolomite, nickel, iron) as catalysts in biomass gasification are given by Dayton (1), Abu El-Rub et al. (2) or Yung et al. (3). Investigations focussing on olivine as tar removal catalyst have been carried by Devi (4) or Devi et al. (5), (6), whereas olivine is assessed as catalyst in biomass gasification. Devi et al. (5-6) observed that the tar conversion (naphthalene) depends on the pre-treatment of olivine at high temperatures and is related to the iron content on the surface. The pre-treatment of olivine effects an enrichment of iron at the surface due to iron segregation. As iron is present at the surface, different oxidation states are possible depending on the surrounding reaction conditions.

Two different olivines differing in their iron content were investigated by Rauch et al. (7). The investigations at a commercial operating dual fluidised bed gasifier of 8 MW fuel input reveal different catalytically activity toward tar reduction, which is related to the presence of iron oxide at the surface.

EXPERIMENTALS

Material characteristics

Olivine is a natural occurring mineral, whose silicate tetrahedra contains iron and magnesium, chemically expressed as $(Mg,Fe)_2SiO_4$. Depended on the geographical origin the Mg and Fe content differs marginally. The natural olivine used within the experiments was provided by Magnolith GmbH (Austria) and is identified by a high forsterite fraction similar to olivine from Norway. Drying of the water of crystallisation and sintering has been carried out by the manufacturer, whereas the bulk material passes through a rotary kiln for approximately 4 hours at 1600 °C. The chemical composition of the olivine is reported in table 1.

Olivine is a non-porous material as a BET surface area of $< 0.5 [m^2g^{-1}]$ is reported Devi et al. (5), but has due to its hardness of 6.5 – 7.0 at Mohs scale a high attrition resistant. Beside high attrition resistance, high availability at low costs makes the olivine advantageous for fluidised bed applications.

The particle size distribution of the olivine used for the experiments ranges mainly from 400 to 600 $[\mu m]$, Figure 1 displays the cumulative size distribution. These rather large particles regarding circulating

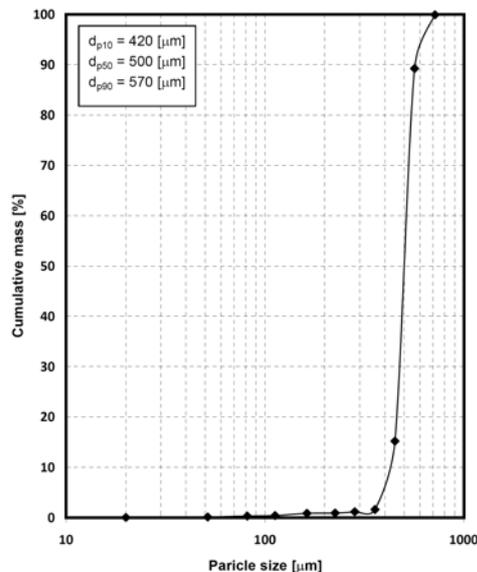


Figure 1: Size distribution of the olivine of 6.5 – 7.0 at Mohs scale a high attrition resistant. Beside high attrition resistance, high availability at low costs makes the olivine advantageous for fluidised bed applications.

Table 1: Chemical composition of natural olivine in [wt.-%]

MgO	SiO ₂	Fe ₂ O ₃	CaO
47.5 – 50.0	39.0 – 42.0	8.0 – 10.5	< 0.4

fluidized bed processing are originated from a bubbling bed application and are applied at the DCFB system for upcoming comparisons.

Dual circulating fluidised bed (DCFB) reactor system

The DCFB pilot rig consist of two interconnected circulating fluidised bed reactors, named as fuel reactor (FR) and air reactor (AR), allowing continuously circulating of solid material between the reactors, see Figure 2. The pilot rig with a fuel power of 120 kW has been developed for chemical looping combustion or chemical looping reforming processes for gaseous fuels with focus on scalability to large size application, whereas the circulating solids act as oxygen carrier or reforming catalyst. Beside these functions heat transfer between the reactors is enabled by the circulating bed material.

