Chemical **L**ooping G**a**sification fo**r** Sustain**a**ble Production of Biofuels

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Deliverable D3.2:

Investigation of fate of tar surrogates with oxygen carrier materials

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1. **Introduction**

Gasification produces a range of gaseous species, see Figure 1. Also, during biomass gasification, it is well known that there could be a significant formation of condensable hydrocarbons, or tars. These species, which could contain a significant part of the fuel heating value, are problematic as they could condense on components downstream of the gasification unit.

Figure 1. Products of biomass gasification.

It is expected that a major advantage with the utilization of oxygen carrier (OC) materials in a gasification process is that the tar species could be converted to syngas, either by:

1) The OCs provide oxygen for partial oxidation of tars to syngas
2) OCs' particles provide catalytic sites for the conversion of tars.

Thus, chemical looping gasification (CLG) can enhance syngas production and suppress tar formation compared to other technologies for biomass gasification (Table 1). This will lead to increased overall fuel efficiency by enhancing carbon conversion in the fuel reactor and increasing the carbon content in the syngas. It also reduces costs for gas cleaning after gasification.

Table 1. Comparison of different gasification technologies

Gasifier	***Oxygen consumption***	***Carbon conversion***	***Tar formation***
Moving/fixed bed	Moderate	Moderate	High
Entrained flow	Very high	High	Very low
High temperature Winkler	High	Low	Low
Circulating fluidized bed	Moderate	Low	High
Dual fluidized bed	None	High	High
Chemical looping	None	High	Low

The objective of this task is to investigate the fate of tar surrogates on OCs selected from Task 3.1. For this study, benzene has been selected as a tar precursor produced during CLG. Previous research indicates that benzene is suitable to evaluate the propensity to convert tar components (Hildor et al., 2019; Mattison et al., 2019).

CTH carried out the tests in a batch fluidized bed reactor using the benzene together with oxidizing gas of steam as well as simulated gasification gases. The gas conversion was determined as a function of solid conversion, and thus the selectivity towards syngas is determined.

2. Methodology

2.1. Materials

OCs were selected from Task 3.1. All samples were calcined at 900 °C in air and were sieved to a size range of 125–180 μm before use in the batch fluidized bed reactor, see Section 2.3.

2.2. Materials characterization

The samples were analyzed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) in a FEI Quanta 200 Field Emission Gun ESEM equipped with the Oxford Inca EDX system.

2.3. Experimental setup and procedure

The experiments were carried out in a fluidized-bed quartz reactor. An overview of the system can be found in previous works as described in Figure 2 (Keller et al., 2016). The reactor's inner diameter is 22 mm and the OC particles were placed on a porous quartz plate in the middle of the reactor. This plate also acts as the distributor plate, as the reducing and oxidizing gases are introduced from the bottom of the reactor. The entire reactor is enclosed in a high temperature furnace, and the temperature was measured inside the bed with a K-type thermocouple enclosed in a quartz cover. The pressure drop over the reactor was measured by Honeywell pressure transducers.

