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## Advanced Gas Cleaning using Chemical-Looping Reforming (CLR)

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### 1. Introduction

When using a fluidized bed gasification technology to gasify biomass for the downstream synthesis to biofuels or chemicals, the biggest challenge is associated with the reforming of hydrocarbons into desirable gas components. These unwanted hydrocarbons are formed during the primary conversion step of the biomass. They range from ethylene to larger aromatic components or even methane if it is not the desired product, and introduce numerous problems to the operation, but also require additional process steps that significantly influence the competitiveness of the overall process. An efficient way to tackle this problem is to provide catalytic surfaces for hydrocarbon reforming directly inside the gasifier by using a catalytic bed material and/or in one or several secondary reactors. In this work, a concept based on this principle and named Chemical-Looping Reforming (CLR) is presented and it is discussed how this concept has the potential to be implemented for both primary and secondary reforming of hydrocarbons.

### 2. Technology description

The basic idea is to separate the bed material used in the fluidized bed to spread and distribute the heat and to mix the fuel from the bed material used to reform hydrocarbons. In a gasifier in particular, this separation could have several advantages, since it can open up

the possibility to independently optimize the conversion of the solid biomass to a raw gas and of the raw gas into a desired gas composition.

The CLR technology uses a metal oxide as catalytic material. The objective is to find a suitable ore that fulfils the following criteria: (i) it is inexpensive, (ii) it can be used in a fluidized bed, (iii) it has a low tendency of agglomeration, (iv) it provides a sufficient catalytic activity, and (v) it does not create a hazardous waste. The process itself mimics the Fluid Catalytic Cracking (FCC) process as it allows the catalytic material to be continuously deactivated by mainly carbon deposition at the same time as it acts as a catalyst in one of the reactors and is continuously reactivated in the other. At Chalmers, this process has been experimentally investigated in two reactor systems and the results from these have previously been published, e.g. in [1, 3]. In these systems, a two inter-connected fluidized beds configuration has been used, where in the first reactor system the catalytic conversion has taken place in a bubbling bed and the reactivation in a circulating bed, while in the second reactor system the beds were switched. At a first sight, the impression of this technology is that it is dedicated to a separate process step after the reactor and - if successful - this would most likely be the case in long-term and for large scale deployment. Meanwhile, the concept can be implemented to the already existing

processes and this for both direct and indirect gasifiers. The most straightforward option is to introduce the concept into an indirect gasifier. In an indirect gasifier, the process is usually schematically presented as in Fig 1.

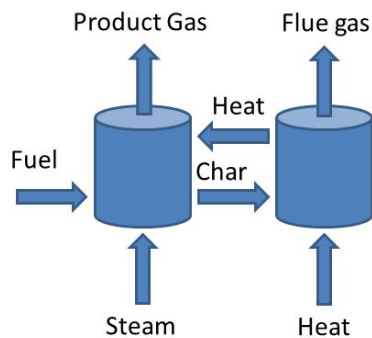


Figure 1: Schematic picture of the indirect gasification process

The fuel is introduced into the gasification reactor, where the heat for the gasification is provided by the bed material, which can also be used to catalyse the conversion of the gas. The gas is released from the fluidized bed and leaves the reactor for downstream usage. The colder bed material together with the char (that is not converted) leaves the gasification reactor for the combustion reactor, where the char is burned to heat up the bed material before it is recirculated to the gasifier. If one considers the bed material as a catalyst, this dual fluidized beds system is similar to that of the CLR process mentioned above as the bed material will act as a catalyst in the gasifier at the same time as it will be deactivated. Thereafter, the bed material will be transported to the combustion reactor and reactivated. However, applying this strategy, the selection of the bed material will be a compromise as the main function of the bed material in this loop is to transport the heat and fuel between the reactors. This provides significant limitations to the window of optimization. There are in principle two

