COMPARATIVE TESTS OF CATALYSTS FOR REFORMING OF TARS AND METHANE IN BIOMASS-DERIVED SYNTHESIS GAS FROM FLUIDIZED BED GASIFICATION

C. Hamel, H. Lohmann, *T. Schulzke, C. Unger
Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT
Department of Energy Carrier and Recycling Materials
Osterfelder Strasse 3, 46047 Oberhausen, Germany
*Tel. +49 208 8598-1155, Fax +49 208 8598-221155, E-Mail tim.schulzke@umsicht.fraunhofer.de

ABSTRACT: Several different commercially-available and recently-developed catalysts were tested for the reforming of model tar compounds and methane in a simulated producer gas from allothermal biomass gasification in a laboratory scale test rig at Fraunhofer UMSICHT. Monolith and bulk catalysts were compared with respect to their conversion performance in a synthetic syngas in a first project step without typical poisoning substances like e.g. sulfur. Precious-metal catalysts were able to almost completely remove aromatic compounds even at 800 °C and very short residence times over 5 hours of test time. If similar conversion rates can be reached for the upcoming tests in the presence of sulfur as well, the catalysts would be applicable for allothermal gasification systems. The best of the nickel catalysts also showed high conversion levels for both methane and aromatics, but could not totally convert all tar components. One catalyst doped with a promoting compound specifically converted the tar components without showing high activity towards methane. Some first results of the influence of added H_2S as the major sulfur component in the gas are also reported here as part of detailed investigations for the most promising catalysts.
Keywords: tar removal, catalyst, monolith, allothermal gasification

1 INTRODUCTION

Despite intensified efforts of research within the past years, a lot of technical challenges remain for large-scale gasification and downstream syngas utilization. With the choice of fluidized-bed processes, a reasonable compromise seems possible regarding efficiency on the one hand and moderate tar levels in the effluent gas on the other. It has already been shown that it is feasible to attain gas qualities clean enough to be used in gas engines by a combination of primary measures such as specific choice of (partly) active bed materials and downstream catalysts [1-3]. In recent years, interest in the substantial use of syngas has grown and hence allothermal gasification with its advantageous gas composition has gained attention [4-6]. These processes take place at temperatures about 50–100 °C lower than autothermal ones. In combination with H_2S present in the gas, the activity of common catalysts no longer suffices for ultra-low tar levels [7].

The small economic benefit of biomass combined heat and power (CHP) gasification systems compared to co-combustion in power plants has limited the choice of catalysts to low-cost ones. With the goal of substantial gas utilization, precious-metal catalysts come into focus again, due to their increased activity at low temperatures, a better sulfur tolerance [8] and additionally, a high resistance to carbon formation [9]. It depends on the desired product whether a simultaneous reforming of lower hydrocarbons like methane is desired. In case of synthetic natural gas (SNG) production, for example, no methane conversion is desired at all. Therefore, not only total tar reduction should be taken into consideration but also different aspects of the whole process.

This contribution gives an overview to the reforming capability and behavior of about 20 different nickel- and precious metal-based catalysts investigated in a laboratory test rig with predefined gas mixtures. As the catalytic reformation should be placed directly after the gasifier to achieve the highest possible conversion temperature in conjunction with the highest possible activity of the catalyst, the real syngas will be loaded with a considerable amount of particles (attrited bed material, coke and ash). Therefore, monoliths are preferred as catalyst support and are thus mainly examined here. Bulk catalysts with a preparation method that can be transferred to monoliths are considered, too.

2 EXPERIMENTAL

2.1 Catalysts

The catalysts shown in this article were provided by Süd Chemie AG. The variety of catalysts included nickel and precious-metal (PM) catalysts in both monolithic and bulk type. The monolith catalysts had a diameter of 17 mm by a length of 34 mm and had 100 cpsi (cells per square inch). The bulk samples consisted of 3x3 mm pellets.

