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ORIGINAL ARTICLE

Manganese oxide as catalyst for tar cleaning of biomass-derived gas

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Abstract The possibilities to upgrade raw gas with the use of a manganese oxide have been investigated in an application for secondary tar cleaning of biomass-derived gas. Experiments were conducted in a reactor system where a novel technique that combines tar cleaning with catalyst regeneration is applied. Raw gas from the Chalmers non-catalytic steam biomass gasifier—containing roughly 32 g_{tar}/Nm_{gas}^3—was fed to the tar cleaning reactor. The tar reforming qualities of the manganese oxide were evaluated in the reactor system using a mixture of 23 wt.% catalysts in silica sand at the temperatures 700 and 800°C. Experiments showed that the catalyst was continuously regenerated from carbon deposits and that the total amount of tars was decreased by as much as 44.5 % at a gas residence time of 0.4 s in the bed. The catalyst showed activity in water–gas shift reaction and the H_2/CO ratio increased from 0.6 in the raw gas to a peak value of 1 in the reformed gas at 800°C. Only a slight decrease in methane and acetylene content was observed for both operating temperatures.

Keywords Biomass · Tar · Gas cleaning · Catalysts · Gasification · Dual fluidized bed

1 Introduction

Biomass is a resource that can be used as fuel in various applications in order to replace fossil fuels. For example, biomass can be synthesized to transport fuels such as: synthetic natural gas, dimethyl ether, or methanol [1]. In order to process biomass to bio-fuels, there is a need to first convert the solid biomass to, for example, gas. This step can be done in a thermo-chemical conversion process called gasification. As biomass is gasified, condensable hydrocarbons, often referred to as tars, are formed as a by-product [2–6]. Tars start to condense already at 350°C [7] and are associated with operation problems such as clogging and blockage of equipment downstream the gasifier. The tars propensity to condense precludes direct use of the raw gas as feedstock for fuel synthesis or as a fuel in gas turbines/engines without implementation of a sufficient tar cleaning. The development of efficient tar cleaning systems is, therefore, a crucial parameter for commercializing the biomass gasification technology.

In principle, there are two available routes for cleaning the raw gas from tars: wet or dry gas cleaning. Wet cleaning is performed in scrubber units where the raw gas is rapidly cooled by a liquid. In this process, the tars are physically removed from the gas by condensation onto water or oil droplets. The wet cleaning—based on scrubber technology—is a well-established technology but is associated with significant amounts of waste water/solvents and thermodynamic penalties coupled to the rapid cooling of the raw gas [8]. Dry cleaning most often refers to catalytic or a high temperature cleaning (thermal cracking of tars). Catalytic cleaning can be integrated with the gasifier outlet temperature, whereas high-temperature cleaning needs to be performed at elevated temperatures (>1,100°C) to reach high conversion efficiencies [6]. Some of the product gas needs to be consumed together with additional oxygen to increase the exit temperature of the gasifier (from around 800 to 1,100°C). Therefore, catalytic tar cleaning is the preferred method as the heat losses can be minimized [6] and the chemically stored energy within the tars can be recovered in the product gas. However, so far catalytic

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systems have not been feasible for use in industrial applications. This is mainly because of problems associated with deactivation of the catalysts. It is known that catalysts with long-term exposure from components such as sulfur, chlorine, alkali, etc., can be deactivated, but the catalyst can also lose its activity after only a short operating time if carbon is depositing on the active surfaces [3, 6, 8]. In this work, a method that combines tar cleaning with regeneration of carbon deposits on the catalyst is applied to investigate the possibilities of using manganese oxide as a reforming catalyst. In this first experiment, a well-defined manufactured catalyst was used to study the tar decomposing activity of the manganese oxide itself, whereas the long-term goal is to use naturally occurring ores containing manganese.