restrictions that are difficult to overcome: to ensure a good gas-particle contact meanwhile avoiding transport of oxygen. The first restriction means that one in practice needs to use particle sizes that are larger than those that would be beneficial for a catalytic process; the second restriction implies that the available ores that could have a high catalytic activity are very limited. Indeed, if the bed material has high oxygen carrying capacity, which is the case for most metallic material of interest, the transport of oxygen between the two reactors will be in such an extent that merely all fuel combustion needed to provide the heat for the process is achieved by burning part of the product gas in the gasifier; even though the heat generation still would occur in the combustion reactor by the oxidizing of the bed material. Applying this to the schematic process shown in Fig 1, this would mean that the char flow from the gasifier to the combustor would be exchanged by a reduced bed material and the combustible products in the flue gases leaving the combustion reactor would instead be diluting the product gas leaving the gasifier.

Thus, in order to introduce the CLR concept into an indirect gasifier without adding a second reactor, one needs to design the process in such way that one creates two circulating flows in the system: the first flow mainly is optimized towards the heat and fuel transport and the second is optimized towards the catalytic process. The simplest way to achieve this is to take advantage of the natural segregation in particle sizes that take place in fluidized beds. In practice, this mean that one can accomplish a circulation of fine particles, which should be optimized towards providing catalytic surfaces and gas particle contact; and a

circulation of coarse particles that carry the heat and provide the mixing and transport of the fuel particles. In e.g. the Güssing and the GoBiGas plants, this is to some extent already done as there exists an external loop of the fine material. More precisely, the fine material leaving the gasifier is collected in a filter after cooling and then transported and injected into the combustion reactor. The fines that leave the combustion side are collected in another filter and part of this stream is directed to the ash bin while the rest is transported and re-injected into the gasifier. However, this system is mainly introduced to burn unconverted carbon from the gasifier into the combustor and to provide condensation kernels for tars in the cooling section of the product gas downstream the gasifier.

The ambition and aim of the work at Chalmers is to optimize the flow of fines, to select proper materials and develop an injection (into the gasifier) strategy to yield significant reduction of the tars leaving the gasifier, thereby minimizing the consumption of oil in the downstream oil-scrubber and the consumption of activated carbon in the cleaning beds prior to gas compression.

#### **4. Results**

The proof of concept for the CLR process in the context of upgrading biomass-derived producer gas has been demonstrated in previous studies conducted at Chalmers and using Geldart B particles [2, 3]. The reactor system operated was a dual fluidized bed reactor featuring a circulating fluidized bed regenerator chamber (AR) and a bubbling bed forming the reformer chamber (FR). In the regenerator, carbon deposited on the catalyst is removed with nitrogen diluted air and in the reformer fluidized with raw gas, tar reduction and gas composition

adjustment occurs. The catalyst materials tested in these studies were: two natural ores, an iron-titanium based ore called ilmenite and a manganese-based ore; and a manufactured nickel catalyst. As a well-documented catalyst, Ni was chosen to serve as a reference for comparison with other results reported in the literature. All three materials showed an ability to reform the tars and adjust the gas composition of the permanent gases [4]. Moreover, owing to the particle circulation and the catalyst regeneration in the dedicated reactor section, no catalyst deactivation was observed and these materials were thus promising for use in fluidized bed applications and raw gas upgrading.

Pursuing from these encouraging results and with inspiration from Fluid Catalytic Cracking in the petrochemical industry, the idea arose to use fine materials (Geldart A type) for their comparatively higher active surface for catalysis compared to the coarser materials above; this in combination with a longer available gas-solid contact time provided by a new reactor setup featuring a riser-shaped reformer. Moreover, the natural segregation by particle size also opened up for the possibility to decouple the heat carrier circulation between boiler and gasifier from the catalyst circulation that uses lighter particles, as introduced earlier.

So far, the later research phase has mainly focused on identifying proper bed materials for the fine particle circulation. For the CLR process, the most interesting ones identified are ilmenite and various manganese ores, which so far fulfil all process requirements. As in the coarser particles used in the previous reactor configuration, they showed clear decomposition activity towards all tar components and are quite inactive

towards methane, which is positive, as methane is the intended end-product.