For confidentiality reasons detailed information about catalyst composition and preparation cannot be given in the following.

2.2 Test setup

The tar reforming tests were carried out in a laboratory scale test rig. A flow sheet of the test rig can be found in [10].

In the first step to produce artificial syngas, three different gas mixes are blended by mass flow controllers (MFC). The first one is preheated and used as carrier gas in combination with an HPLC pump (Knauer Smartline Pump 100) to vaporize an exact amount of water. This system allows constant water vapor levels up to 40 vol%.

To add the model tar components, a 2-syringe pump doses naphthalene dissolved in benzene to a second vaporizer (180 °C) where it is mixed with the preheated second gas mix. These model tar compounds were chosen due to their high abundance in real fluidized bed product gas and because they are the most stable aromatic hydrocarbons of their class [11].

Both gas streams are combined in a heated mixing chamber. A third gas line that bypasses both vaporizers is also connected to this chamber. For the sulfur poisoning tests, this bypass was used to feed a 4 vol% H_2S in CH_4 gas mixture to the artificial syngas.

The syngas is fed to a combined gas heater-reactor system, which is placed inside a 3-zone vertical split-tube furnace that is capable of heating up to 1000 °C. Figure 1

shows details of the combined gas heater and reactor. The former is manufactured of a 6x1.5 mm stainless steel (EN steel no. 1.4878) tube helix (1). The reactor is a 22x2 mm stainless steel tube (EN no. 1.4828). A type-K thermocouple placed just at the entrance to the reactor measures the reactor inlet temperature (2). These temperatures are defined as set points for the process steps.

The catalyst is positioned on a small steel cylinder (3), needed for inserting and retrieving the catalyst sample, and a thin quartz glass frit (4) which is designed to ensure a highly uniform gas distribution over the transversal section of the reactor.

A thermocouple on the outer side of the reactor in the axial centre of the catalyst (5) and a thermocouple approx. 1 cm above the catalyst (6) are used to give an insight to the energetic conditions in the reactor. A VICI Valco multi-position valve is used to select a gas stream fed to an online quadrupole mass spectrometer (InProcess Instruments GAM 200). The mass spectrometer has a direct input, i.e. the capillary is positioned in the center of the selected gas stream. This input system allows a parallel, quasi-continuous and quantitative gas analysis of the whole gas matrix, ranging from the ppmv to the vol% level.
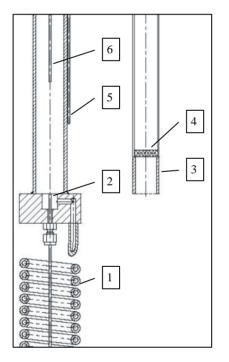

Figure 1: Detailed view at the gas heater and reactor

2.3 Test procedure

The test program for the sulfur-free benchmark tests comprised the following steps:

In a first step, the furnace is heated up to 900 °C (temperature of the first thermocouple) under a CO_2 gas stream. If a Ni catalyst is used, heating-up is interrupted for a three-hour reduction step at 650 °C by a mixture of 10 % H_2 in Ar. Thereafter, the heating process is continued up to 900 °C. When 900 °C is reached, the gas is changed to syngas and the raw gas composition (before the reactor) is analyzed for about one hour. Average values of the raw gas composition are shown in table I. Then the multi-position valve is changed to measure the output gas (after the reactor). The temperature is

decreased in 50 °C steps down to 700 °C. On every step the temperature is kept constant for one hour. After the 700 °C step, the temperature is increased to 900 °C again to check whether the catalysts reach their initial activities. This measurement allows drawing conclusions about possible non-reversible deactivation of the catalysts during the temperature program. A subsequent five-hour step at 800 °C provides a first hint at the long term stability of the catalyst. At the end of the test, the raw gas composition is measured again to indicate a possible drift of the mass spectrometer.

