INVESTIGATION OF COMBINED CATALYST AND OXYGEN CARRIER SYSTEMS FOR THE PARTIAL OXIDATION OF TARS FROM BIOMASS GASIFICATION

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ABSTRACT: In this paper, catalytic partial oxidation is applied as a thermo-chemical method to remove tar from biogas and convert it into fuel gas by using a combined catalyst and oxygen carrier system. In this method, the amount of oxygen needed for the partial oxidation of tar will be supplied by an oxygen carrier, which will also serve as a carrier of the catalyst. Based on the results of laboratory tests, the perovskite material CSFM ($Ca_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_{3-\delta}$) and ilmenite exhibited promising properties as oxygen carriers. They can supply a sufficient amount of oxygen for the oxidation of tar and show excellent redox properties for the regeneration. As a potential catalyst material, NiO showed high catalytic activity. During testing, the combined system of these two materials showed high ability for the removal of naphthalene, which was used as a model component for tar. In order to prevent the catalyst (NiO) from being poisoned by H_2S, H_2S sorbent were used. In combination with the combined catalyst and oxygen carrier system, the use of H_2S sorbent further enhanced the performance of the catalyst. In conclusion, the suitable oxygen carrier materials, catalyst and sour gas sorbent could be identified, which in combination enable the proposed tar removal process.
Keywords: Adsorbent, Biomass gasification, Catalytic conversion, Oxidation, Tar removal.

1 INTRODUCTION

Nowadays, with an increasing requirement for the reduction of fossil related CO_2 emissions, the energetic use of biogenic fuels is becoming increasingly important as a replacement for fossil fuels. The main purpose of using biomass for energy generation is to protect the environment by reducing the CO_2 emission within the limit range of Kyoto Protocol and to conserve limited fossil resources.

The gasification technology provides a method for the energetic use of biomass. The application of gasification technology to generate electricity and heat makes it possible to realize small, decentralized plants with regional energy-supply structure and a higher efficiency. One disadvantage of gasification is the formation of undesired high boiling hydrocarbons and tars [1-3]. This limits significantly the use of gas in a CHP unit (combined heat and power unit) and delays the establishment of this technology in the market. The current state of development for tar removal is still not sufficient to guarantee a safe and economical operation. For instance, by using the produced fuel gas for gas engines, very high requirements are made on the quality of the fuel gas. These requirements are at present either not reached, or only will be reached with a very high expense on apparatus and operational techniques. As a physical process, gas scrubbing can remove disturbing components from the gas [4]. However, the disadvantage of this method is the yielding of PAH-containing sludge and phenol-containing wastewater. These must be further processed by appropriate operation, which needs either a large amount of technical effort or high costs.

One more effective method with little sludge and wastewater for tar removal and conversion is the catalytic partial oxidation method, which is a catalytically active thermo-chemical process. Partial oxidation means that the reaction will take place with a sub-stoichiometrical amount of oxygen, so that the CH- and CHO-compounds (tars) will be partially oxidized to CO and H_2 instead of completely oxidizing to CO_2 and H_2O. An oxidative

catalytic tar removal can be achieved by using a catalyst and injecting air to the fuel gas [5, 6]. Nevertheless, the use of air as oxidant brings also some drawbacks, such as dilution of the fuel gas and total oxidation of fuel gas components.

In this paper, a combined system of an oxygen carrier material (OCM) and a catalyst for the partial oxidation of tars will be introduced. OCMs are able to incorporate oxygen ions into the crystal lattice. The oxygen stoichiometry of the ceramic material depends significantly on oxygen partial pressure and temperature. Therefore, such compounds can be used in a process called CAR (Ceramic Auto-thermal Recovery) based on a cyclic variation of the oxygen partial pressure [7]. Oxides based on the perovskite structure type show very high oxygen storage capacity [8]. The OCM releases the necessary oxygen and the partial oxidation of the high boiling hydrocarbons (tars) can be activated by the catalyst. Meanwhile, the OCM also serves as a carrier for the catalyst. There are so far hardly any systems known for this specific application in the literature. In accordance with the CLC process (chemical looping combustion) [9, 10], a gas processing apparatus was developed, which comprises of two reactors. The reactors operate alternately with tar-containing biogas and with air. While the operation with tar containing biogas removes tar and consumes oxygen in the combined catalyst and OCM system (catalytic partial oxidation), the operation with air regenerates the combined catalyst and OCM system so that it can be used again for the next tar removal process. During the tar removal, the oxygen will be released from the OCM. When reaching or just about to reaching the oxygen depletion in the OCM, the gas media in the two reactors will be switched. The oxygen-depleted carrier will now be regenerated by the oxygen in air; while simultaneously the regenerated OCM will operate with the tar-containing biogas. In this way, a continuous tar removing process can be achieved. A model has already been developed, which describes the condensation of tars, the oxygen release during heat up and the reaction between tars and oxygen [11]. By this