The tar reforming properties of the catalyst are evaluated in a system of dual fluidized beds [9], which is based on the chemical looping reforming (CLR) technique originally presented by Mattisson et al. [10]. The CLR system is fed with raw gas—containing about 32 $g_{tar}/Nm_{raw\ gas}^3$—from the Chalmers 2–4 MW biomass research gasifier [11, 12]. The idea with the tar cleaning method is to reform tar components (C_nH_m) into useful gas molecules. The reactor system consists of two reactors: a regenerator reactor also called air reactor (AR) and reformer reactor (FR) fluidized with raw gas (Fig. 1). Two loop seals, fluidized with inert gas or steam, prevent gas cross-contamination of the effluents from respective reactor, while enabling the catalyst to circulate between the two reactors. In the reformer reactor, the Me_xO_y is reduced to Me_xO_{y-1} during the partial oxidation of the tar components (C_nH_m) in the raw gas according to reaction (1), which usually is an endothermic reaction [13]. Besides the desired tar reforming reaction, additional carbon-forming reactions cause carbon to deposit on the Me.

$$C_nH_m + (n - n_1)Me_xO_y \rightarrow (n - n_1)CO + (0.5\,m)H_2 + (n - n_1)Me_xO_{y-1} + n_1C \tag{1}$$

The reduced metal oxide Me_xO_{y-1} is also acting as catalyst for tar reforming in the presence of reforming media* such as water steam or carbon dioxide in the raw gas according to the simplified reaction (2).

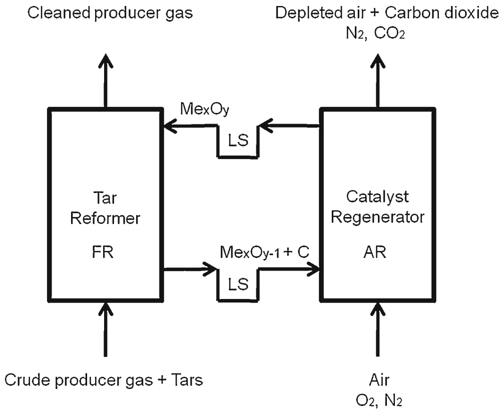

Fig. 1 Dual fluidized bed system for tar removal

$$C_nH_m + Me_xO_{y-1} + H_2O^* + CO_2^* \rightarrow Me_xO_{y-1} + C_iH_j + H_2 + CO \tag{2}$$

Simultaneously, as Me_xO_{y-1} is re-oxidized to Me_xO_y in a strongly exothermic [13] reaction in the AR, carbon deposits on the catalytic surfaces are oxidized to CO_2 according to reaction (3)

$$n_1Me_xO_{y-1} + n_2C + (n_1/2 + n_2)(O_2 + 3.77N_2) \rightarrow n_1Me_xO_y + n_2CO_2 + (n_1/2 + n_2)(3.77N_2) \tag{3}$$

The concept of reforming tars in the CLR system was proven by Lind et al. [9] using ilmenite ($FeTiO_3$) as tar reforming catalyst.

The catalyst (M4MgZ1150) used in this work consists of 40 % manganese oxide (Mn_3O_4) supported on 60 % stabilized magnesium–zirconium oxide ($MgZrO_3$) and was originally developed as an oxygen carrier for the chemical-looping combustion process (CLC) [14]. Johansson et al. [15] investigated the potential of the M4MgZ1150 as oxygen carrier in CLC operations and confirmed that the material was suitable as it could withstand continuous redox reactions and in the same time showed high reactivity. This implies that the material is even suitable for the CLR system where the catalyst is continuously exposed to reduction and oxidation reactions. Mendiara et al. [16, 17] investigated the tar reforming activity of the M4MgZ1150 in batch experiments with toluene as representative tar component at 600 and 800°C. They concluded that the material showed high reactivity towards toluene, which was decomposed to a large extent at both temperatures. In this work, the tar reforming properties of M4MgZ1150 is investigated in a system that has been developed one step closer to an industrial application. The experiment gives additional information about the catalyst activity, as more than 170 tar components are present in the raw gas from the gasifier and 21 of them are analyzed. The fundamental investigated criteria to assess the tar reforming quality of the catalyst and the suitability to use the catalyst in the CLR system are:

- How reactor temperature variations influence the tar reforming activity
- How various oxygen loads on the catalyst influence the tar reforming activity
- The possibilities to regenerate active surfaces from carbon deposits while remaining of catalytic activity
- How reactor temperature and oxygen load influences the permanent gas composition