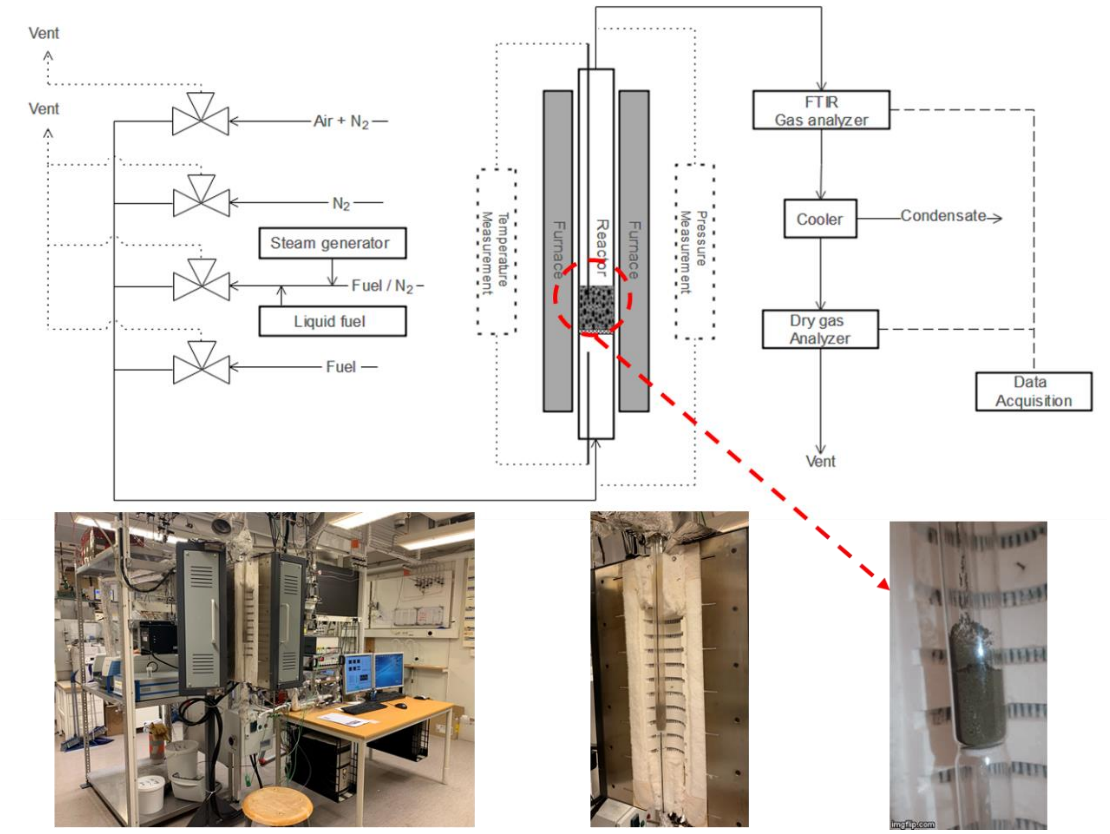

Figure 2. Schematic overview of the laboratory batch reactor system.

Heating up of the equipment was performed in oxidizing conditions with 5% O_2 until stable temperatures and gas concentrations could be measured at 850 °C. After full oxidation, the bed material was exposed to oxidizing and reducing conditions in a cyclic manner at different temperatures, with intermediate inert flushes performed under 180 s with 1000 ml_N/min N_2. Each cycle was made up of fully oxidized particles that were flushed with inert N_2 followed by a reduction, inert again to flush the reactor and ended with the oxidation of the bed material until fully oxidized. The alternating conditions of gases were used to simulate the conditions the bed material would be exposed to in a CLG process, where both oxidizing and reducing zones are present. The oxidizing atmosphere was composed of a mixture of synthetic air and N_2 so that the total flow through the reactor was 1000 ml_N/min with a concentration of 5% O_2. The reducing gas was composed of 500 ml_N/min steam mixed with either syngas (50/50 CO/H_2 mixture), CH_4 or C_6H_6 according to concentrations given in Table 2 to total gas flow of 1000 ml_N/min. The C_6H_6 -N_2 mixture was obtained via bubbling of the gas throw a beaker containing C_6H_6 at room temperature and then cooled down to 6 °C to reach a C_6H_6 stream with a concentration of 1.4 mol%. C_6H_6 was used as a reference tar, hydrocarbons formed during gasification and combustion.

Table 2. Operating conditions for the experiments.