These particles were tested in two different reactor configurations: a dual fluidized bed and a batch reactor. The dual fluidized bed reactor was used for the experiment with manganese. It comprises a bubbling bed regenerator chamber (AR) and a riser forming the reformer chamber (FR) fluidized with raw gas. This gives a gas-solids contact time four times that for the previous reactor configuration where the reformer was a bubbling bed. Fig. 2 shows the scaled reactor setup with the two loop seals SLS and ILS that create two different gas atmospheres in the reactor sections.

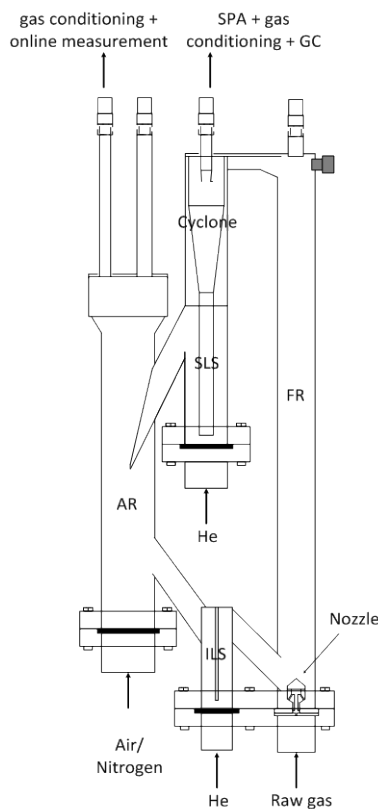


Figure 2: CLR reactor setup for the manganese experiment

For the ilmenite experiment, a fluidized bed batch reactor was used where the catalyst is subject to alternating redox conditions. The reasons behind the choice of this reactor configuration are detailed

in the ilmenite section below. Fig. 3 shows the reactor setup with the raw gas line from the gasifier.

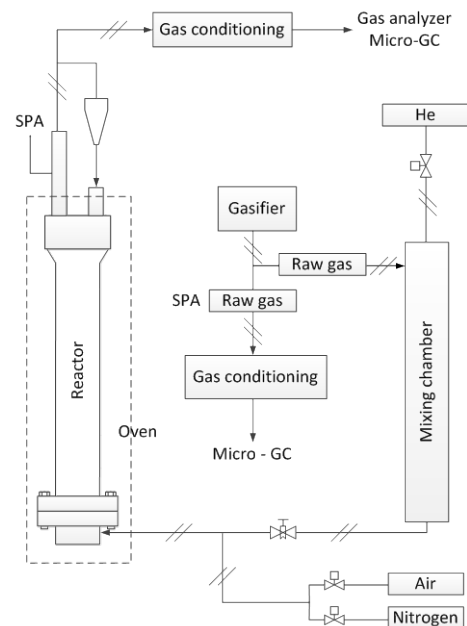


Figure 3: Batch reactor setup for the ilmenite experiment

The slip stream of raw gas used to assess the catalysts efficiencies originated from the Chalmers 2-4 MW indirect gasifier. Details on the indirect gasifier system are provided elsewhere, e.g. in [5]. Note that this gas contains roughly 50-60% of steam. The grain size investigated in this second phase of the CLR project was in the range 45-90  $\mu\text{m}$  while the temperature interval was between 800 and 880°C in the reformer reactor. Below are some key results from the corresponding investigations.

### Manganese experiment

The manganese catalyst in this study was a natural ore from Brazil containing in particular 45% Mn, 6% Fe, and 11% SiO<sub>2</sub>. Experiments totaled 4.5 h of stable conditions. Elements of the results presented below are taken from [1].