2 Experimental

A drawing of the 0.5 meter high CLR system is shown in Fig. 2. In this bench-scaled CLR system, the FR (1) is designed as a bubbling fluidized bed to provide a good estimation of the gas/solid contact, but the concept could also be applied to two circulating fluidized beds. The regenerator reactor (AR) (2) is a circulating fluidized bed and gas/solid separation is achieved in a cyclone. The gases (Table 1) enter the reactor system via wind boxes, which are placed beneath the porous plates in FR, AR, superior loop seal (SLS), and inferior loop seal (ILS) in order to reduce pressure fluctuations in the gas feed. The tar reforming reactions and regeneration reactions can, with respect to temperature, be optimized separately with a temperature difference up to above 200°C. The temperature control is achieved by separate heating of the two oven halves (3), together with an air-cooled jacket on the FR (4). The gas feed to the AR is controlled by two separate mass flow regulators (5), which enable operation with air and/or nitrogen. Downstream the AR, the gas is cooled and dried in a gas conditioning system (6). The content of CO, CO_2, and O_2 in the gas exhausting from the AR are analyzed online by non-dispersive infrared analyzers for CO and CO_2, respectively paramagnetic analyzer for O_2 (7). The gas flows of Helium to the SLS and ILS are controlled by two separate mass flow regulators (8). The FR in the CLR system is connected to the Chalmers gasifier, which is operated at a pressure slightly lower than the atmospheric pressure, due to safety reasons. As a consequence, the CLR operating pressure is −4 to −6 kPa and

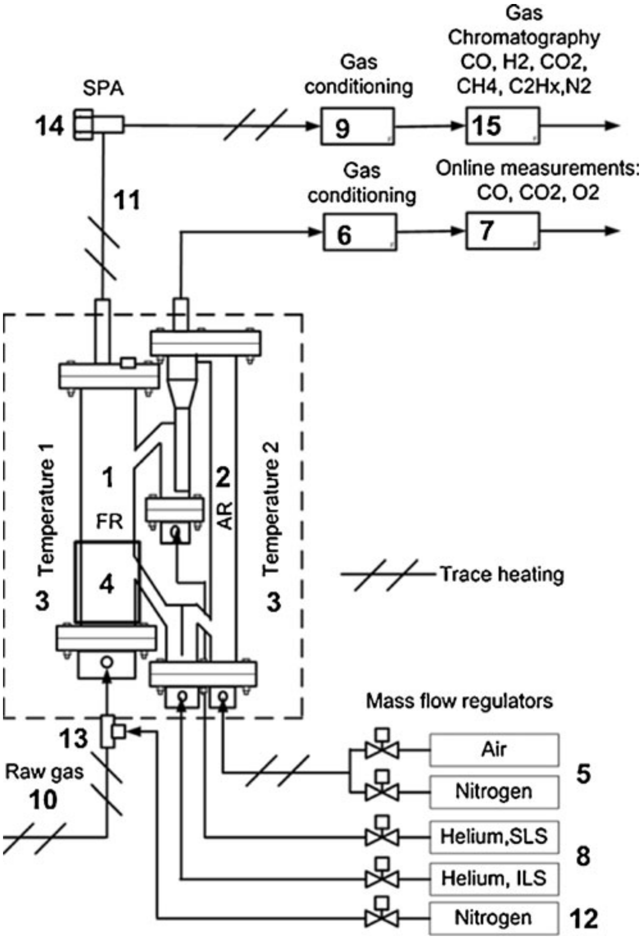

Fig. 2 Drawing of the CLR setup

Table 1 Operation conditions in gasifier and chemical looping reforming (CLR)

Properties	Units	700°C in CLR		800°C in CLR	
Gasifier					
Fuel	–	Wood pellets		Wood pellets	
Bed temperature	°C	830		825	
Bed material	–	Silica sand		Silica sand	
Dry raw gas composition					
Hydrogen	mol%	21.02		20.42	
Carbon monoxide	mol%	35.35		35.40	
Carbon dioxide	mol%	14.47		14.37	
Methane	mol%	12.85		12.85	
Acetylene	mol%	0.41		0.38	
Ethylene	mol%	4.45		4.40	
Ethane	mol%	0.40		0.43	
Nitrogen	mol%	11.06		11.75	
Tars	g/nm^3	32.89		32.90	
Steam content. raw gas	mol%	50.71		51.25	
CLR					
Temperature	°C	700		800	
Air feed in AR	l/min	0.26	0.56	0.26	0.56
Nitrogen feed in AR	l/min	5.04	4.74	5.04	4.74
Helium feed in ILS	l/min	0.29		0.29	
Helium feed in SLS	l/min	0.37		0.37	
Raw gas feed FR (dry)	l/min	≈2.5		≈2.5	
Silica sand					
Particle diameter (mean)	Mm	230		230	
Solids density (bulk)	kg/m^3	1,470		1,470	
Amount silica sand	G	388		388	
Gas residence time (reactor)	s	≈3.0		≈3.0	
Gas residence time (bed)	s	≈0.4		≈0.4	
M4MgZ1150					
Particle diameter (mean)	µm	230		230	
Solids density (bulk)	kg/m3	1,560		1,560	
Amount catalysts	g	116		116	
wt.% of total bed inventory	%	23		23	