Table I: Composition of Simulated Syngas

Gas Component	Unit	Value
H_2	Vol%	26
CO	Vol%	16
CO_2	Vol%	14
CH_4	Vol%	7
Ar	Vol%	4
H_2O	Vol%	33
Naphthalene	ppmv	370
Benzene	ppmv	1 500

For the tests with added sulfur, the test program was slightly altered. The temperature steps were prolonged to about three hours each and the long-term step at 800 °C was canceled. In the sulfur tests described in this article, the H_2S concentration was always 150 ppmv. This concentration correlates to raw syngas with a significant amount of bark in the gasified wood.

In all tests, the total gas flow was 2 L/min at STP conditions (0 °C, $1 \cdot 10^5$ Pa), resulting in an gas hourly space velocity (GHSV) of approx. 16000 h^{-1}. At 800 °C e.g., the residence time is about 0.05 seconds which is approx. ten times lower than in large scale applications. The high GHSV was firstly chosen to reduce the necessary testing time per catalyst and secondly, to test the catalysts under very rough conditions to clearly point out differences. It also has to be borne in mind that the ratio of active monolith channels to the cross-sectional area of the reactor is quite low and would not be transferred to a large-scale reforming system. Table II summarizes the test conditions and relevant dimensions.

Table II: Summary of test details

	Unit	Value
Reactor inner diameter (ID)	mm	18
Catalyst (bed) length	mm	34
Volumetric flow rate (STP)	L/min	2
Space velocity at STP (GHSV)	h^{-1}	16 000
Steam-to-carbon ratio (S/C)	-	0.86

2.4 Data analysis

For the comparative tests, the main criteria were the conversion levels of naphthalene, benzene and methane. These were calculated according to the following formulas.

$$X(CH_4) = \frac{n_0(CH_4) - n(CH_4)}{n_0(CH_4)} \cdot 100\%$$

$$X(C_6H_6) = \frac{n_0(C_6H_6) - n(C_6H_6)}{n_0(C_6H_6)} \cdot 100\%$$

$$X(C_{10}H_8) = \frac{n_0(C_{10}H_8) - n(C_{10}H_8)}{n_0(C_{10}H_8)} \cdot 100\%$$

Therefore, a molar balance was set up. The volume flows of the MFCs as well as the volume flows of the two liquid dosing systems were used to calculate the total molar input. The raw gas composition measured in each test was used to calculate the molar flow of the elements. As argon could be considered as inert, the change in volume could be deduced from the different fractions of argon in raw and product gas.

In the vast majority of the tests, the elemental molar balances could be closed with an error below 5%.

3 RESULTS AND DISCUSSION

3.1 Blank value measurements

With blank value measurements, it could be shown that the used reactor materials have no significant quantitative effects regarding the tar reforming activity in the applied conditions and therefore do not influence the concluded results.

3.2 PM catalyst tests without sulfur

The performances of different PM catalysts were compared with respect to their conversions of methane (CH_4), benzene (C_6H_6) and naphthalene ($C_{10}H_8$). Figures 2, 3 and 4 show the conversions of the hydrocarbons methane, benzene and naphthalene of eight PM monolith catalysts on the y-axis versus the progress of the testing program on the x-axis. There are two points given for the 800 °C long term step. The first one is taken at the beginning of the process step, the second one at the end. To improve readability, the exact relative times are not used here. For the same purpose, a different scaling was used for the three diagrams.
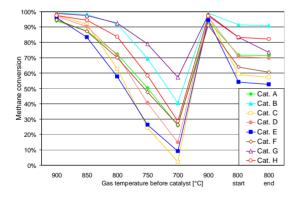
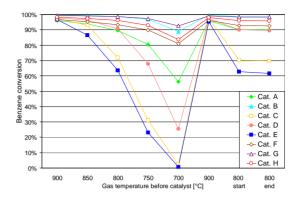**Figure 2:** Methane conversion versus the temperature before the catalyst

