
Iron based catalysts for tar removal – downstream tests in real producer gas

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Abstract:

Gasification is considered to be a promising way of upgrading biomass to a valuable secondary energy carrier. A major problem is hereby the presence of condensable hydrocarbons (tars) in the producer gas which complicate the further use of the gas. One possible solution to the problem is catalytic tar removal. When commercially available Ni-based catalysts are used, problems like carbon deactivation, sintering or sulphur poisoning have to be faced. Furthermore the in-situ usage of Ni-based catalysts in fluidized bed gasifiers is problematic due to Ni-contaminated dust load. Fe-based catalysts have the potential to solve some of the aforementioned problems and need to be tested under real conditions. In this study we show the ability of three newly developed Fe-based catalysts to reduce total tar content as well as the number of tar species in biomass gasification derived producer gas. The catalysts were tested downstream in the producer gas of a fluidized bed gasifier and a reduction of total tar content of 82% could be achieved. Furthermore all three catalysts enhance H₂ yield and reduce the CO amount by promoting the water gas shift reaction.

1. Introduction:

Biomass is a renewable energy carrier and through gasification it can be made applicable for a large number of processes. The producer gas can be used in heat & power production, the production of hydrogen, synthetic natural gas (SNG) or liquid biofuels [1]. One of the major problems in the producer gas utilisation is the tar content [2]. When the gas temperature is falling below the tar dew point fouling and blocking of equipment will occur [3]. Primary (inside the gasifier) or secondary (downstream) methods can be used for tar removal [4]. Besides gas scrubbing [5] the tar can be removed by catalytic processes. They have the advantage that no contaminated scrubbing fluid has to be disposed and that the heating value of the tar compounds is not lost in the producer gas thus leading to a higher cold gas efficiency. An overview over recent research in catalytic tar destruction is given e.g. in [6], [7], [8] and [9].

Catalysts can be used inside the gasifier or in downstream processes [4]. A lot of work in the field has been done by Corella et al. who investigated catalysts (for primary and secondary processes) and suggested kinetic models for the tar destruction [10]. For instance, Ni-based monoliths placed in downstream reactors, although less active than commercial Ni-based ring catalysts in the tar removal, can be used in particulate containing producer gas [11]. Catalysts for secondary processes have also been tested e.g. by Pfeifer et al. [12] and Rönkkönen et al. [13]. Pfeifer et al. tested Ni based catalysts downstream a fluidized bed gasifier and report an almost total tar conversion for GC detectable tar compounds at >850 °C [12]. On the other hand, Rönkkönen et al. [13] tested several precious metal catalysts (Rh, Ru, Pt, Pd based) with model tar compounds (naphthalene, toluene) under the presence of H₂S and compared them to a Ni based catalyst. They found Rh-based catalysts to be the most promising for tar

destruction reaching a conversion of aromatic hydrocarbons of 98% at 900 °C. Fluidized bed gasifiers are especially suited for the in-situ use of catalysts as bed materials or additive. In fact, Fe-containing olivine, a natural mineral, is nowadays widely used as bed material during fluidized bed gasification. It can decrease the tar content and favour the water gas shift reaction, thus resulting in a H₂-rich, tar reduced producer gas [14]. The selection of the olivine plays a key role since minerals do not have a fixed composition and not all naturally occurring olivines contain enough Fe. Kuhn et al. [15] investigated four different olivines on their reforming abilities of model tar compounds (naphthalene, toluene). The pretreatment and the origin of the olivine had a large impact on the catalytic activity. Dolomite and olivine were compared in air gasification [16], dolomite was 1.4 times more active but producing 4-6 times more particulates due to its softer consistence. Pecho et al. [17] compared natural olivine and calcite to synthetic perovskite-type compounds during the tar reforming of toluene under fluidized bed conditions. In a sulphur free atmosphere the synthetic catalysts outperform the natural materials. Nevertheless under the presence of sulphur the natural materials are advantageous concerning activity. Their study shows the potential of synthetic in-situ catalysts, but also possible limitations. Therefore catalysts have to be tested thoroughly in real tar containing producer gas. Rapagna et al. [18] prepared Fe-impregnated olivine catalysts that show an increase of 61% tar removal compared to pure olivine as bed material in fluidized bed gasification. Świerczyński et al. [19] prepared synthetic Ni/olivine catalysts and tested their tar removal abilities in fixed beds using toluene as a model compound. In this work, we propose synthetic Fe-

containing catalysts obtained from hydrotalcite-type (HT) compounds as an alternative or additive to olivine bed materials. HTs are layered materials constituted by positively charged layers usually with divalent and trivalent cations; the charge excess is balanced by anions located in the interlayer. The general chemical composition can be written as $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^b)_{b/x}nH_2O$ [20]. After calcination at high temperatures catalysts formed by oxide and spinel phases are obtained. In this work, catalysts were prepared from Mg/Al/Fe HTs containing silicates or carbonates as anions in order to adjust the properties of the catalysts such as crystalline phases, specific surface area, iron reducibility and mechanical stability. In this sense, materials with tailored properties could be prepared.