model, the demands on the capacity and temperature dependant release behaviour of the OCM can be determined.

2 EXPERIMENTAL

2.1 Materials selection

As OCM, CSFM ($Ca_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_{3-\delta}$) and ilmenite were selected. CSFM is a perovskite material known for its reversible oxygen stoichiometry and phase stability [12, 13]. It has been synthesized by solid state reaction of the appropriate amounts of the oxides. The oxygen for the partial oxidation of the tars will be released from the perovskite lattice of this material. Ilmenite (Rio Tinto Group, Fer et Titane, Sorel-Tracy/Québec, Canada) contains a large proportion of Fe_xO_y (Table I), which serves as reversible OCM in the CLC process [9, 10]. Compared to CSFM, ilmenite is a natural and more cost effective material. As the catalyst material, NiO was selected. It is a common catalyst material, widely used in the field of SOFC (solid oxide fuel cell) as the catalytic ingredient of the anode materials and catalyses the oxidation of the fuel [14, 15]. The 2-aromatic ring molecule naphthalene ($C_{10}H_8$) was used as a tar model compound for the following reasons: first of all, it is the most difficult component in tar to be decomposed by catalytic reforming. Besides, naphthalene contains the major portion of the 2-ring components in tar [16]. Moreover, naphthalene is often used as tar model compound in the literature [16-21].

In addition to the organic impurities such as tars, the inorganic tracer H_2S will also be released during biomass gasification, which would initiate and accelerate the deactivation of catalysts [22]. In order to prevent the catalyst from being deactivated by H_2S, CuO was used as a sorbent in some experiments to reduce the trace gas [23, 24]. The regeneration of Cu can be performed with air advantageously together with the OCM.

Table I: Chemical composition of the ilmenite

Composition	Weight [%]
Fe	36.7
Ti	14.9
Al	3.02
Ca	1.22
Cr	0.091
Mg	2.97
Mn	0.11
Na	0.50
Ni	0.061
Si	5.16
Zr	0.081
O	33.69

2.2 Preparation of the combined catalyst and OCM systems

For preparation of the combined catalyst and OCM system, the OCMs were first shaped into mini honeycomb structure and then coated with catalyst on the surface. By use of an extrusion tool and a cutting device, the OCMs were first extruded into mini honeycomb structure and then cut into small pieces. The extruded structure has nine flow-through channels, as can be seen in Fig. 1.


Figure 1: OCM in the shape of mini honeycomb

In the next step, the formed OCMs were sintered at 1350 °C (2 h dwell times) for CSFM and at 1300 °C (2 h dwell times) for ilmenite, respectively. Both materials were then coated with the catalyst. In the coating process, the honeycombs were immerged into a catalyst slurry suspension. At the same time, a slight low pressure was applied to deaerate the remained air from the channels of the mini honeycombs. Afterwards, the honeycombs were removed from the catalyst slurry by a sieve and placed individually on an absorbent pad. After drying in air for 48 hours, the honeycombs were sintered again at 1000 °C for 1 hour.

In this way, 3 batches of CSFM and 1 batch of ilmenite coated with different weight portions of NiO were produced as combined catalyst and OCM systems for tar removal (Table II). Fig. 2 shows the scanning electron microscope (SEM) analysis of the catalyst-coated OCM. It can be seen that the material has a large contact surface with the catalyst. The fine grained catalyst penetrated deeply into the pores of the honeycomb structured OCM and is equally distributed. The layer thickness of the catalyst is in the micrometre range.