Tars samples were taken in the raw and reformed gas using the SPA method. The results are presented in Figure 4 comparing the concentrations in  $\text{g}/\text{Nm}^3$  between inlet of the reactor and outlet at three temperatures: 800, 850 and 880°C. For clarity reasons, the tars are gathered into six representative groups ranging from phenolic compounds to 3-rings and larger molecules [6]. From Fig. 4, one can see a drastic decrease in the tar levels after the raw gas passed through the reformer. Higher temperature enhanced tar degradation with a maximal measured conversion of 72 % at 880°C. Another aspect is that benzene and naphthalene were produced in the reformed gas, most likely through decomposition of larger tar structures. For naphthalene though, increasing temperature slightly reduced the output in the cleaned gas.

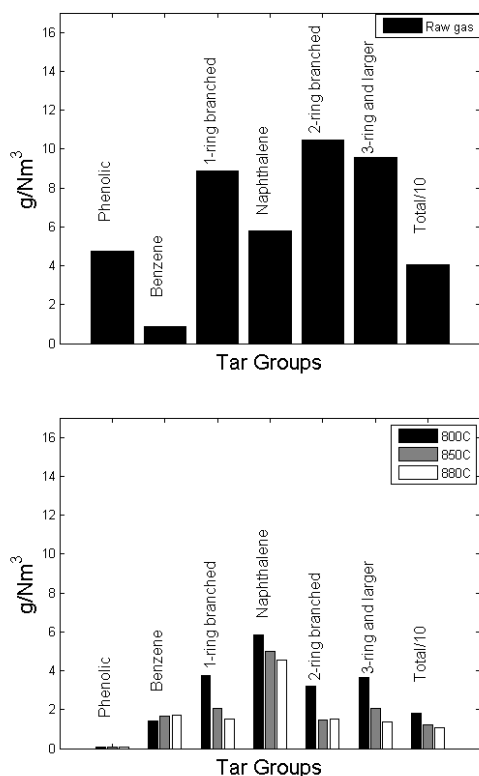


Figure 4. Concentrations of tar groups in  $\text{g}/\text{Nm}^3$  in: (above) raw gas; (below) reformed gas downstream the CLR unit [1]

Tar decomposition together with other catalytic reactions at the prevailing conditions was expected to change the permanent gas composition in the resulting reformed gas. Figure 5 compares the distribution of permanent gas compounds in the raw and reformed gases for the three cases. The decrease in inert  $\text{N}_2$  concentration in the reformed gas indicates it was diluted by the production of permanent gases, see Fig. 5. These can for instance originate from tar reforming into lighter measurable compounds.  $\text{C}_2\text{H}_x$  were also mitigated with a similar trend as for the tars when temperature was augmented.  $\text{H}_2$  and  $\text{CO}_2$  increased in the reformed gas while  $\text{CO}$  was divided by 2. This suggests that the Water-Gas Shift (WGS) played a role in the gas composition adjustment. The  $\text{H}_2/\text{CO}$  ratio was increased from 0.7 in the raw gas to nearly 3 in the reformed gas at the temperature 800°C; an interesting ratio for the downstream methanation. The manganese catalyst showed no  $\text{CH}_4$  reforming ability and the  $\text{CH}_4$  content in the reformed gas was actually increased by ~19 %.

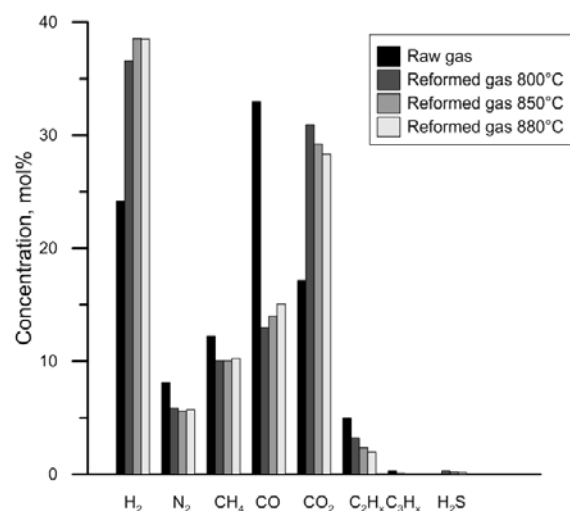


Figure 5: Gas composition of raw gas and reformed gas at examined temperatures [1]

