The use of ilmenite as oxygen carrier with kerosene in a 300W CLC laboratory reactor with continuous circulation

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Abstract – An ilmenite oxygen carrier was tested in a laboratory scale chemical-looping reactor with a design thermal capacity of 300 W. Ilmenite is a mineral iron-titanium oxide, which has been used extensively as an oxygen carrier in CLC. Two different kinds of fuels were used, a sulfur-free kerosene and one that contained 0.57 mass-% sulfur. Both fuels were continuously evaporated and directly fed into the chemical-looping reactor. Experiments were conducted for 50 h with the sulfur-free kerosene and for 30 h with the sulfurous kerosene. CO_2 yields above 99% were achieved with both types of fuel. It seems that a significant and lasting improvement in the oxygen carrier's reactivity was achieved by using sulfurous kerosene. No evidence of sulfur was found on the particles' surface.

1 Introduction

In chemical-looping publications, the use of liquid fuels is rare and processes with gaseous and solid fuels are predominant. Recent overviews over developments, advancements and operational experience in chemical-looping were given by Hossain and de Lasa [1], by Fang et al. [2], by Lyngfelt [3] and by Adánez et al. [4]. However, only a handful of articles have been published that focus on the use of liquid fuels in chemical-looping applications. Pimenidou et al. used waste cooking oil in a batch packed bed reactor to produce a synthesis gas [5]. Addition of calcined dolomite as CO_2 sorbent added to the bed material was investigated to capture CO_2 and increase the concentration of hydrogen [6]. Cao et al. gasified bitumen and asphalt in a separate pyrolysis unit before feeding the synthesis gas into a batch fluidized-bed reactor [7]. Forret et al. and Hoteit et al. conducted chemical-looping combustion experiments, where liquid fuel was injected into a batch fluidized-bed reactor with a nickel-based oxygen carrier. The investigated fuels included n-dodecane [8], a domestic fuel oil and a heavy fuel oil [9]. Mendiara et al. investigated reforming of tar with different oxygen carriers by feeding nitrogen saturated with toluene into a batch fixed-bed reactor [10]. The production of hydrogen from pyrolysis oils in a batch packed bed reactor was investigated by Lea-Langton et al., who used waste lubricating oil [11] and two biomass pyrolysis oils [12], and Giannakeas et al., who used scrap tire pyrolysis oil [13]. Moldenhauer et al. conducted both reforming and combustion experiments of sulfur-free kerosene in a fluidized-bed reactor with continuous circulation of oxygen carrier [14, 15].

This study focuses on the influence of sulfur in kerosene on a mineral ilmenite oxygen carrier. The experiments were conducted in a laboratory scale chemical-looping reactor with two interconnected fluidized beds. The sulfur measurements that were conducted during the experiments will be presented in a later version of this paper.

2 Experimental Details

2.1 300W Laboratory Reactor

An illustration of the reactor, which was used in this work, is shown in Fig.1. The injection system for the liquid fuel, which is not visible in Fig.1, is connected to the inlet of the fuel reactor. A more detailed description of both reactor and injection system can be found in [15].