Figure 3: Benzene conversion versus the temperature before the catalyst
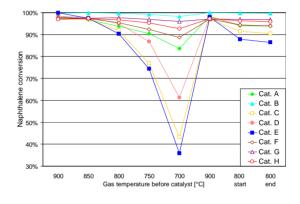
Figure 4: Naphthalene conversion versus the temperature before the catalyst

All shown catalysts were able to nearly completely convert naphthalene at high temperatures, but differed in their performances at lower temperatures, especially at 700 °C. It has to be remarked here that these results are obtained without catalyst poisons or competing compounds like NH_3. To approach realistic conditions and applications, it is crucial to extend the test matrix with catalyst poisons and other impurities.

To assess the results, especially with a view to economical feasibility, it is necessary to know about the relative amounts of each active component. Table III summarizes the relative amounts of the PM catalysts shown in the figures. As all of them are based on the same cordierite carrier, the amounts can be directly compared.

Table III: Summary of test details

Catalyst	PM 1	PM 2
A	1	1
B	1	1
C	1	1
D	0.4	1
E	0.2	1
F	4	0
G	8	0
H	0	1

Regarding the catalysts with just one active component (F, G, H), catalyst G with at least twice the amount of active component of all other catalysts performs best in converting methane and benzene. A

reason could be the absolute amount of highly active centers available that are required for the methane reforming reaction. It is also possible, that the activity is too high and thus the catalyst tends to do cracking instead of reforming which would result in carbon formation. This could explain the loss in activity over the five hours at 800 °C. Adding sulfur will probably help to assay this issue.

Catalyst H was prepared with a different precious metal. Though having the least amount of active component, it performs very well in both reforming aromatics and methane. So far, it was not possible to assay the reason for the high activity of this catalyst, but the relations may change when using sulfur loaded gas in the next project steps.

The stability at 800 °C could be in line with the results of catalyst B, as cracking was nearly not present on this catalyst.

Comparing the use of one versus two active components, no clear tendency can be seen so far.

Different synthesis routes lead to diverse results as can be seen for catalysts A, B and C, which differ only in the preparation method but exhibit the same total loading. Either the precursor was varied or the order in which the active components were coated. The results indicate heavy influences of these preparation factors, as catalyst B shows the best results of all catalysts and catalyst C seems to be very inactive.

Catalysts A, D and E are made with the same preparation route but differ in the amount of PM 1. Within one type of preparation, there seems to be a direct correlation between the amount of PM 1 and the activity. For all three compounds, catalyst A performs best and catalyst E is less active.

3.3 Ni catalyst tests without sulfur

One main goal of this project is to develop nickel catalysts that are able to compete with PM catalysts at lower temperatures, thus being economically more feasible due to their lower price. For the comparative tests, commercially-available catalysts were tested, as well as catalysts from recent developments.

Figure 5 shows the results of three Ni bulk catalysts. Catalyst K, a commercially available methane steam-reforming catalyst, was used as a reference for the tests, due to its standardized preparation route. All three catalysts show high conversions regarding the aromatic compounds but were not able to completely remove them. The catalysts I and K also show high conversions of methane, in opposition to catalyst J. A reason for that could be the additional doping of this catalyst with a promoting compound. With a view to the aim to develop catalysts that can be applied for different downstream applications, this catalyst may be a good choice for SNG or gas engines. These applications benefit from a high methane slip but still need very low concentrations of aromatics. When returning to 900 °C, all three plotted catalysts lose about 5 % of their methane conversion ability but show stable results for benzene and naphthalene. In comparison to the PM catalysts that show no significant deactivation, this leads to the conclusion that the Ni catalysts underwent deactivation as a result of possible coking. The results of the long-term tests also lead to this conclusion, as all catalysts visibly show a loss in activity over the five hours at 800 °C. The deactivation behavior will be further discussed in the following section.
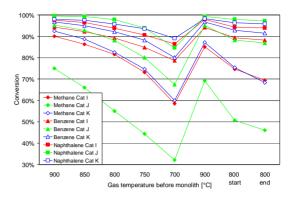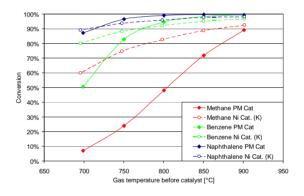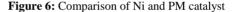