Phase	**Gas mixture**	**Gas Flow [ml_N/min]**	**Temperature [^{o}C]**	**Time [s]**
Oxidizing	5% O_2 +95% N_2	1000	800-950	300-1200
Inert	100% N_2	1000	800-950	180
Reducing-Activation	100% Syngas (1:1)	1000	800-950	20
Reducing-Syngas	50% steam, 45% Syngas (1:1), 5% N_2	1000	800-950	20
Reducing- CH_4	50% steam, 35% CH_4, 15% N_2	1000	800-950	20
Reducing- C_6H_6	50% steam, 30% N_2 containing 1.4% C_6H_6, 20% N_2	1000	800-950	20-60

The OC content of the bed material was 5 g for syngas and C_6H_6 cycles. To obtain 15 g of bed material in the reactor silica sand with a size between 180 µm and 250 µm was added to the bed. The reason why only 5 g of OC was used for syngas and C_6H_6 experiments was due to that almost full conversion of the gases, at any temperature, was obtained with 15 g of the OCs, meaning that it would be difficult to assess the reactivity of the OC. Cooldown was performed after full oxidation in oxidizing conditions.

Before investigating the reactivity of the different bed samples, activation cycles were performed. These cycles have been used in earlier studies regarding LD slag (Xu et al., 2017) and have also been shown to have an effect on the performance of other iron-based OCs, such as ilmenite (Leion et al., 2008). Activation cycles, with reducing gas composition as described in Table 2, were performed until the conversion of CO was stable for the material, 3–8 cycles depending on the material. This was performed on all materials used in this study and after these activation cycles the material was considered to be activated. After activation, the experiments with steam and a reducing component were performed three times at every temperature setting to confirm the repeatability of the results.

2.4. Gas analysis

The gas analysis was performed on the hot gas from the laboratory reactor with a Thermo-Scientific IS50 Fourier Transformed Infrared (FTIR) analyzer. The gas cell in the FTIR and the connecting tubing was heated to 120 °C to prevent condensation. The FTIR was calibrated for quantification of CO, CO_2, CH_4, H_2O, C_6H_6. Downstream from the FTIR, the off-gas from the furnace was cooled and condensate removed. The dry gas was then analyzed in a Rosemount NGA 2000 equipped with thermal conductivity and paramagnetic gas sensors for H_2 respective O_2. The NGA 2000 was also equipped with IR/UV sensors for CO, CO_2 and CH_4 as a reference for the FTIR.

2.5. Evaluation

The total conversion of C_6H_6, CO and H_2 were based on the molar balance over the inflow and the outflow of respective gas. The concentration was determined from either the FTIR or NGA 2000 and the conversion of each fuel component was calculated according to Eq. 1

$$Conversion\ of\ fuel = \int_{t_{red}=0}^{t_{red}=end} \frac{x_{Fuel,in}\times\dot{n}_{in} - x_{Fuel,out}\times\dot{n}_{out}}{x_{Fuel,in}\times\dot{n}_{in}}\,dt \times 100\% \qquad \text{Eq. 1}$$

Where, $\dot{n}_{in}$ and $\dot{n}_{out}$, are the inlet and outlet molar flow rates to the reactor, respectively. The molar outlet flow was calculated for the dry and wet gas flow from the gas composition in the measured outlet gas composition compared to the set composition in the inlet.

The oxygen capacity, R_{0C}, was also calculated for the investigated samples:

$$R_{0C} = \frac{m_{ox}-m_{red}}{m_{ox}} = \frac{n_O\times M_O}{m_{ox}} \qquad \text{Eq. 2}$$

Where, M_O is the molar weight of oxygen. The uptake for the last of the activation cycle for each material was used as a guideline regarding oxygen capacity at 850 °C after reduction with syngas.

3. Results

From the elemental analysis of the OCs, shown in Table 3, it can be observed that the main differences between the OCs are the iron and manganese content. The reactivity, or oxygen transfer rate, was highest for the manganese ores, followed by ilmenite. The two manganese ores, Sibelco and Egyptian ore, displayed similar reactivity, as seen with respect to the oxygen transfer to the gas phase, or degree of gas phase oxidation as a function of the degree of solid reduction. LD slag has the lowest R_{OC} of 0.46 which is expected, considering the low content of Fe and Mn in the sample, see Table 3.