The flow regime in AR is fast fluidisation and in the FR turbulent fluidisation. Mixing of gas phases is avoided by steam or nitrogen fluidised loop seals. Downstream of each reactor, gas and solids are separated in cyclone separators. After solid separation, the gas streams pass a common post combustion chamber equipped with a support burner for complete combustion. The exhaust gas stream is cooled down, cleaned in a bag filter and sent to the chimney. The pilot rig and further auxiliary units are detailed by Kolbitsch et al. (8) or Pröll et al. (9). A solid sampling system is installed at the pilot rig and allows solid sampling from the lower and upper loop seal. The solid sampling system consists mainly of a pipe which is installed into the each loop seal and a solid deposit, which is connected to the pipe. The sampling system is further detailed by Kolbitsch et al. (10). Solid sampling is carried out under inert atmosphere (argon) in the solid deposit to avoid undesired reactions of the solids with ambient air.

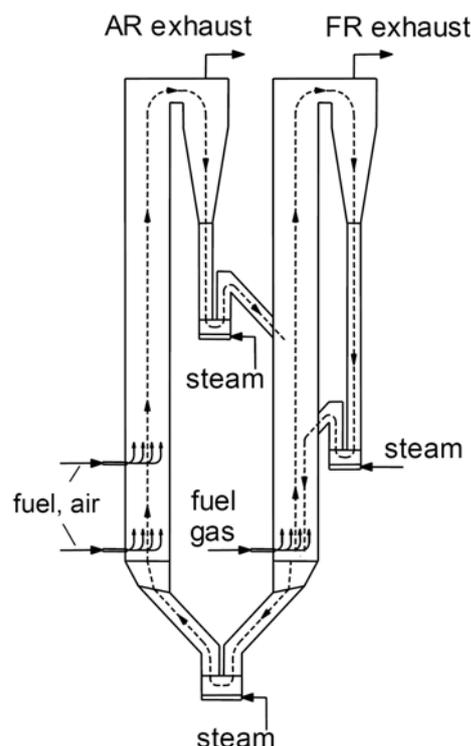


Figure 2: Sketch of the 120 kW DCFB pilot rig for chemical looping processes

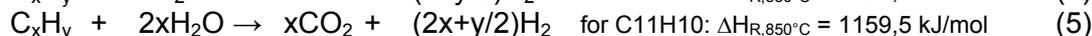
Gas measurement system

For determination of fuel reactor exhaust gas concentrations a Rosemount NGA 2000 (CO: 0–100%, CO₂: 0–100%, O₂: 0–25%, H₂: 0–100%, CH₄: 0–100%) is used and, additionally, an online gas chromatograph Syntech Spectras GC 955, which allows cross-checking of carbon species and determination of the N₂ content for evaluation of possible gas leakages from the air reactor to the fuel reactor. The air reactor exhaust stream is analyzed using a Rosemount NGA 2000 (CO: 0–100%, CO₂: 0–100%, O₂: 0–25%). Tar measurement has been carried out in the fuel

reactor exhaust gas stream to determine the tar concentration and tar conversion, respectively. The tar measurement method was developed at Vienna University of Technology and is based on the tar protocol given by Neeft et al. (11) focusing on tars originated from biomass gasification. Further details are given by Pfeifer (12).

Reactions and definitions

The fuel reactor is fed with a gas mixture of the gas species H₂, CO₂ and CH₄. 1-methylnaphthalene (C₁₁H₁₀) is added as tar compound in vaporised form. Generally, gaseous reactions take place into the FR, see reaction (1) – (5).



Assuming, that Fe, FeO (Fe_{II}) and Fe₂O₃ (Fe_{III}) are possible Fe-phases on the surface, the following gas-solid reactions can occur alternately between the AR and FR. Reactions (6) and (7) are expected to occur but to a low extent with consequent oxidation of the present gaseous species in the fuel reactor.



To characterise the oxygen capacity, different numbers (equation I to III) are introduced: the oxygen ratio (ω), the oxygen capacity (R_0) and the oxygen load (X_s):

$$\omega = \frac{m_{act}}{m_{oxid}} \quad (I) \quad R_0 = \frac{m_{oxid} - m_{red}}{m_{oxid}} \quad (II) \quad X_s = \frac{m_{act} - m_{red}}{m_{oxid} - m_{red}} \quad (III)$$

with the molar masses of the fully oxidised (m_{oxid}), the fully reduced (m_{red}) and the mass of the actual particle (m_{act}).