2. Concept and methodology:

Catalysts:

HT compounds with similar divalent to trivalent ratio, $M^{2+}/M^{3+} = 2.125$, containing carbonates (HT-CO₃) and two different amounts of silicates (HT-xSil and HT-1.25xSil, where x and 1.25x refers to the amount of silicate) were prepared by co-precipitation at pH constant [21]. A solution containing the salts of the metals (Mg(NO₃)₂ 6H₂O, Al(NO₃)₃ 9H₂O, Fe(NO₃)₃ 9H₂O) in the appropriate ratio was drop wise added to a solution containing the anions (carbonates or silicates). The pH was kept constant by NaOH addition (10.5 ± 0.2). After washing and drying the solids, catalysts were obtained by calcination at 900 °C for 12 h (exHT-CO₃, exHT-xSil and exHT-1.25xSil). The Fe load in the catalysts was ca. 15-18 wt%. The tar removal activity of the exHT-xSil (Catalyst 1), exHT-1.25xSil (Catalyst 2) and of a 50:50 mixture exHT-xSil and exHT-CO₃ (Catalyst 3) was studied.

Characterization techniques:

Powder X-ray Diffraction (PXRD) analyses were carried out using a Philips PW1050/81 diffractometer equipped with a graphite monochromator in the diffracted beam and controlled by a PW1710 unit (CuK α - Ni filtered, $\lambda = 0.15418$ nm). A 2θ range from 10° to 80° was investigated at a scanning speed of 70° h^{-1} . Temperature Programmed Reduction (TPR) analyses were carried out with an H $_2$ /Ar (total flow rate 20 ml/min) gas mixture in the 100-950°C temperature range in a ThermoQuest CE instruments TPDRO 1100.

Gasifier:

The catalysts were tested with producer gas of an allothermal bubbling fluidized bed gasifier at the Technische Universität München. A scheme of the gasifier can be seen in Figure 1. The gasifier vessel has an internal diameter of 154 mm, a length of 1500 mm and is made of high temperature resistant steel (German material number 1.4841). As bed material ~ 15 -17 kg of olivine was used, the height of the bed was ~ 700 mm. The fluidization number throughout the experiments was ~ 5.3 . During the experiments 2 kg/h of wood pellets were fed into the bottom of the gasifier while the bed was fluidized with a steam flow of 2 kg/h, thus leading to a steam to biomass ratio (S/B) of 1.0 kg/kg.

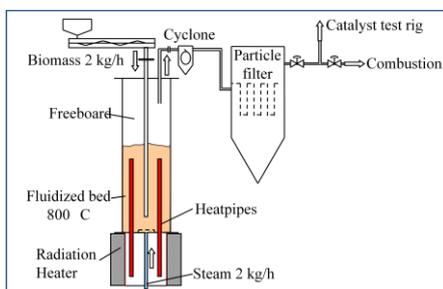


Figure 1: Scheme of the allothermal bubbling fluidized bed gasifier

The gasifier is heated by alkali metal heat pipes to 800 °C. To compensate the pressure losses through piping and the catalyst test rig the gasifier was operated under slight overpressure at ~ 1.15 bar absolute. Particles in the gas are removed in a cyclone and a ceramic candle filter. They are heated to >340 °C to prevent tar condensation. After the filter a slip stream is channelled into the catalytic test rig.

Catalytic test rig:

A sketch of the catalytic test rig can be seen in Figure 2.