Table 3. Elemental analysis of the OCs

Elemental Composition	**Sibelco**	**Egyptian Ore**	**Ilmenite**	**LD slag**
(wt%)	Mn ore	Mn-Fe ore	Fe-Ti ore	Fe waste
Mn	49.9	32.3	0.2	2.2
Fe	5.2	21.6	33.1	13.7
Si	3.4	4.7	0.9	4.8
Al	4.2	1.2	0.3	0.5
Ca	1.9	1.7	0.2	27.3
R_{OC} (%)	4.7	4.5	4.2	0.46

Each OCs in Table 3 has been investigated under the experimental condition given in Table 2.

Dry-gas analysis of the gas composition for an entire reduction-oxidation cycle with ilmenite at 850 °C has been shown in Figure 3. The reducing phase is syngas according to Table 2. Each cycle starts with an inert phase (Inert) to flush the reactor with N_2, followed by a reducing phase (R). After reduction, the reactor is flushed with N_2 and then an oxidizing phase (Ox) is introduced to oxidize the particles.

The conversion of 20 seconds injection of CO, H_2, CH_4, and C_6H_6 was investigated in the temperature interval of 800 to 950 °C, and the results are presented in Figure 4.

During the reducing phase of each cycle in the batch reactor, the oxidized bed material reacted with a reducing gas resulting in a high initial concentration of H_2O and CO_2, associated with a high degree of oxidation gases. The degree of oxidation of gases decreases as a function of time, until there is no oxygen transfer from OCs to the gas phase, i.e., only catalytic reactions are occurring. This period, where there is little or no oxygen transfer, is related to partial oxidation processes, such as chemical-looping reforming (CLR) or chemical-looping gasification (CLG). At the end of the reduction period, there was no oxygen transfer to the gas phase at all, and all reactions are catalytically or thermally activated. After the reducing phase of each cycle, the reactor was flushed with N_2 and then the bed material was oxidized by synthetic air.

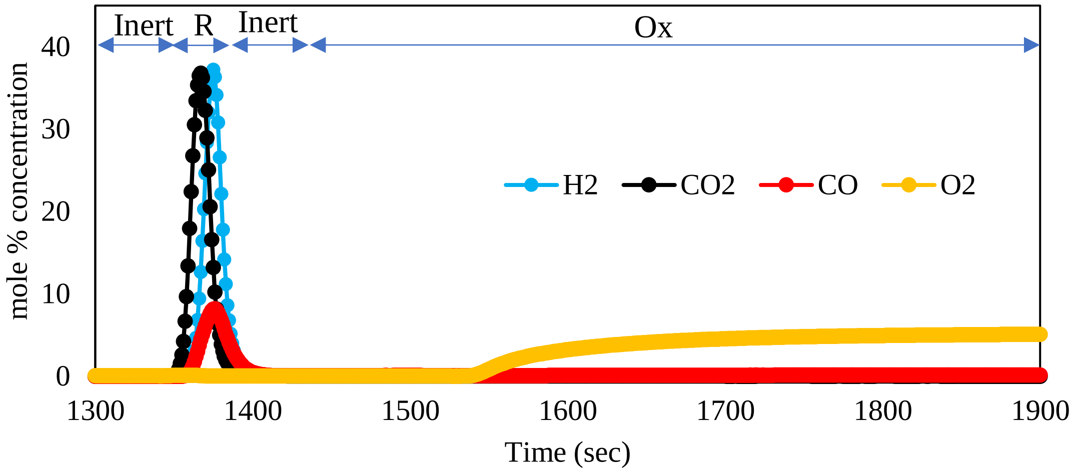

Figure 3. Dry-gas analysis of the gas composition for an entire reduction-oxidation cycle with ilmenite.

During the inert phase between the oxidizing step and reducing step there is an oxygen release from manganese ores. This is likely due to the capability of the material to release oxygen to the gas phase, or the so-called oxygen uncoupling (CLOU). This has been seen previously for manganese ores (Sundqvist et al., 2018).