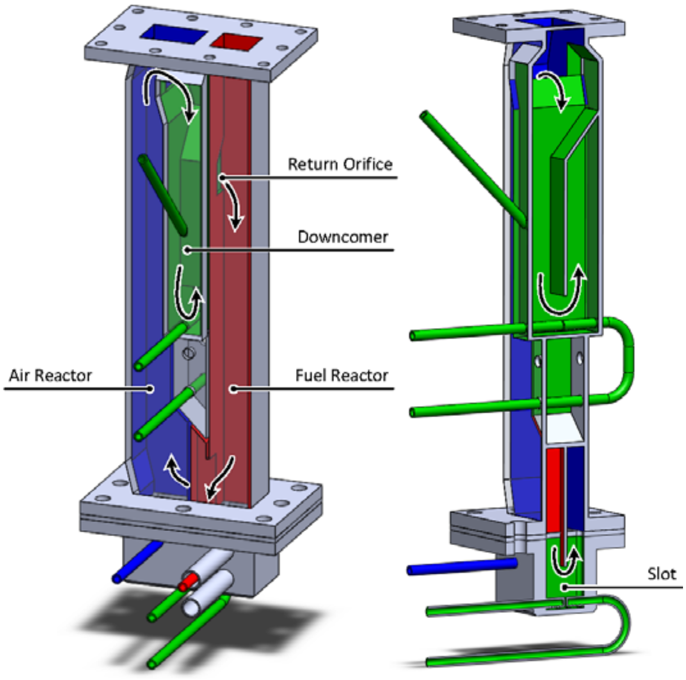


Fig.1: Schematic three-dimensional illustration of the 300W chemical-looping reactor

2.2 Fuel

In this study, two similar types of fuel are used: sulfur-free kerosene and sulfurous kerosene. Both types were provided by courtesy of Preem AB in Gothenburg, Sweden. By definition, kerosene consists of different hydrocarbons with evaporation temperatures between 150°C and 320°C. The sulfur-free kerosene is produced through catalytic desulfurization of the sulfurous kerosene. Table 1 and Fig.2 show analyses of the two types of kerosene.

Table 1: Fuel analysis of sulfur-free and sulfurous kerosene

Fuel property	Sulfur-free kerosene	Sulfurous kerosene	Analysis method
C content (mass-%)	86.2 ±0.5	85.9 ±0.5	ASTM D 5291
H content (mass-%)	13.5 ±0.4	13.5 ±0.4	ASTM D 5291
N content (mass-%)	<0.1 ±0.03	<0.1 ±0.03	ASTM D 5291
S content (ppmw)	<1	5700 ±400	ASTM D 1552
Lower heating value (MJ/kg)	43.34 ±0.21	42.66 ±0.20	ASTM D 240
Higher heating value (MJ/kg)	46.20 ±0.22	45.52 ±0.22	ASTM D 240
Density at 20°C (kg/dm^3)	0.792	0.860	–
Hydrogen-to-carbon ratio (mol/mol)	1.87	1.87	–

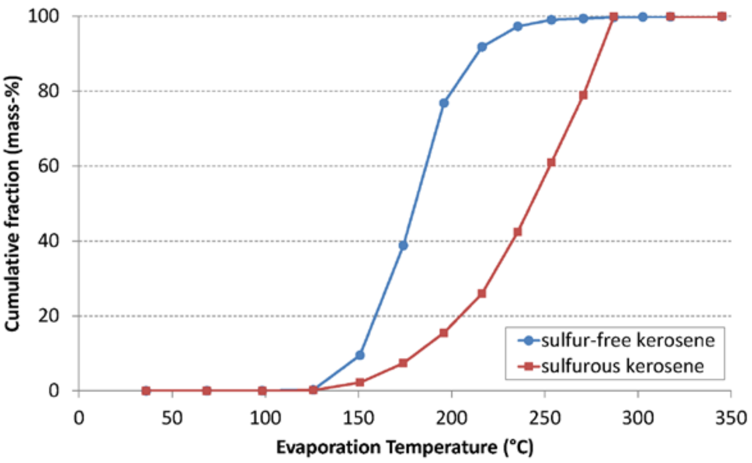


Fig.2: Kerosene analysis according to ASTM standard D-2887-08

2.3 Measurements

Fig.3 shows a schematic of the gas measurement system. The top parts of the air and fuel reactors are connected to a gravitational solid/gas separator. Part of the hot flue gases of the fuel reactor are diverted and led through a heated line, at 155°C, to a flame ionization detector (FID). The FID measures the content of organic carbon as CH_4 equivalent, without giving information about the hydrogen content. The flue gases of both air and fuel reactors are separately filtered and cooled down to 5°C, before they pass through gas analyzers. The dry-gas content of CH_4, CO and CO_2 is measured by IR analyzers and the content of O_2 by a paramagnetic sensor. Additionally, the dry fuel reactor gas is analyzed in a gas chromatograph (GC), which measures, besides the previously mentioned gases, H_2, N_2, and hydrocarbons up to C_3H_8. The GC used is equipped with two columns, Molsieve MS5Å 10m x 0.32mm (ID) and PoraPLOT Q 10m x 0.15mm (ID), in which the gas sample is injected in parallel.