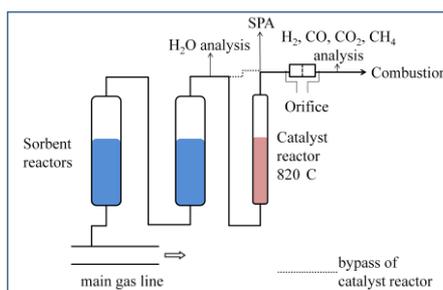


Figure 2: Experimental setup

In these preliminary tests in producer gas the ability of the catalysts for tar conversion without possible deactivation by other contaminants was tested. Therefore sulphur and chlorine were removed upstream by 200 ml of commercial available sorbents. During test of Catalyst 1 the temperature in the sorbent reactors was between 380°C-450°C, during the tests of Catalyst 2&3 the temperature was between 330°C-380°C. Catalyst and sorbent material were placed in fixed bed reactors with 25 mm and 47 mm internal diameter respectively. The catalyst reactor can be bypassed to analyse the initial tar load. 40 ml of pelletized catalyst (2.3-1.41 mm particle size) was used in each test. The tests were performed at ~ 820 °C and a gas hourly space velocity (GHSV) of 12.000 h^{-1} (calculated at standard

conditions). The flow was measured after the catalytic reactor using an orifice plate.

Biomass feedstock:

As biomass feedstock wood pellets were used. The pellets are commercially available under the trading name Agrol and are a blend of ~80% spruce and 20% pine. Proximate and ultimate analysis (Vario Macro CHNS analyzer) of the pellets is given in Table 1. The volatile content is relatively high and the pellets have a low moisture and ash content.

Table 1: Biomass feedstock elemental and proximate analysis in [wt%]

C waf	H waf	N waf	S waf	O waf
49.9	6.8	0.1	0.1	43.2
Water	Ash db	Volatile db	Fix C db	
4.8	0.1	85.6	14.3	

Experimental procedure:

Prior to the catalyst test the gasifier was operated for ~2.5 h to ensure stable operating conditions. Each catalyst was reduced before use with a mixture of H₂/N₂ (42.3/57.7) for a period of ~2 h at ~800 °C. The catalyst reactor was bypassed in the first part of each test for the analysis of the untreated gas. In the second part of each test the producer gas was channelled through the catalyst reactor before analysis. The tar analysis was performed by taking SPA samples that were later analysed at the laboratories of KTH (Sweden). All SPA samples were taken at an access point after the catalyst reactor (the bypass respectively) like indicated in Figure 2, the temperature at this point was ~300-330 °C. For one SPA sample 100 ml of producer gas was drawn up with a syringe over an amino phase column. The results of the analysis are given by KTH as μg_{tar}/sample. With the assumption that the steam in the gas is condensed in the amino phase and does not enter the syringe in vapour form, this value was converted into g_{tar}/m³_{dry} in this work. The SPA samples were taken in the untreated as well as in the gas after the

catalyst to determine the tar conversion. For the initial tar concentration one SPA sample was taken (referred to as no Catalyst), for the treated gas two samples were taken (referred to as Catalyst' & Catalyst''). The values of toluene and other tars with low boiling points have to be regarded carefully (see [22]). Between sampling and analysis of the tar samples passed a longer time period, therefore parts of these tars will have already been evaporated. The main gas components of the dry producer gas (H₂, CO, CO₂, CH₄) were monitored online using a gas analyser type S700 from SICK|MAIHAK. The concentration of steam in the producer gas was monitored online using a Hygrophil-H from BARTEC.

3. Results and discussion

Catalysts characterization:

The catalyst obtained from the carbonate intercalated HT (exHT-CO₃) is constituted by MgO- and spinel-type phases containing the Fe³⁺ species (MgFe₂O₄ or MgFe_{1-x}Al_xO₄). A forsterite (Mg₂SiO₄) phase was also observed in the catalysts containing silicates (Catalyst 1 and 2). The amount of forsterite is larger in the Catalyst 2 as expected by the higher amount of silicates in the precursor. Moreover, it should be remarked that the MgO/spinel ratio is related to the nature of the anion, silicate or carbonate, and to the amount of silicate. The reducibility of the iron species depends on the catalyst composition, the reduction temperature of the samples follows the trend: exHT-CO₃ ≈ Catalyst 2 < Catalyst 1.

Gas analysis:

In Figure 3 the gas composition during the complete test of Catalyst 3 is given as an example. The concentrations of H₂, CO, CO₂ and CH₄ are measured in the dry gas and H₂O is the total steam content in

the producer gas. The sum to 100% of the dry gas is assumed to be mainly N₂ from purge gas.