CLR chemical looping reforming, *AR* air reactor, *FR* reformer reactor, *SLS* superior loop seal, *ILS* inferior loop seal the gas flow through the reactor is controlled by a gas pump in the gas conditioning system (9). The raw gas pipe between the FR and the gasifier (10), as well as, the connecting pipe between the FR and the gas conditioning system (11) are electrically heated to 400°C to avoid tar condensation. A T-connector for nitrogen supply (from a mass flow regulator (12)) is mounted on the raw gas pipe upstream the inlet to the FR (13). This enables inert conditions in the FR before and after the introduction of raw gas. The concentrations of tars in the raw gas and the reformed gas are measured by solid phase adsorption [18] (SPA). The tar samples for the reformed gas are collected in the heated pipe between the FR and the gas conditioning system (14) while an additional system is used for tar sampling of the raw gas [9]. The adsorbed tars are dissolved in a solvent and sent for analysis in a gas chromatography followed by flame ionization detector (GC-FID). The reformed gas leaving the FR is cooled and dried in the gas conditioning system (9) and thereafter, analyzed by a micro gas chromatograph (15), micro-GC (Varian 4900). A detailed description of the analysis equipment, CLR and the gasifier measuring system can be found in Lind et al. [9].

3 Experimental procedure

A reference experiment with silica sand was carried out at 740 and 815°C to ensure that no catalytic effects was induced by the sand or the reactor material itself (containing 10 % nickel). The experiment which was performed by comparing the dry gas composition and tar content in and out of the CLR system showed that the silica sand and the reactor material had negligible effect on both gas and tar composition. Detailed description and results from the reference experiment can be found in Lind et al. [9].

The manganese experiments were conducted with a mixture of 23 % M4MgZ1150 in 77 % silica sand as bed inventory to investigate how the tar decomposing/reforming properties are influenced by a change in temperature and oxygen load. A detailed description of the catalyst preparation can be found in Johansson et al. [15]. The catalyst activity and the regeneration of the catalyst was evaluated at 700 and 800°C with two different oxygen concentrations—1.0 and 2.2 mol% O_2—in the inlet feed to the AR (Table 1). The same bed material was used in both experiments.

The bed material mixture was poured into the FR, which was heated to 800°C, and the raw gas pipe connected under nitrogen purging. Thus, the raw gas was gradually replacing the nitrogen until the nitrogen was fully exchanged to raw gas.

The regeneration of carbon deposits on the catalysts was investigated by measuring CO_2 and CO concentration from the outlet of the AR. For the start-up sequence in both 700 and 800°C cases, and during nitrogen fluidization in the FR, the CO_2 and CO concentrations were below the detection limit of the instrument. Table 2 shows the measuring interval and detection limit for the analysis instruments downstream the AR. The amount of carbon deposits that was regenerated from the catalysts $Y_{\mathrm{c,AR}}$ has been calculated as the ratio between total integrated mass of carbon at the outlet of the AR and total mass of carbon fed to the FR during steady-state operation in the CLR, according to Eq. 4. Where $m\mathrm{CO}_{2,\mathrm{ARout}}$ and $m\mathrm{CO}_{,\mathrm{ARout}}$ is the carbon contribution from the carbon dioxide and carbon monoxide at the outlet of the AR and $\mathrm{mC}_{i,\mathrm{FRin}}$ denotes all the carbonaceous species in the raw gas.

$$Y_{C,\mathrm{AR}} = \frac{\int_{t_{\mathrm{start}}}^{t_{\mathrm{stop}}} \left(\overset{\bullet}{m}\,\mathrm{CO}_{2,A\mathrm{R\,out}} + \overset{\bullet}{m}\,\mathrm{CO}_{A\mathrm{R\,out}} \right) \mathrm{d}t}{\int_{t_{\mathrm{start}}}^{t_{\mathrm{stop}}} \left(\sum_{i=j}^{n} \overset{\bullet}{m}\,\mathrm{C}_{i,\mathrm{FR\,in}} \right) \mathrm{d}t} \tag{4}$$

The oxygen content in the feed to the AR was kept at 1.0 mol% for 1 h. Sampling of O_2, CO, and CO_2 in the outlet of the AR was performed every second during the entire experiment. Sampling of the reformed gas composition out from the FR was performed every third minute and 6 tar samples were collected by SPA when stable operation was achieved. Thereafter, the oxygen concentration was switched from 1.0 to 2.2 mol% during 1 h. Sampling of tars and dry gas components was conducted in the same manner as in the 1.0 mol% oxygen case.