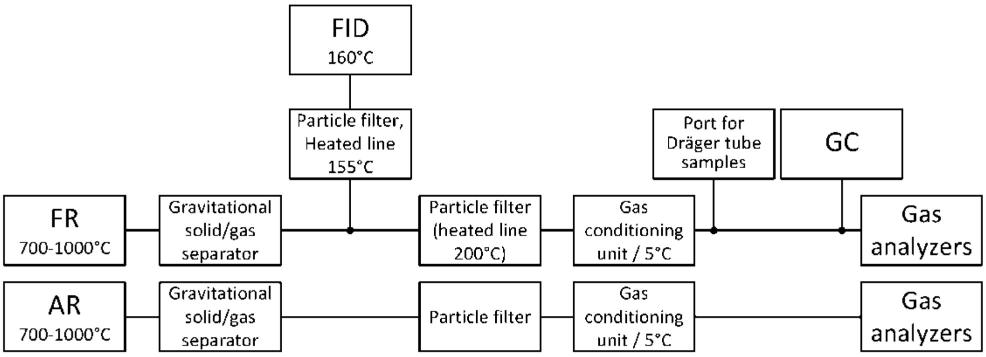


Fig.3: Schematic measurement layout

Before and after the experiments, the ilmenite particles were analyzed using SEM/EDX and XRD. The bulk density and the BET surface area (through gas adsorption) of the oxygen carrier particles were also measured before and after the experiments.

2.4 Oxygen Carrier

Ilmenite is a mineral that consists mainly of iron-titanium oxides. In order to be used as an oxygen carrier, ilmenite is physically beneficiated and ground. Ilmenite has been studied in chemical-looping applications with solid fuels [16-19] and gaseous fuels [17, 20-27]. Compared to synthesized oxygen carriers, ilmenite is cheap. The ilmenite used here was supplied by Titania A/S, Norway. The reactor was filled with about 380 g of ilmenite in the size range of 90-212 µm.

2.5 Conducted Experiments and Calculations

This paper presents the results from two series of experiments. During all experiments particles in the air reactor were fluidized with 8 L_n/min air and a total of 0.85 L_n/min argon was added to the loop-seals. In the injection system 0.93 L_n/min steam were mixed with the different amounts of fuel used.

In the first series, the ilmenite oxygen carrier was used with sulfur-free kerosene. Bed temperatures in the fuel reactor between 750°C and 950°C were investigated and the fuel flow was varied between 0.25 ml_{liq}/min and 1.00 ml_{liq}/min (143-572 W_{th}). During this series experiments with addition of sulfur-free kerosene were performed for 41 h.

For the second series of experiments, both sulfur-free and sulfurous kerosene were used as fuel. A set of experiments with sulfurous kerosene was performed between two sets of experiments with sulfur-free kerosene with the purpose to investigate whether the reactivity of the oxygen carrier changes during exposure to sulfur components. The flow of sulfurous kerosene was varied between 0.164 ml_{liq}/min and 0.654 ml_{liq}/min (100-400 W_{th}) at fuel reactor bed temperatures between 850°C and 950°C. During the second series, 30 h of experiments were performed with addition of sulfurous kerosene and 9 h with sulfur-free kerosene.

Before the first test series was started, the ilmenite oxygen carrier particles were carefully oxidized in air by slowly increasing the temperature and maintaining a fast fluidized bed regime. Then the batch of oxygen carrier was activated by continuously oxidizing and reducing the particles. Syngas, consisting of 50% H_2 and 50% CO, was used as a reducing agent for 1 h and sulfur-free kerosene for 8 h. The batch of oxygen carrier used for test series 2 consisted of 95% of material from series one and 5% of fresh material.

The evaluation uses data from three different analyzers, IR analyzers, GC and FID. Carbon fractions are calculated, which are the fractions of fuel-C in the fuel reactor converted to CO_2, CO, CH_4 and hydrocarbons higher than CH_4 (C2…C9).