Table II: Composition of the four combined catalyst and OCM systems

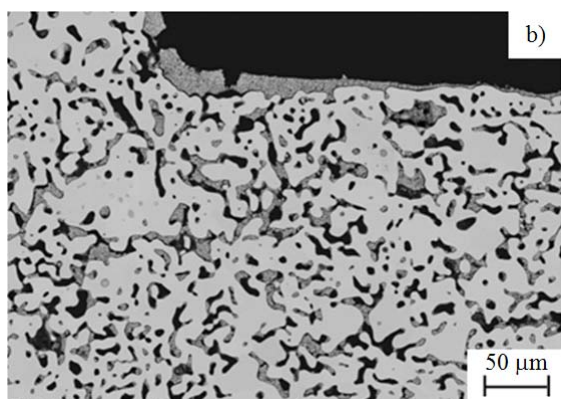| Material systems	Weight of catalyst [%]	Weight of OCM [%]
NiOC7	NiO - 7.05%	CSFM - 92.95%
NiOC4	NiO - 4.77%	CSFM - 95.23%
NiOC3	NiO - 3.72%	CSFM - 96.28%
NiOI7	NiO - 7.61%	ilmenite - 92.39%
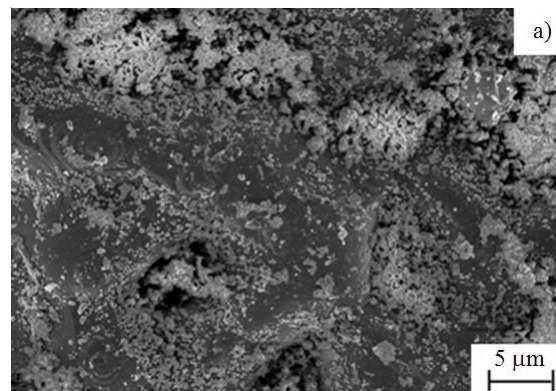
Figure 2: Scanning electron microscope pictures of the catalyst-coated OCM NiOC7: (a) surface; (b) cross section

2.3 Testing of OCMs

The redox properties of the OCMs were determined by thermogravimetric analyses. By using this method, the mass change of the OCM can be continuously measured as a function of temperature and/or time. In this study, a magnetic suspension balance from Rubotherm Präzisionsmesstechnik GmbH is applied for the mass measurement, which also allows measurements under harsh conditions [25].

The properties of the OCMs were examined in a long-term four-cycle experiment. In the first cycle the pre-oxidation phase occurs. In this phase, the OCM was fully oxidized during heating up to 900 °C with 25 ml/min air flow. After that, the material was cooled down to 100 °C in the same gas atmosphere. In the next cycle, the gas flow was changed to Ar/H$_2$ with a flow rate of 25 ml/min. The OCM was then heated up to 800 °C in this reducing atmosphere. Because of the low O$_2$ partial pressure, the oxygen stored in the OCM would then be released in this reduction phase. Afterwards, a re-oxidation phase (the 3rd cycle) with air flow and a further reduction phase (the 4th cycle) with Ar/H$_2$ gas flow were repeated to test the reversibility of this material. Through this cyclic long-term experiment with gas exchange of air and Ar/H$_2$, the oxygen storage capacity, reversibility and stability of the OCM can be identified. The materials were characterised by XRD before and after the experiments.

2.4 Testing of the catalyst activity and tar removability of the combined catalyst and OCM systems

The ability for tar removal of the combined catalyst and OCM systems as well as the catalyst activity was examined by using molecular beam mass spectrometry (MBMS). The MBMS can provide effective in situ analysis of high-temperature condensable and non-condensable gases [26, 27]. The experimental setup is shown in Fig. 3.