The composition of the raw gas fed to the FR was determined via the gasifier sampling system for 2 h following the CLR experiment. Dry gas composition was sampled every third minute via the GC and tar composition was sampled by one set of six SPA samples after 1 h. The same procedure was repeated for the 700°C experiment, except that the bed material was already in the CLR during the start-up.

4 Results and discussion

The aim of this work was to evaluate if the M4MgZ1150 could be suitable as a reforming catalyst in a system for secondary continuous catalytic tar cleaning. The tar reforming activity of the catalyst was evaluated at the temperatures

Table 2 Gas-analyzing instruments downstream of the AR

Instrument	Measuring interval (mol%)	Detection limit (ppm)
O_2	0–25	1,250
CO	0–1	50
CO_2	0–100	5,000

of 700 and 800°C by comparing the tar components in the raw gas with the reformed gas after the CLR system. Table 3 summarizes the concentrations (g_{tar}/Nm^3) of the 21 analyzed tar components from the SPA-samples, in the raw gas, as well as in the reformed gas leaving the CLR. The table is organized in accordance to: the two investigated temperatures (cases), the position for tar measuring (measure position) and the oxygen concentration in the inlet feed to the air reactor (mole% O_2 in AR). The highest degree of tar reduction (44.5 %) was achieved at a CLR operating temperature of 800°C. At a temperature of 700°C in the CLR the highest reduction of tar was nearly 22 %. These values can seem low if compared with, e.g., values for tar reforming with a nickel based catalyst, where tar conversions can be close to 100 %. However, in this experiment the amount of catalyst was only 23 wt.% of the total bed inventory and consequently the gas solid contact was very restricted.

In addition to the total amount of tars, the SPA samples also provide information about the different tar molecules and how the tar structures change. Figure 3a, b shows the overall changes in tar composition—divided into seven groups—between the raw gas and the reformed gas at 700 and 800°C. The groupings display the general patterns for the catalytic decomposition of the tars. The tar groups are as follows: phenols, benzene, one-ring aromatic compounds with branches (1-ring), naphthalene, two-ring aromatic compounds with branches (2-ring), three- to four-ring aromatic compounds without branches (3- and 4-rings), and finally "unknowns." The results from experiment performed at 800°C (Fig. 3a) show how the amount of phenols and 1-ring tars decreases, while the amount of benzene increases for both oxygen concentrations. This implies that the decomposition of phenols and1-ring tar molecules takes place via a reaction stripping off the hydroxyl or alkyl group from the branched molecule to form pure benzene. Almost all phenols (98 %) and more than half (55 %) of the 1-ring branched aromatic compounds are converted at 800°C with oxygen concentration of 2.2 mol% in the AR.

Table 3 Tar composition for raw gas (gasifier) and reformed gas at 700 and 800°C leaving the CLR using 23 wt.% M4MgZ1150 in silica sand

Cases	700°C in CLR (g_{tar}/Nm^3)			800°C in CLR (g_{tar}/Nm^3)		
	Measure position (mol% O_2 in AR)					
	Gasifier (–)	CLR (1.0)	CLR (2.2)	Gasifier (–)	CLR (1.0)	CLR (2.2)
Phenol	1.39	0.88	0.39	2.18	0.09	0.07
o-cresol	0.06	0.08	0.03	0.26	0.00	0.00
m-cresol	0.20	0.02	0.00	0.48	0.00	0.00
p-cresol	0.06	0.00	0.00	0.15	0.00	0.00
Benzene	0.75	0.80	0.77	0.51	1.18	1.18
Toluene	0.81	0.82	0.72	0.66	0.68	0.60
m/*p*-xylene	0.21	0.20	0.15	0.19	0.08	0.07
o-xylene	1.33	1.23	1.05	1.10	0.83	0.85
Indan	0.04	0.08	0.06	0.06	0.17	0.16
Indene	3.85	2.08	1.32	3.76	0.65	0.61
Naphthalene	8.01	7.97	8.69	7.54	9.68	8.41
2-methylnaphthalene	1.29	1.03	0.90	1.32	0.52	0.37
1-methylnaphthalene	0.83	0.64	0.55	0.83	0.24	0.17
Biphenyl	0.56	0.58	0.71	0.54	0.81	0.65
Acenaphthylene	2.46	2.13	2.16	2.40	1.51	1.24
Acenaphthene	0.17	0.09	0.08	0.18	0.06	0.04
Fluorene	0.86	0.55	0.42	0.86	0.14	0.09
Phenanthrene	1.71	1.75	2.17	1.77	2.02	1.50
Anthracene	0.51	0.51	0.61	0.53	0.47	0.33
Fluorantene	0.52	0.49	0.61	0.53	0.51	0.36
Pyrene	0.58	0.56	0.71	0.60	0.53	0.36
"Unknowns"	6.72	4.25	3.60	6.43	2.00	1.21
Total tar	32.90	26.73	25.70	32.89	22.18	18.27
Conversion (%)	–	18.8	21.8	–	32.6	44.5