Figure 5: Conversions of 3 different Ni catalysts versus the temperature before the catalyst

3.4 Comparison between PM and Ni catalysts

As written above, the development of competitive Ni catalysts is one of the major aspects of this project. A direct comparison between two bulk catalysts (3x3 mm pellets) is given in Figure 6.

Figure 6: Comparison of Ni and PM catalyst

The PM catalyst is able to nearly totally convert naphthalene down to 700 °C but the conversions of methane compared to Ni are lower. Benzene conversion shows a drop at 700 °C. The Ni catalyst also reaches high conversion levels for the aromatic compounds but, as already discussed above, is not able to convert all naphthalene even at high temperatures. The activity for methane remains high even at temperatures below 800 °C.

Figure 7 gives a first impression about the behavior of the catalysts regarding their long-term stability. In the diagram, the concentrations of H_2 (left side) and the tar compounds (right side) are plotted over the absolute test time. The horizontal offset between the curves is due to the pre-reduction of the Ni catalyst. It is clearly visible that the Ni catalyst loses its activity over the whole length of time in contrast to the PM catalyst, which reaches its final activity after about one hour and constant conversion thereafter. The described behavior could be seen for all Ni catalyst samples over the five hours step at 800 °C.

It has to be remarked that this test was aimed to give a first impression about long-term operation. To further assess this topic, there will be separate long-term tests in the next project steps.

Summarizing the comparison, it can be said that both catalysts work as they were designed. The PM catalyst seems to be good for removing the aromatic compounds;

the Ni catalyst has a high activity for methane but should not be used for full tar conversion, even without sulfur.
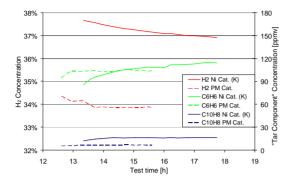

Figure 7: Comparison of Ni and PM catalyst in long-term step

3.5 Comparison between bulk and monolith catalyst

The project is focused on developing monolith catalysts due to the designated application in heavily dust-loaded producer gases. Catalyst development, in contrast, primarily uses bulk catalysts as they are easier in synthesis and handling. For the project, it is therefore necessary to be able to compare both types of preparation.

The PM catalysts shown in figure 8 both have the same fraction of active compound per volume and thus can be compared to each other.

While the monolith has a higher conversion rate for methane, the bulk catalyst removes more naphthalene, particularly at 750 - 850 °C. Regarding benzene, the bulk catalyst achieves higher conversions at higher temperatures, whereas the monolith has a higher activity at 700 °C. These phenomena could possibly be explained by diffusion-controlled kinetics. A laminar flow profile is reached quickly within the channels of a monolith which results in diffusion controlled kinetics. This could explain the lower conversions for the larger molecules naphthalene and benzene.
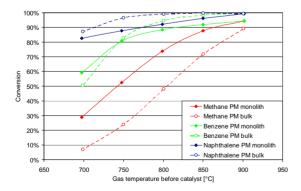

Figure 8: Comparison of monolithic and bulk catalyst

3.6 Tests with sulfur

The addition of sulfur is the most important step towards a more realistic simulation of the syngas. By the time of this article's writing, just a few measurements with sulfur were done, so these results should give a first impression about the influence of 150 ppmv H_2S at the used conditions.