3 Results and Discussion

3.1 Conversion of Sulfur-free Kerosene (Series 1)

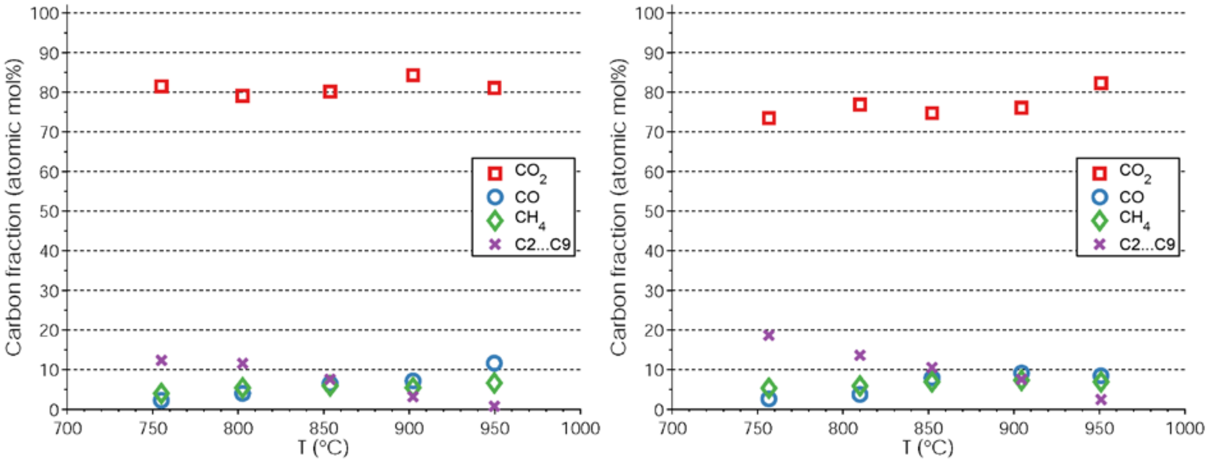
The results of the series with sulfur-free kerosene are shown in Fig.4. One trend that can be observed clearly is that the fraction of C2…C9 decreases with increasing temperature, while the fraction of CO increases. Hydrocarbon decomposition is known to increase with increasing temperatures. Additionally, the presence of steam, from the injection system and as a product of fuel conversion, triggers steam reforming of hydrocarbon according to reaction (R1).

$$\mathrm{C}_m\mathrm{H}_n + m\,\mathrm{H_2O} \rightarrow m\,\mathrm{CO} + \left(m + {}^{n}\!/_{2}\right)\mathrm{H_2} \tag{R1}$$

For the fuel flows in Fig.4, the flow of steam in the injection system is above the minimum needed to reform the fuel fully to CO and H_2. The fact that hydrocarbons are detected shows that equilibrium is not reached in the injection system.

The maximum fuel carbon conversion to CO_2 was about 84% at 900°C and 143 W_{th} fuel equivalent, see Fig.4, of all fuel flows and all temperatures tested in series 1. This value is quite low and would probably be unacceptable for an industrial plant. Whereas the CO_2 yield does not follow a clear trend when the temperature is varied, the overall degree of oxidation of fuel increases with temperature.

It can be concluded that the combustion of kerosene is a combination of hydrocarbon decomposition, steam reforming, and oxidation of H_2 and CO. Direct oxidation of CH_4 or other hydrocarbons seems less likely. Coke formation and gasification of coke is likely to play a role in the fuel conversion process. The overall fuel combustion is likely to improve if the reforming step, (R1), could be completed. The use of a catalyst in the injection system could improve the reformation. However, if this would benefit the overall process cannot be said with certainty.