The experiments were conducted in a high density alumina tube in order to avoid side reactions. The mini honeycombs to be tested were placed in the alumina tube as a fill and the tube was then placed in the 5-zone furnace. The carrier gas (helium with 4 mol-% hydrogen) was first loaded with a naphthalene concentration of 2 mg/l by flowing over a fixed tar source (naphthalene). The naphthalene loaded carrier gas was then lead via a flange into the reaction tube and flows constantly (3 l/min) through the mini honeycomb fill. To make a direct analysis of the remained naphthalene concentration in the carrier gas after reacting with the mini honeycomb fill, the 5-zone furnace was connected to a MBMS. During the experiment, the furnace temperature rose from 300 °C with a heating rate of 10 K/min up to 600 °C. In this heating process, O$_2$ was released from the OCM in the mini honeycomb fill and led to the catalytic oxidation/partial oxidation of naphthalene. The intensities of the gas species after this catalytic oxidation process were then examined by MBMS at the exit of the furnace and the conversion ratio of naphthalene by each combined system can be identified. Finally, the mini honeycombs were cooled down to 300 °C and regenerated with air. Catalyst activity was tested in a similar experimental procedure as described above, only with oxygen provided by the inflow gas (He + naphthalene + O$_2$) instead of the OCMs.
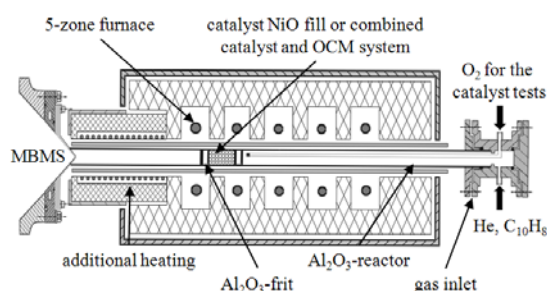

Figure 3: Experimental set up for catalyst tests and the combined catalyst and OCM system tests

The H$_2$S adsorption test was also carried out under the same experimental conditions. The CuO sorbent to be tested was placed upstream of the catalyst fill. The two fills were separated by an Al$_2$O$_3$ frit. During the test, the naphthalene loaded carrier gas was first mixed with 140 ppm$_{Vol}$ H$_2$S at the gas inlet, then the gas mixture was lead sequentially through both fills, where an adsorption of H$_2$S by the CuO sorbent and a conversion of naphthalene by the catalyst fill took place simultaneously. Before every experiment, the CuO sorbent was regenerated by air.

3 RESULTS AND DISCUSSION

3.1 Redox properties of the OCMs

The experimental results of the cyclic thermogravimetric measurements of the OCM (CSFM and ilmenite) are presented in Fig. 4. The weight change of the OCMs (absorption and release of O$_2$) was influenced by temperature and atmosphere, as can be seen in Fig. 4. Different temperature profiles during the oxygen release cycles (2nd and 4th cycles) were applied to both OCMs. The weight change of the OCMs indicates the release and absorption of O$_2$. The oxygen release capacity of CSFM exhibited no significant increase at temperatures higher than 600 °C, while that of ilmenite shows increased oxygen storage capacity with increasing temperature. After the cyclic test, the main phase of CSFM converted into a tetragonal Ruddlesden-Popper phase Sr$_3$Fe$_2$O$_7$, while the main phases of ilmenite showed no obvious changes.

The starting temperature, above which the oxygen-release first occurs, is listed together with the released or

regenerated portion of oxygen in different cycles of the two OCMs in Table III. For CSFM, oxygen was released in the second and the fourth cycle above an almost identical temperature of about 301 °C. The starting temperature of oxygen-release for ilmenite is about 327 °C. By comparing the amount of oxygen being released and regenerated in different cycles, it can be seen that both materials showed excellent reversibility. In comparison with CSFM, ilmenite has a higher oxygen storage capacity under the same experimental conditions.
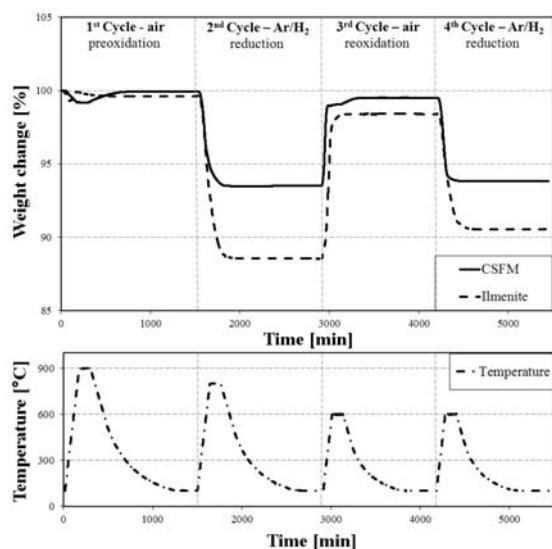