To summarize this section, the manganese ore used in the study showed promising catalytic properties on the raw gas. This is in terms of activity towards tar components, but also in the actual upgrading of the gas composition and methane yield. Finally, no loss of activity was observed during these tests even though longer operation would be required to properly assess the attrition aspect.

### *Ilmenite experiment*

Ilmenite is an iron-titanium oxide ( $\text{FeTiO}_3$ ) that has gained much interest in the past 10 years owing to its favourable ability to carry oxygen for Chemical-Looping Combustion (CLC) processes with fossil fuels, see in e.g. [7-8]. It was also used in successful campaigns in the Chalmers 12 MW boiler fired with biomass and revealing its propensity to enhance the distribution of oxygen along the boiler riser [9, 10]. Another advantage of this material relies in the fact that it can be magnetically separated, which has the potential to considerably facilitate disposal of spent ilmenite from these applications and add to its competitiveness in the catalyst choice.

The use of ilmenite as a tar reforming catalyst was detailed in earlier studies showing the potential of this material for CLR application [2, 3]. More recently, a test campaign was conducted using the fluidized bed batch reactor in Fig. 3 where the catalyst is subject to alternating redox conditions. The idea was to decouple the effect of oxygen transport inevitable in the aforementioned dual bed configurations from the actual catalysis achieved by the fully reduced particles. In particular, the iron content at the surface of activated ilmenite is known to catalyse tar reforming in presence of reforming agents such as steam and  $\text{CO}_2$  [11].

One experiment cycle starts with fluidization of the batch with nitrogen-diluted air to fully oxidize the ilmenite. Then the system is flushed with nitrogen before the reducing sequence is initiated with raw gas. The oxygen-laden particles oxidize part of the raw gas until no oxygen is left and the fully reduced ilmenite can catalyse tar reforming and act as gas upgrading catalyst. One shall precise that both the reactor system and the gasifier are operated at sub-atmospheric conditions, for safety reasons. The pump inducing the driving force to let the raw gas stream in is located downstream the reactor in Fig. 3. This together with the reactions gas-solids that produce or consume permanent gases make stable operation difficult to achieve under longer reduction periods. Generally this was the limiting factor for aborting the reduction sequence instead of issues with the ilmenite bed itself.

In the experiments reported here, one temperature case of  $800^\circ\text{C}$  was investigated with three different gas-solids contact times (RTs): 0.6, 0.8 and 1.1 s. Detail in the experiments is provided in [12].

Fig. 6 shows the change in tar yields (expressed in  $\text{g}/\text{Nm}^3$ ) between the raw and reformed gas for the case  $\text{RT}=1.1$  s. In

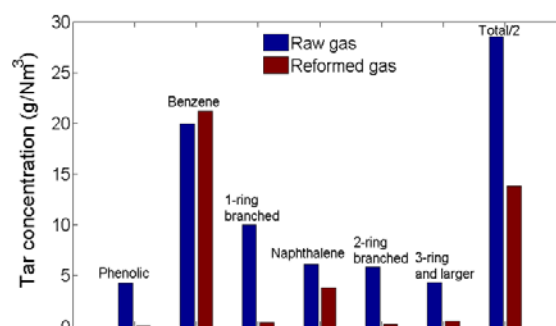


Figure 6. Concentrations of tar groups in  $\text{g}/\text{Nm}^3$  in raw gas/reformed gas; reactor temperature of  $800^\circ\text{C}$  and RT of 1.1 s [12]