CLR chemical looping reforming, *AR* air reactor

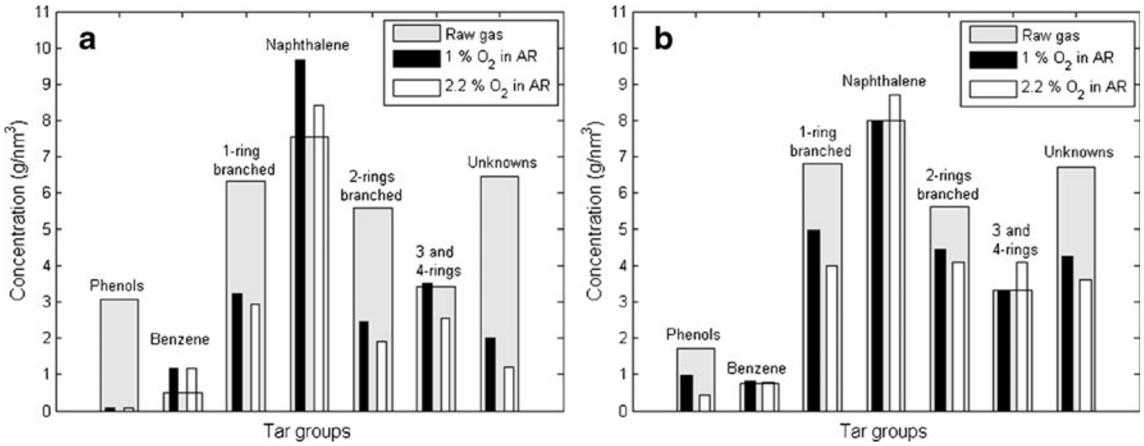

Fig. 3 **a** Composition of tar divided into seven groups for raw gas and reformed gas at 800°C. **b** Tar group composition for raw gas and reformed gas at 700°C

A similar tar decomposing pattern can be seen for the 2-ring tar molecules, where the alkyl group is stripped off forming pure naphthalene. The 2-ring compounds are decreased by as much as 66 % at an oxygen concentration of 2.2 mol% in the AR. Besides the decomposition of phenols and 1- and 2-rings, the decomposition of tars from the group "unknowns" also contributes to the increase in benzene and naphthalene. The "unknowns" comprise at least 150 unidentified tar molecules with molecular weights spread from that of benzene to molecular weights greater than pyrene. The reforming of unknown molecules greater than pyrene may explain why the amount of 3- to 4-rings is higher in the reformed gas than in the raw gas for the 1.0 mol% oxygen case. The elevated concentrations of 3- and 4-rings may well also origin from the decomposition of the heaviest tar molecules, so called non-GC detectable, i.e., not possible to measure via GC-FID.

A general trend for the 800°C case (Fig. 3a) is that increased oxygen concentration increases the conversion of phenols, 1- to 2-rings and "unknowns." In other words, the tar reforming reactions benefit from increased oxygen transfer from the AR to the FR. The tar decomposition pattern of forming pure aromatic compounds (benzene and naphthalene) from branched aromatic compounds and phenols agrees well with results from an experiment involving ilmenite as a tar reforming catalyst in the same system [9].