Figure 4: Weight change of the OCMs and temperature profile during the cyclic thermogravimetric measurements

Table III: Released or regenerated oxygen portion in the last three cycles and starting temperature of oxygen-release in the oxygen release cycles

Item	CSFM	Ilmenite
released O_2 in 2nd cycle [l/kg]	45.05	77.7
regenerated O_2 in 3rd cycle [l/kg]	42.01	69.05
released O_2 in 4th cycle [l/kg]	39.72	55.02
T of O_2-release in 2nd cycle [°C]	300.6	326.5
T of O_2-release in 4th cycle [°C]	301	327

3.2 Catalyst activity and H_2S-sorption experiments

The catalytic activity of the selected catalyst NiO was investigated by MBMS. Fig. 5 (curve a) shows the naphthalene conversion ratio as a function of temperature by using 20 g NiO. The curve indicates that the naphthalene conversion ratio increases with increasing temperature. At 400 °C, a naphthalene conversion ratio of over 80% was achieved; at 600 °C, about 95% naphthalene was removed; at a temperature higher than 700 °C naphthalene was completely removed and converted to synthesis gas. With the help of XRD analysis, it was verified that the catalyst NiO remains as monophase after the measurements. The excellent naphthalene conversion ratio of NiO demonstrates its suitability as catalyst for the combined catalyst and oxygen carrier system.

To determine the influence of H_2S on the catalytic activity of NiO and the H_2S removal efficiency of CuO sorbent, 20 g catalyst fill with an additional CuO sorbent

fill was tested under the mixed gas flow (He + 140 ppm$_{Vol}$ H_2S + naphthalene + O_2). In Fig. 5, the naphthalene conversion ratios under different experimental conditions are shown as a function of temperature. The curve b shows the influence of H_2S on the conversion ratio of naphthalene catalysed by NiO. Compared to the conversion ratio in non-contaminated gas (curve a), the conversion ratio under H_2S containing gas flow was lowered by 6.9% points at 600 °C. In particular, the conversion ratio at 400 °C was lowered by 27.8% points under H_2S containing gas flow. As expected, the trace gas H_2S caused a deactivation of NiO and thus led to a very low naphthalene conversion ratio.
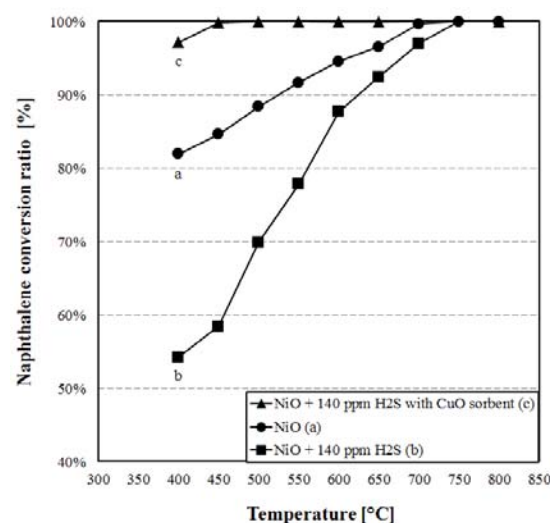

Figure 5: Conversion ratios of naphthalene with temperature catalysed by NiO under different testing conditions

The curve c in Fig. 5 represents the naphthalene conversion ratio for NiO together with a CuO sorbent under the mixed gas flow (He + 140 ppm$_{Vol}$ H_2S + naphthalene + O_2). Obviously, the CuO sorbent can not only absorb the trace gas H_2S, but also partly catalyse the oxidation of naphthalene [20, 21, 28].