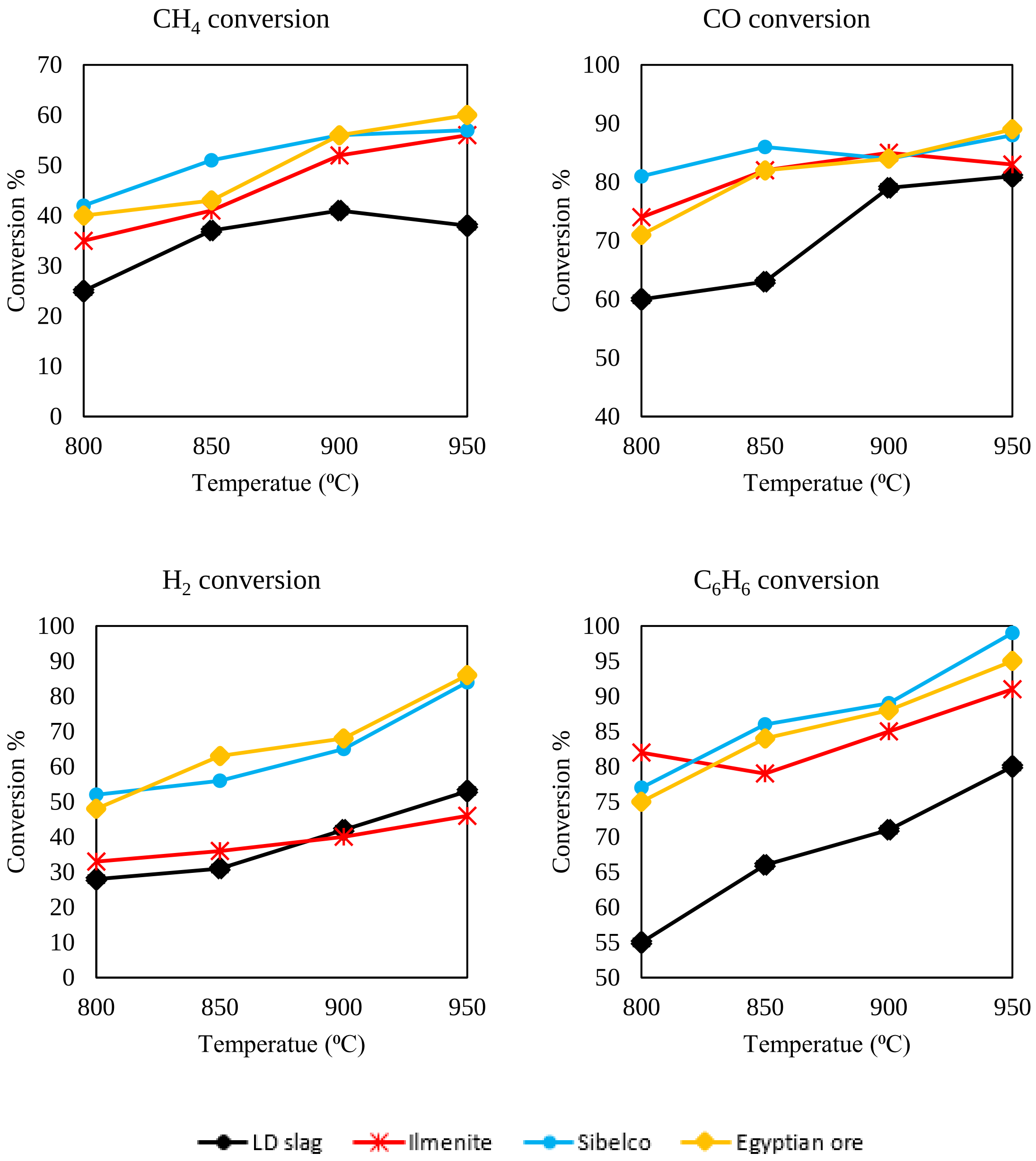

Figure 4. conversion of reducing gases at different temperatures.

Based on the results, the conversion of C_6H_6 is improved significantly by temperature and full conversion of the benzene is possible at the highest temperature for manganese ores.