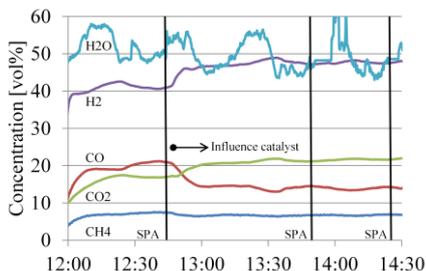
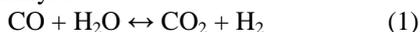


Figure 3: Gas composition during test of Catalyst 3. H₂, CO, CO₂, CH₄ in dry gas, H₂O of total producer gas

While H₂, CO, CO₂ and CH₄ at the exit of the gasifier are relatively stable whereas the H₂O concentration is fluctuating between 45-55%. This is due to fluctuations in the steam supply. In the first period of the test the catalyst reactor was bypassed and a SPA sample was taken at ~12:40. After that the gas was channelled through the catalyst reactor and SPA samples were taken at ~13:45 and ~14:25. One can clearly indicate the influence of the catalyst on the main gas components when the gas was channelled through the catalyst reactor. The H₂ and CO₂ content increases and CO decreases which is due to the promotion of the water gas shift reaction (eq. 1) by the catalyst.



Contrarily the CH₄ concentration does not show appreciable changes before and after the catalytic reactor. This behaviour could be related to a low reforming activity of the catalyst or to the formation of CH₄ by tar decomposition. Moreover, the change in the dry gas volume should be considered. Lastly, an influence of the catalyst on the H₂O content cannot be observed due to the above mentioned fluctuations. Tests with Catalysts 1&2 were performed in a similar manner. In Figure 4 to Figure 6 average values of the

gas composition during the three catalyst tests are given. The mean value of the gas composition was calculated within the time of 10 or 20 minutes prior to the SPA sample. It should be pointed out that the influence on the water gas shift is similar for all catalysts resulting in a H₂ rich gas.

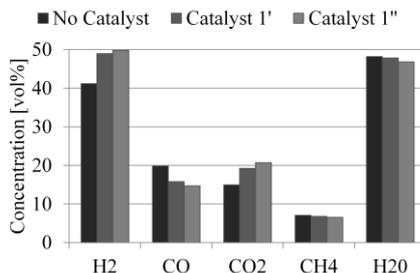


Figure 4: Average gas concentrations during test of Catalyst 1. H₂, CO, CO₂, CH₄ in dry gas, H₂O of total producer gas

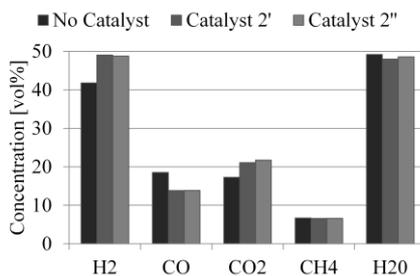


Figure 5: Average gas concentrations during test of Catalyst 2. H₂, CO, CO₂, CH₄ in dry gas, H₂O of total producer gas

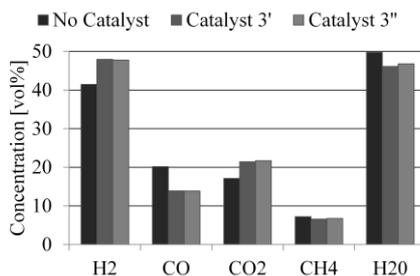


Figure 6: Average gas concentrations during test of Catalyst 3. H₂, CO, CO₂, CH₄ in dry gas, H₂O of total producer gas

Tar analysis:

The major objective of the experiments was to determine the tar removal abilities of the three catalysts. Therefore the influence on the total tar content as well as on the different tar species is considered. The total tar content in this study is defined by the sum of all tar species detected in the SPA samples, which is the sum of the GC-detectable tar compounds. When the 5 class system from ECN [14] is considered, class 1 the GC-undetectable very heavy tars are not included in this definition. In Figure 7 the total tar reduction by the three different catalysts is displayed. The total reduction was calculated with the mean value of the two values for the treated gas. Catalyst 1 and Catalyst 3 are the most promising ones, reducing the total tar content by 82% and 75% respectively. Catalyst 2 is less active and reduced the total tar content by 51%.