Experimental approach

The FR was fueled with a surrogate gas mixture of 20 Nm³/h containing: H₂: 52 vol.-%, CO₂: 40 vol.-% and CH₄: 8 vol.-%. The surrogate gas mixture is related to a syngas composition derived from steam biomass gasification as reported by Koppatz et al. (13), assuming that CO is generated in the FR according to reaction (1). Additionally 1-methylnaphthalene was added as tar model compound in the FR. Propane (C₃H₈) is used as fuel in the AR. Depending on the operation point, the AR was operated at a stoichiometric air/fuel ratio (λ) > 1 or < 1.

The temperature in the FR was kept at approximately 850 °C and the AR was operated at temperatures about 920 – 960 °C. Within the investigations different operation points were performed, see Table 2.

Table 2: Overview on accomplished operation points

Operation point		OP1	OP2	OP3	OP4	OP5
λ in air reactor	[-]	> 1	> 1	< 1	> 1	< 1
Tar feed	[g/Nm ³]	-	~ 40	~ 40	~ 10	~ 10

RESULTS AND DISCUSSION

Figure 3 displays the pressure profile of the DCFB reactor system similar at all operation points. An exponential decay of pressure is found in the air reactor, but is less developed compared to circulating fluidised bed risers due to the application of large particles. The pressure profiles indicate the decrease of solids concentration with reactor height in air and fuel reactor.

The fuel reactor shows high concentration of solids in the bottom region, whereas the upper part is lean in solids. Due to minor fluidisation and gas velocities, a weak circulating fluidised bed is developed into the FR.

The following figures highlight the global operation conditions (operation point OP 1 to 5), whereas the profile of exhaust gas composition in the FR, the excess of O₂ or CO in the AR and the temperatures in the AR and the FR are shown.

Main operation characteristics are the exothermic reaction of combustion in the AR and the overall endothermic reactions in the FR. The AR exhaust gas is mainly characterised by an excess of O₂ or CO, which indicates operation points at $\lambda > 1$ (Figure 4-6, 8) or $\lambda < 1$ (Figures 7, 9) in the AR. Since the heat demand in the FR is supplied by the circulating solids, the temperature in the AR is higher at about 80 to 120 K.

The FR exhaust gas composition is characterised by the species H₂, CO, CO₂ and CH₄. CO is formed in the FR due to the reaction of H₂ and CO₂, see reaction (1), whereas also H₂O is formed, but not measured with online measurements. The fluctuation in the FR exhaust gas composition during operation point 3 (Figure 7) is caused by a short-term interruption in the surrogate gas feed to the FR. However, this has not been considered within the mean values. The FR exhaust gas composition as displayed within the figures is diluted by about 20 vol.-%_{db} of nitrogen due to the fluidisation of the loop seals and consequently mixing of nitrogen to the FR gas stream. Further dilution of the FR gas stream is caused by argon flushing of the pressure measurements and is quantified to about 5 vol.-%_{db}.

Figure 5 (OP 1 to OP2) highlights the influence of tar feed on the FR exhaust gas composition. Mean values for each operation point are reported in Table 3. The temperatures were kept at about 850 °C with minor deviations of less than ± 10 K. Operation point 1 is characterised by a nearly similar quantity of CO₂ and CO. This indicates quasi-equilibrium status of CO-shift reaction (reaction 1), since at temperatures of about 850 °C the CO-shift equilibrium is at the side of CO and H₂O. At operation point 1 the CH₄ conversion is at approximately 50 %. Tar feed results in shifting of the exhaust gas composition (see Figure 5), which is similar to all operation points with tar feed. The CH₄ content increases from 2.5 vol.-% to ~ 5 vol.-%, since CH₄ is also a product of tar cracking.