Figure 9 directly compares the results of the bulk catalyst K in both sulfur-free and sulfur-containing syngas. The conversion performance, especially for methane, was greatly influenced by the addition of 150 ppmv H_2S. It has to be emphasized that the used GHSV in these tests is more than double what would be applied in large-scale systems, especially when using bulk catalysts. The test with sulfur also showed that the catalyst is able to reach its starting activity of methane after undergoing the low temperatures in contrast to the test without H_2S-addition. This might be due to a lower coking tendency as a result of partially-occupied active nickel centers as it was reported by [12]. According to this paper, the occupation of high-activity centers can result in a higher selectivity for other components as it can be seen in figure 9.
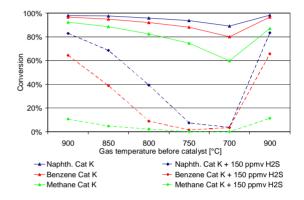

Figure 9: Influence of 150 ppmv H_2S on Ni bulk catalyst

As described in the experimental section (see figure 1), the temperatures in the axial center of the catalyst (5) and approx. 10 mm after the catalyst (6) were measured by thermocouples. These measurements give information about the thermal conditions as a consequence of the reactions taking place at the catalyst. The reforming reaction is highly endothermic and therefore it was expected that the temperatures outside the reactor (5) and after the catalyst (6) are lower than at the entrance of the reactor (2). The measured temperatures versus the nominal set point are plotted for the test without H_2S (Figure 10) and with 150 ppmv H_2S (Figure 11). In both tests, the temperature gradient is decreasing from 900 °C to 700 °C. When methane conversion is depressed (as it can be seen in Figure 9), the reactor is nearly isothermal when highly endothermic reforming of low concentrated tar is balanced by slightly exothermic shift reaction.
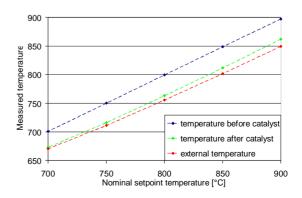

Figure 10: Measured temperatures versus nominal set points without H_2S
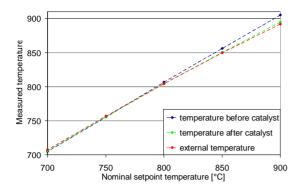
Figure 11: Measured temperatures versus nominal set points with 150 ppmv H_2S

4 SUMMARY AND OUTLOOK

A broad variety of different catalysts were tested in a simulated syngas for the reforming of model tar substances and methane.

The PM catalysts differed in the amount of active components and in preparation route. A high amount of PM 1 had a direct positive effect on the conversion of the hydrocarbons though the catalyst having only PM 2 also showed high activity. Most PM catalysts could completely remove aromatic components from the gas even at temperatures of 800 °C and five hours of test time. These catalysts could be a choice for allothermal gasification systems as they keep good performance in tar reforming at relatively low temperatures.

The Ni catalysts were not able to convert all tar compounds but reached higher conversion results for methane than the PM catalysts. One catalyst additionally doped with a promoter showed high conversions for the aromatics in combination with low conversions of methane and thus could be applied for downstream applications like SNG.

It can be concluded that PM catalysts should be applied when a total removal of higher tars is required for downstream applications like Fischer-Tropsch syntheses.

The differences between bulk and monolith catalysts mostly were also examined. Probably due to diffusion controlled kinetics, the bulk catalyst showed higher conversions for naphthalene whereas the monolith catalyst performed better in reforming methane.

The addition of 150 ppmv sulfur heavily effected the conversions of the Ni catalyst. Methane was affected over the whole temperature range and the tars were influenced beginning from 800 °C downwards. It has to be kept in mind that the applied test conditions are very rough.

After determining an operation window in which at least some of the PM catalysts lead to acceptable tar conversion rates in the presence of 150 ppmv H_2S other contaminants will be added to the gas matrix to stepwise approach to the challenges of raw producer gas from biomass gasification in fluidized beds.

5 ACKNOLEDGMENTS

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