Among the materials, the two manganese ores exhibit higher reactivity than ilmenite and LD slag, with higher conversion of CH_4, CO, H_2 and C_6H_6. This can be explained by a higher degree of oxygen transfer for the manganese ores. However, Sibelco shows higher reactivity than Egyptian ore, converting hydrocarbons better.

Regarding the experiments with C_6H_6, the bed materials were exposed to a longer injection of the reducing gas from 20 seconds to 60 seconds, to better understand the OCs' behaviour both in the CLC and CLG period. The latter is characterized by a higher degree of oxidation to CO_2 and H_2O in CLC compared with CLG/CLR where only small amounts of oxygen are to be transferred to the gas phase. In the batch reactor, the material was reduced to a point where there are only homogeneous or catalytic reactions occurring. In a real unit, it is expected that there will be some oxygen transfer from the particles as the particles from the air reactor will be oxidized, and it is likely advantage with respect to obtaining proper syngas.

The results in Figure 5 indicate that when increasing the benzene injection time from 20 seconds to 60 seconds, the total conversion of benzene will significantly decrease. This indicates the catalytic effects of OCs to crack benzene is less dominant compare to initial conversion due to partial oxidation of benzene during by the oxygen available in the oxygen carrier. However, manganese ores still showed a better performance compare to the ilmenite and LD slag due to their high oxygen transport capacity and their CLOU properties.

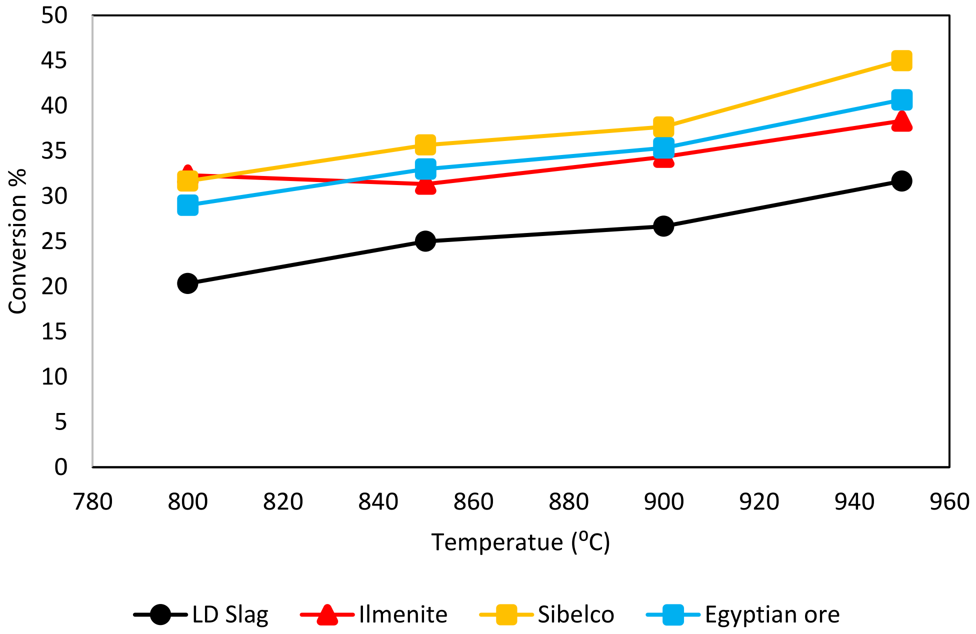

Figure 5. Conversion of benzene as a function temperature for the selected OCs during 60 sec benzene injection.

4. Conclusions

The use of oxygen carriers in gasification of biomass can reduce tar formation with partial oxidation of tar compounds to syngas. The tar conversion will increase with increasing temperature. However, the investigated OCs showed conversion of tar surrogates due to partial oxidation is more dominant compared to catalytic cracking of tar. Manganese ores exhibit better performance regarding tar conversion due to their higher oxygen transfer capacity.

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