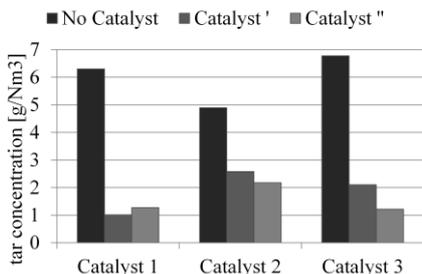


Figure 7: Total tar reduction by the catalysts

The analysed SPA samples give an insight in the tar species that are affected by the catalyst. In Figure 8 the detailed results for Catalyst 1 can be seen. Most of the tar species are removed by the catalyst beyond the detection limit of the analysis. Without catalyst 19 tar species have been detected, with catalyst only 4 (toluene, o-xylene, naphthalene and biphenyl). Naphthalene is the major tar species still present after the catalyst and it increases with time-on-stream. This behaviour may be related to the stability of naphthalene

against reforming or cracking. Moreover, it should be remarked that naphthalene can be produced by cracking of heavier tars.

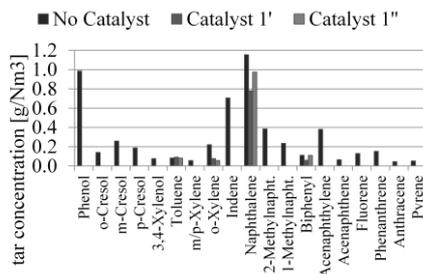


Figure 8: Concentration of tar species during test of Catalyst 1

In Figure 9 the detailed results obtained with Catalyst 2 are summarized. Without catalyst 15 different tar species are detected, whereas with catalyst the number of species has been reduced to 9. From these 9 species in the treated gas 2 are near the detection limit of the GC. The major tar species in the treated gas is again naphthalene. Anthracene, not detected in the untreated gas, has been measured in low amounts in the treated gas. Toluene, naphthalene and biphenyl have been detected in lower amounts in the untreated gas compared to the treated gas. Biphenyl could be produced by dimerization of benzene [14]. The plus in toluene and naphthalene could be due to partial cracking of heavier class 1 tar species or the cracking of substituent groups, which would lead to an increase in aromatic tar compounds without substituent groups and a parallel decrease in compound with substituent groups [23]. Therefore, here the cracking of heavier tar species may take place leading to the formation of lighter tars and the Catalyst 2 seems to be not active enough to completely remove them.

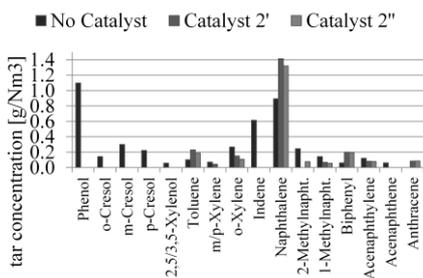


Figure 9: Concentration of tar species during test of Catalyst 2

In Figure 10 the detailed results for Catalyst 3 are displayed. Without catalyst 17 different tar species, with catalyst 8 species have been detected. From these 8 species in the treated gas 4 are near the detection limit of the GC. The major tar species in the treated gas is again naphthalene. In the first SPA sample taken in the catalytically treated gas naphthalene is higher than in the untreated gas. As discussed above this could be due to cracking of heavy class 1 tars or the cracking of substituent groups. The activity of Catalyst 3 is in the same range as Catalyst 1 after activation with time-on-stream.

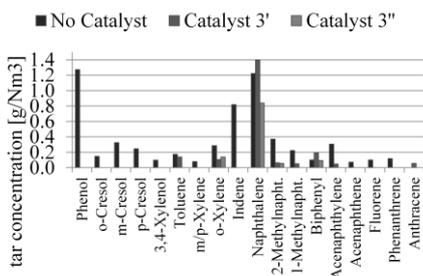


Figure 10: Concentration of tar species during test of Catalyst 3

After catalytic tests PXRD patterns show that in all the catalysts most of the Fe^{3+} species were reduced to FeO , which forms a MgO-FeO solid solution, and/or to Fe_3O_4 . The characterization of the used

catalysts is still under progress to establish a structure-activity relationship.

4. Conclusion and Outlook

Fe-based catalysts obtained from hydrotalcite-type compounds are promising materials for the in-bed tar removal. The activity is dependent on the catalyst composition. Catalyst 1 is the most promising by reducing the total content of GC-detectable tar by 82%. Nevertheless naphthalene is too stable to be efficiently removed by the catalyst. The treated gas after Catalyst 2 contains even more naphthalene than the untreated gas. A possible explanation can be that heavier tar compounds are partially cracked leading to a net formation of naphthalene. In future work the most promising Catalyst 1 will be tested without removal of sulphur and chlorine. A direct comparison of the catalyst and olivine shall be performed. The final test will be the in-situ application of the catalyst in the fluidized bed of the gasification reactor.

5. Acknowledgements

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