Fig. 6, one can witness a decrease in naphthalene concentration by 37% in the reformed gas. The content of the more stable benzene slightly increased as other larger compounds were decomposed into benzene. It accounted for 77% of the overall tar content in the reformed gas. In total - and removing the dilution effect from the dry gas production - the raw gas tar level was diminished from 57.1 g/Nm<sup>3</sup> down to 27.6 g/Nm<sup>3</sup> by passing the bed of ilmenite, corresponding to a 52% removal efficiency, and up to 90% if benzene is excluded from the calculation. This is despite the relatively low temperature of this experiment. Indeed, from previous tests with ilmenite, one can expect an enhanced tar reforming when temperature is increased [2]. The tar content was also clearly lowered when the RT was increased. The previous figure can be compared with tar abatements of respectively 26% for RT=0.6 s and 34% for RT=0.8 s.

As for the permanent gas composition, Fig. 7 summarizes the concentrations of the main components in the raw gas and in the reformed gas for three different RTs.

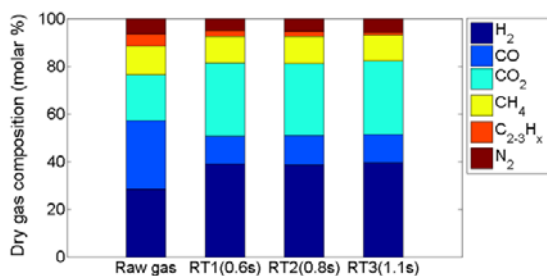


Figure 7: Gas composition of raw gas and reformed gas at examined RTs [12]

The change in gas composition is evident from Fig. 7. The fact that the inert N<sub>2</sub> content decreased in the reformed gas indicates a dilution from produced permanent gases. As seen above, tar

reforming reactions, but also the WGS have contributed to this result. In all, the H<sub>2</sub>/CO ratio was brought to almost 3 in the reformed gas, again a favourable figure for a downstream methanation step. Notably, the levels of C<sub>2-3</sub>H<sub>x</sub> were also decreased when the RT was increased; a trend similar to that of the tars. This could potentially open up for a prediction scheme of the tar contents using the more conveniently measured C<sub>2-3</sub>H<sub>x</sub> concentrations, even if further work is needed. The decrease in ethylene is also interesting from a downstream catalytic process point of view, where olefins are generally problematic. Finally, one shall precise that for the three cases, operation was conducted for about 80 min of reduction in presence of raw gas and no sign of decay in ilmenite activity could be noted. This suggests that in a fully-deployed CLR-based system, the required fines circulation for a given load of tars in a producer gas could be maintained at reasonable levels.

To summarize on these catalysts investigations, one can conclude that both showed reactivity towards tar reduction, but ilmenite has the advantage of offering the possibility for magnetic separation from the ash and attrited bed material used for the heat transport. Depending on the amount of attrited material and ash, the possibility to separate the active fraction can be vital from an economic point of view. However, no show-stoppers have been yet identified that could stop further investigation of the two materials. Particle integrity and stability in the context of long term operation is an issue that needs dedicated investigation, even though no indication from deactivation or contamination was revealed from the Chalmers experiments. This aspect is expected to be the part of an experimental campaign within the

GoBiGas project at Göteborg Energi where the aim is to promote tar conversion by optimizing the recirculation of fine catalyst material and developing a strategy for their injection.

## 5. Conclusions

During the past five years, extensive work has been conducted in connection to biomass gasifiers, particularly with insights on possible bed materials and implementation strategies have been developed. The principal intention of this work is to present how the CLR process can be implemented both as a secondary measure but also how it could be introduced already as a primary measure in order to abate the tar levels in the producer gas and adjust the gas composition. So far, promising catalysts have been successfully tested in bench-scale reactors and no show-stoppers that could hamper their further investigation in e.g. a deployed scale at GoBiGas have arisen. When the fines circulation is fully-optimized in an integrated system with the gasifier, the CLR technique clearly has the potential to reduce the consumption of oil-scrubber and active carbon beds already installed.

## 6. References

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