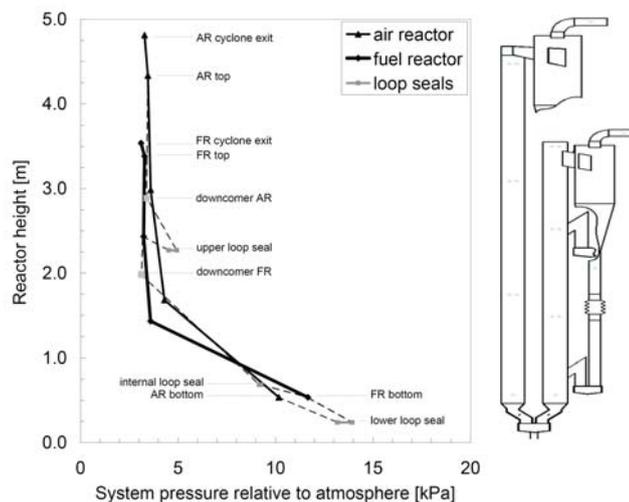


Figure 3: Pressure profile in the DCFB reactor system

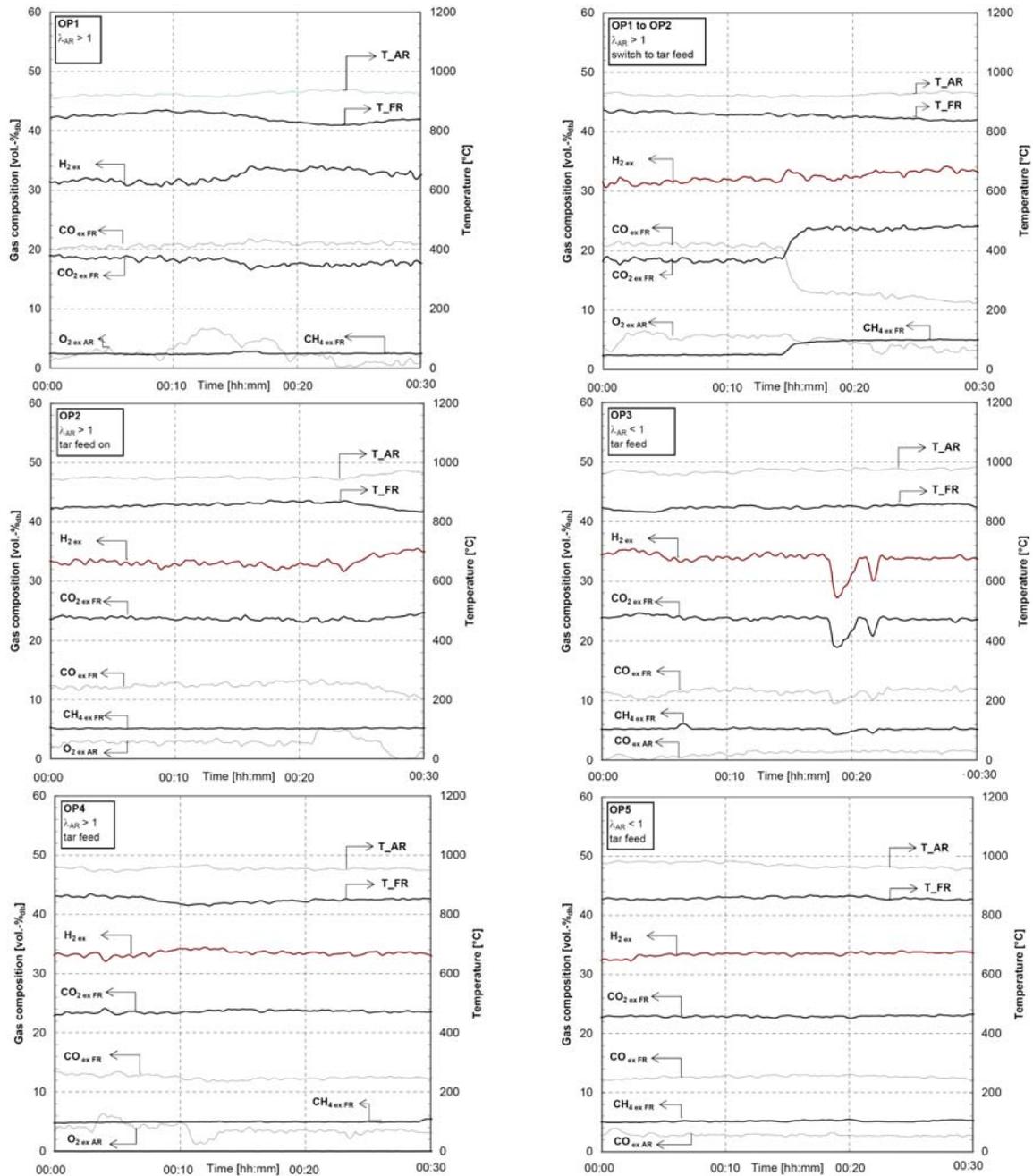


Figure 4-9: (top left to bottom right) operation point 1 to 5; as indicated at the figures

The H₂ content is slightly increased, but remains in the range of 33 – 34 vol.-% for OP2 to OP5. The main shift is observed for the CO and CO₂ content. The CO content decreases to values of 11 – 13 vol.-%, whereas the CO₂ content increases up to 22 – 24 vol.-%. Apparently, this is caused by an interaction of reactions (1), (4-5), whereas the dominating product is CO₂ to the disadvantage of CO formation. The tar conversion is reported in Table 3 and reveals that the conversion rate is higher for lower tar feed.