A similar pattern in reforming phenols and 1-ring compounds can be seen at 700°C (Fig. 3b) but in this case the catalyst activity is lower. At 2.2 mol% O_2 in the AR, the phenols and the 1-ring is reduced by 75 and 41 % in comparison to 98 and 55 % at 800°C. The fraction of benzene is more or less unchanged in comparison to the raw gas for both oxygen concentrations at 700°C. This implies that the rate of benzene decomposition is equal to its rate of formation. A change in oxygen concentration from 1.0 to 2.2 mol% in the AR increases the rate of formation for naphthalene at 700°C (Fig. 3b). The same pattern is seen for the group 3- and 4-rings at the higher oxygen concentration, which can be explained by increased decomposition of "unknowns" and non-GC detectable tars. This implies that the oxygen transfer via the catalyst has greater effect on the decomposition rate of branched molecules than on pure aromatics.

In general, the tar reforming activity of a catalyst decreases and can completely disappear if carbon is depositing on the active sites. As tar cracking and reforming reactions enhance the formation of carbon on the surface of the catalyst, it is therefore important to regenerate and recover the active surface of the catalyst. During CLR operation, the concentration of carbonaceous gases leaving the AR as well as the total gaseous carbon fed to the FR are monitored. The pressure in the AR is kept 200–300 Pa higher than in the FR to preclude raw gas leakage to the AR. The measured CO concentration was below the detection limit of the instrument in both the 700 and 800°C case, which confirms that the deposits of carbon on the catalyst in the FR are nearly fully oxidized to CO_2 in the AR. The measured CO_2 content was in the same order as the detection limit of the instrument, so even though there was a definite increase in CO_2 when comparing the raw gas experiment with the nitrogen fluidization in the FR, the result should be interpreted as trends and not absolute values. However, integrating values under steady-state condition gives an indication of the proportion of carbon deposit actually regenerated in the AR. The calculated mass fraction of carbon in the AR (according to Eq. 4) is shown for the two different oxygen loads at 700 and 800°C in Fig. 4. It can be observed that the increase in oxygen concentration from 1.0 to 2.2 mol% oxygen in the inlet feed to the AR increases the amount of carbon deposits at both 700 and 800°C. This can be explained by the enhanced tar reforming activity in the FR from elevated oxygen transport via the catalyst,

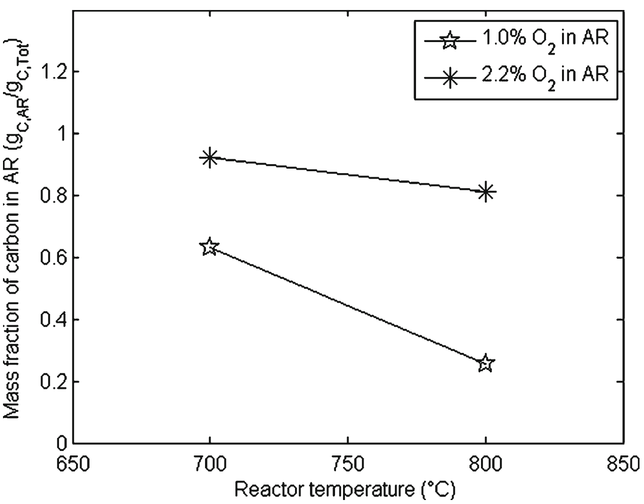

Fig. 4 Mass fraction of carbon in AR

which in turn increases the carbon deposits on the catalyst. The highest amount of carbon deposits were detected at 700°C, where the amount of carbon leaving the AR corresponds to almost 1 % of the total amount of the carbon fed to the FR. The fact that greater amounts of carbon are formed on the catalysts at 700 than at 800°C is a consequence of the endothermic gasification reactions occurring in the FR. The result is that a greater amount of carbon deposits follows the catalysts to the AR where it is converted to CO_2.

The dry composition of the raw gas is compared with the reformed gas after the CLR system, to investigate if the M4MgZ1150 shows any catalytic effect on the permanent gases. The changes in gas compositions are shown for the raw gas and for the reformed gas at 800°C (Fig. 5a). A general trend at 800°C is that the H_2 and CO_2 concentrations increase, while the CO concentration decreases. Furthermore, the concentrations of CH_4 and acetylene decrease slightly. The increase in H_2 can to a large extent be explained by an increased water–gas shift activity (WGS), resulting in that the H_2/CO ratio being shifted from approximately 0.6 in the raw gas to 1 in the reformed gas. However, when comparing the concentrations of the measured gas components in the raw gas and the reformed gas, the decrease in CO, CH_4, and light hydrocarbons is not fully compensated by the increase in CO_2. A possible explanation to this could be that there has been a change in raw gas composition between the measurements on the raw gas and those performed on the reformed gas after the CLR system. Moreover, gas cross-contamination between the AR and the FR—operated at a slightly lower pressure—may have occurred. This would also explain the increased nitrogen content in the reformed gas. Therefore, the changes in gas components between the raw gas and the reformed gas should be regarded as trends and not as absolute numbers.