3.3 Tar removability of the combined catalyst and OCM systems

After being separately investigated in the preliminary experiments, the selected catalyst and OCMs were then investigated in the next step as a combined system. 30 g of each of the four combined catalyst and OCM systems (Table II) were manufactured and tested for their partial oxidation properties of naphthalene using MBMS. During the experiment, the carrier gas (He + 4% H_2) together with naphthalene flew through the chosen system and were partially oxidized. The intensity changes of the product gas species ($^{18}H_2O^+$, $^{29}CO^+$, $^{34}O_2^+$, $^{44}CO_2^+$ and $^{128}C_{10}H_8^+$) with time/temperature are shown in Fig. 6. Hydrogen was not included here, because it has a very small molecular mass and cannot be easily detected by MBMS.

For all four combined catalyst and OCM systems, the intensity of naphthalene reached its maximum value after two minutes from the beginning of the experiment. Then it decreased with increasing temperature, because oxygen stored in the OCMs (CSFM, ilmenite) was released due to heating and naphthalene was thereby catalytically
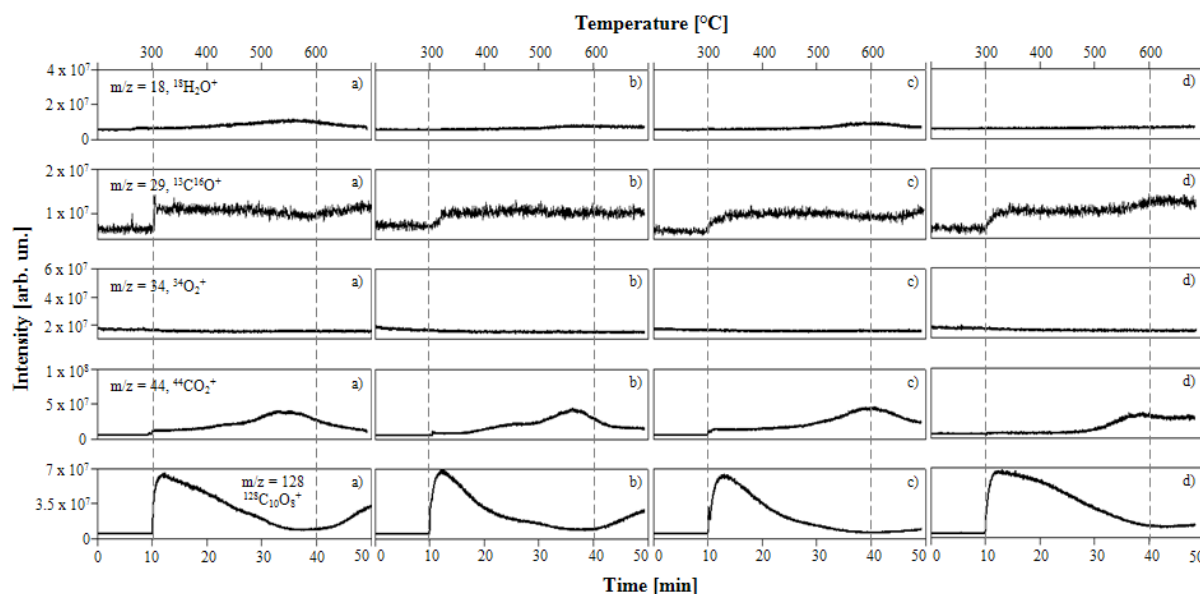
Figure 6: Intensity-Time-Profiles obtained during partial oxidation/oxidation of naphthalene at 300 - 600 °C in mixed gas (He + 4% H_2 + naphthalene) with four different combined catalyst and OCM systems: (a) NiOC7; (b) NiOC4; (c) NiOC3; (d) NiOI7

oxidized. The starting temperature for oxygen-release of CSFM and ilmenite are 301 °C and 327 °C, respectively, as being ascertained in the thermogravimetric experiments in Section 3.1.