Table 3: Mean values of main parameters for OP1 to OP5

Tar feed of about 43 g/Nm³ (OP2 and OP3) results in conversion rate below 70 %, whereas about 73 % are obtained at tar feed about 13 g/Nm³ (OP4 and OP5). GC/MS analysis of the tar show, that about 95 %

Parameter		OP1	OP2	OP3	OP4	OP5
Temperature in FR	[°C]	845	856	848	849	858
Tar feed	[g/Nm ³]	-	43.3	43.2	12.8	13.3
H ₂ in FR _{exhaust gas}	[vol.-% _{db}]	32.4	33.2	34.1	33.5	33.4
CO ₂ in FR _{exhaust gas}	[vol.-% _{db}]	18.0	23.8	23.9	23.6	22.9
CO in FR _{exhaust gas}	[vol.-% _{db}]	20.8	12.4	11.6	12.5	12.7
CH ₄ in FR _{exhaust gas}	[vol.-% _{db}]	2.5	5.2	5.3	5.0	5.2
Tar in FR _{exhaust gas}	[g/Nm ³]	-	13.5	14.3	3.3	3.6
Tar conversion	[%]	-	68.7	67.0	73.7	72.9

is present as naphthalene. Minor constituents are: indene, 1-methylnaphthalene, 2-methylnaphthalene or acenaphthylen.

Solid sampling was carried out, whereas about 100 g of solids were taken from the upper loop seal (ULS) and lower loop seal (LLS). A first solid analysis was accomplished by calcination of the solids in an oven at about 900 °C for 12 hours to determine the residual oxidation potential of the material. Assuming that olivine contains 10 wt.-% of iron in the form of FeO, equation (I) can be expressed as ω_{min} and ω_{max} , whereas m_{act} is m_{red} and m_{oxid} , respectively. Table 4 summarizes the oxygen ratio (ω) regarding the solid samples for OP4 and OP5.

The results reported in table 4 reveal, that higher oxidation of the particle is present in the ULS after the combustion in the AR compared to the LLS after reduction in the reforming zone. Despite AR operation at $\lambda < 1$ during OP5 a certain oxygen load occurs for the ULS sample. This is due to the assumption, that the entire iron is available for the redox-cycling. This is not the case, if the real particle properties are considered, since only a certain amount of iron is present on the particle surface. Furthermore, the influence of residence time with regard to reduction and oxidation is neglected. Thus, reducible Fe-phases are even present after a certain period of operation at $\lambda < 1$ in the AR.

CONCLUSIONS

Olivine is commonly used as bed material for fluidized bed gasification processes. This paper gives important information about the catalytic

Table 4: Solid sampling characterisation

General values	ω_{min} [-]	ω_{max} [-]	R_o [g/g]
	0.977	1	0.022
	OP4 – LLS	OP4 – ULS	OP5 – LLS
ω_{act} [-]	0.996	0.997	0.996
X_s [-]	82.5	87.8	80.5
	OP5 – LLS	OP5 – ULS	
	80.5	85.5	

activity of olivine due to iron resp. oxygen transfer. The results show that quasi-equilibrium of the CO-shift reaction is achieved for operation at 850 °C without tar feed. Tar conversion depends significantly on the tar feed. Tar conversion of nearly 75 % is achieved at a tar feed of about 13 g/Nm³. According to solid sampling analysis, a low amount of oxygen is transferred from the air reactor (AR) to the fuel reactor (FR), but shows only little impact on the gas species composition of the FR exhaust gas. Further experiments will focus on long term test, to investigate the characteristics of olivine with regard to iron behaviour and iron availability on the

surface. As iron is a promising catalyst for tar reforming, further experiments will focus on investigations with iron enriched olivine.

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