In Fig. 5b, the gas compositions are shown for the raw gas and the reformed gas at 700°C. In the 1.0 mol% oxygen case, there is a slight increase in H_2 concentration, and for the 2.2 mol% there is a slight decrease in H_2. This shows that the M4MgZ1150 catalyst also induces some activity in WGS reactions at 700°C, but when the oxygen concentration is increased from 1.0 to 2.2 mol%, the produced H_2 is oxidized to water by the catalyst. Just as in the 800°C case, there is a slight decrease in CH_4 and acetylene.

5 Conclusions

A metal oxide named M4MgZ1150, consisting of 40 % Manganese oxide (Mn_3O_4) supported on 60 % $MgZrO_3$, has been investigated as tar reforming catalyst in an application for secondary catalytic tar reforming. The available amount of catalysts was only sufficient to constitute one fourth of the bed material and silica sand was, therefore, used as filler material. The mixed bed material was circulated in a reactor system of dual fluidized beds, where one of the beds was operated as a tar reformer and the second as a

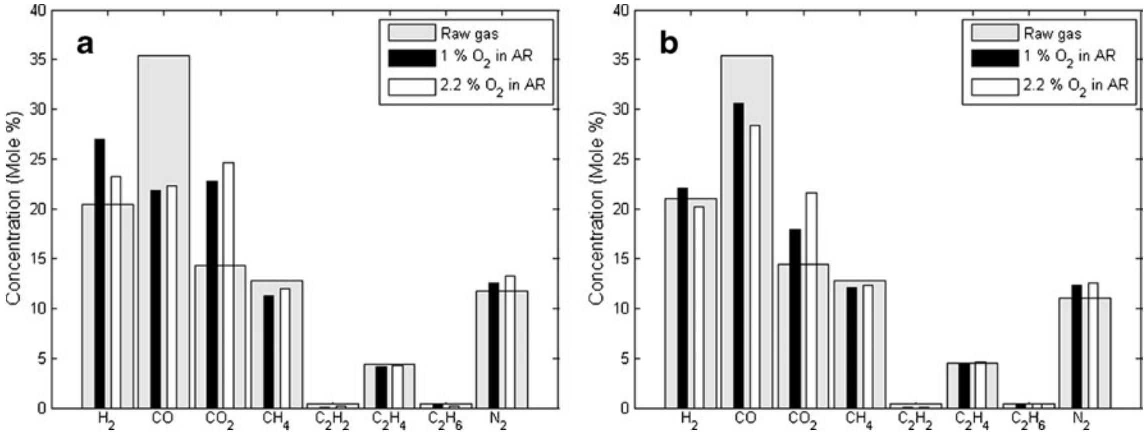

Fig. 5 **a** Gas composition for raw gas and reformed gas at 800°C. **b** Gas composition for raw gas and reformed gas at 700°C

catalyst regenerator. The tar reforming reactor was fed with raw gas from the Chalmers biomass gasifier—containing approximately 32 $g_{tar}/Nm_{raw\ gas}{}^3$—and the regenerator was fed with two different fractions of oxygen in nitrogen. From the results of the investigation, the following conclusions were drawn:

1. The catalyst showed tar reforming activity, where the small bed—consisting of 23 wt.% M4MgZ1150 in silica sand—generating a gas/catalyst residence time of approximately 0.4 s resulted in a total tar reduction of up to 44.5 % at 800°C. The tar decomposing rate was enhanced with increased oxygen load on the catalyst and tar groups containing branched aromatics and phenols were more easily decomposed by the catalyst than the pure ring structures, i.e., benzene and naphthalene.
2. The catalyst was continuously regenerated from carbon deposits via oxidation into CO_2 in the regenerator reactor. No catalyst deactivation due to carbon deposits was detected, even though a maximum of 1 % of the total amount of fed carbon to the FR was regenerated from the catalyst in the AR.
3. A general trend of increased CO_2 and decreased CO was seen with increased oxygen transport via the catalyst. The catalyst showed activity in water-gas shift reaction at both 700 and 800°C and only a slight decrease in methane and acetylene contents were observed at both temperatures.

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