The intensity of oxygen remained constant from the beginning of the experiment, since all oxygen released from the OCM was directly consumed by naphthalene removal. In addition to the products of complete oxidation, such as CO_2 and H_2O, the content of CO also significantly increased during the experiments. This confirms that partial oxidation of naphthalene took place.

At the end of the experiment, the furnace temperature reached 600 ° C and was held at 600 °C for 10 minutes. During the heating period, the intensity of naphthalene started to increase again after reaching the lowest point in the material systems NiOC7 and NiOC4 while the intensity of CO_2 decreased in accordance. NiOC3 shows the same behaviour later, during the dwell time. These phenomena indicate a depletion of O_2 in the OCMs of these three material systems. The reason for the postponed oxygen depletion of NiOC3 might be caused by its larger amount of OCM (larger amount of oxygen) in relation to the amount of catalyst than the other two material systems under the same weight condition. On the contrary, the intensity of naphthalene and CO_2 in the material system NiOI7 did not change during the dwell time because of a higher oxygen storage capacity of the OCM (ilmenite). After the dwell time, the material systems were cooled down to 300 °C regenerated by air and tested in further cycles.

The naphthalene conversion ratios of all four material systems at 600 °C are shown in Fig. 7. The above described cyclic experiments were performed 10 times for each material system to test their reversibility. The results showed that the average naphthalene conversion ratio of the 3 material systems (CSFM + NiO) is over 97%, while that of the material system (ilmenite + NiO) is over 95%. Especially NiOC3 has a naphthalene conversion ratio of more than 99%. The measurement deviation of all experiments is considered to be below
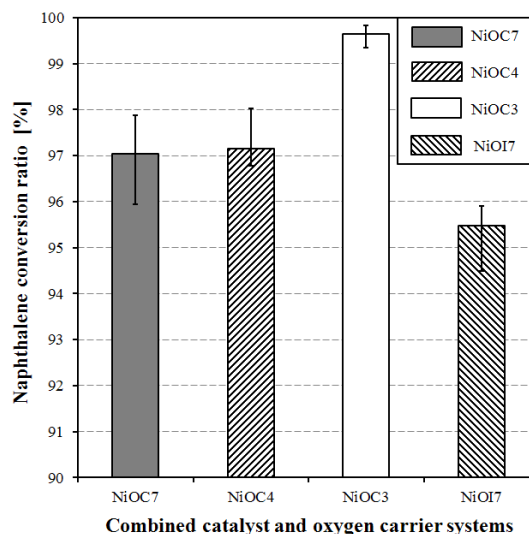
2%.

Figure 7: Conversion ratio of naphthalene at 600 °C with four different combined catalyst and OCM systems

After the measurements, all four material systems were characterized by XRD. As a result, it was found that the main phases of all four material systems did not change after the experiments. Nevertheless, Ni was found in all material systems after the experiments beside NiO.

4 CONCLUSIONS

In order to remove the tar formed during the biomass gasification process, a combined catalyst and OCM system was developed and several combinations of materials were investigated. The results of the four-cycle thermogravimetric measurements showed that both OCMs (CSFM and ilmenite) have very good oxygen

storage capacities and reversible redox properties. It was also proved that the catalyst NiO has an excellent conversion ability of the tar model compound naphthalene.

The oxygen storage capacity as well as starting temperature for oxygen-release of the two OCMs (CSFM and ilmenite) and the catalytic activity of the catalyst (NiO) fit very well to the requirements of the partial oxidation of tar. The use of the perovskite CSFM seems to be more meaningful for lower gas temperatures because of its lower temperature for oxygen generation, but ilmenite tolerates longer reduction time according to its higher oxygen storage capacity.

Results of the cyclic measurements showed that all four systems have very high naphthalene conversion ratios at 600 °C as well as very good reversibility and stability. Partial oxidation/oxidation of the naphthalene happened, which is proved by the observed increased intensities of CO and CO_2 measured by MBMS. CuO sorbent for trace gas (H_2S) elimination showed very good adsorption ability of H_2S and in addition a further catalytic effect for the naphthalene conversion process.

The results of this paper show that the developed combined catalyst and OCM systems are very efficient and reliable for tar removal in the biomass gasification process.

ACKNOWLEDGEMENT

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