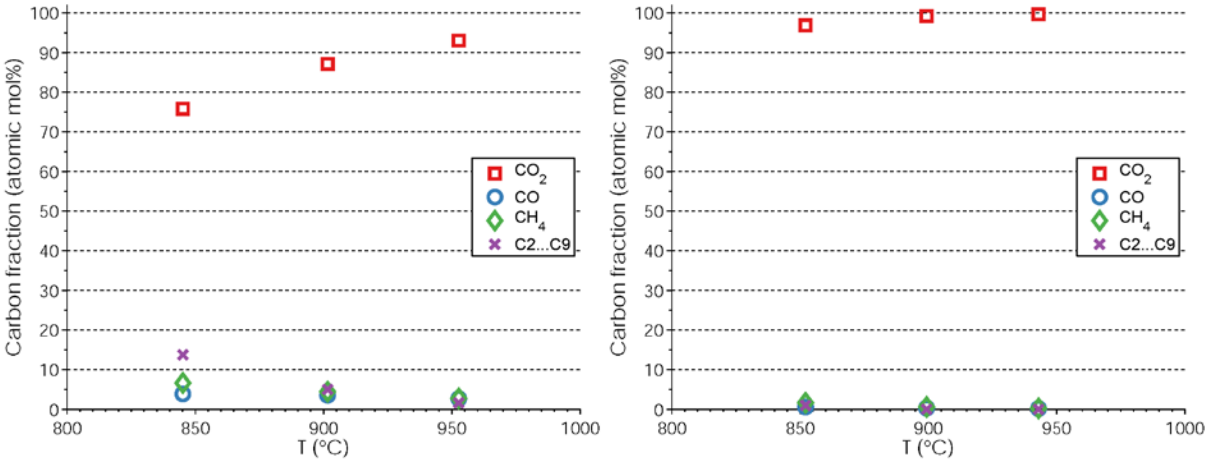


a) 143 W_{th} (0.25 ml_{liq}/min) *b) 286 W_{th} (0.50 ml_{liq}/min)*

Fig.4: Carbon fractions for different flows of sulfur-free kerosene and different temperatures (series 1)

3.2 Conversion of Sulfurous Kerosene (Series 2)

Experiment series 2 was commenced using sulfur-free kerosene, see Fig.5a. The results are similar to the ones from series 1, cf. Fig.4a, except at 950°C. The experiments at 950°C in series 1 were actually carried out a few months after the experiments at temperatures between 750°C and 900°C. In between, experiments with a different oxygen carrier were conducted. The conversion of fuel improved drastically from before, Fig.5a, to after the experiments with sulfurous kerosene, Fig.5b.

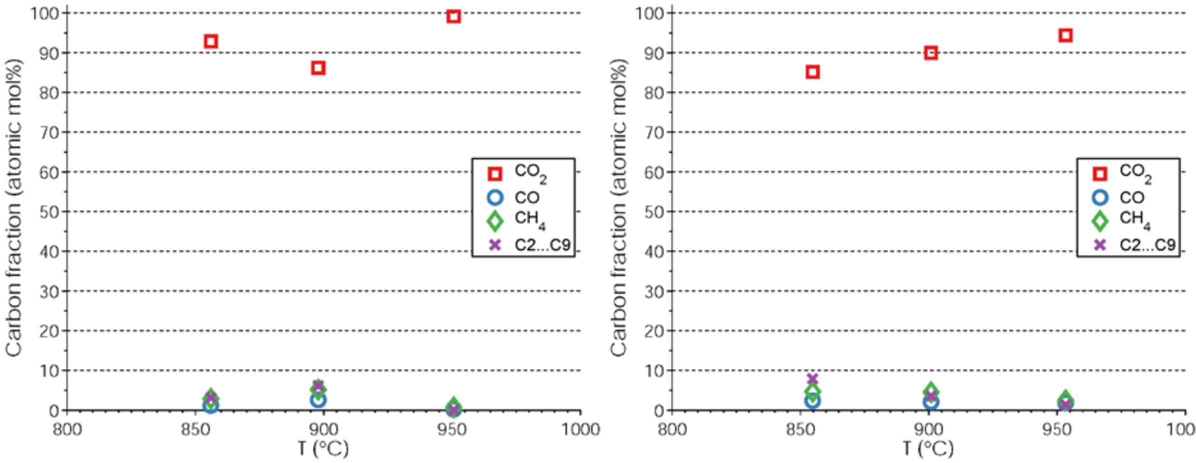


a) Before experiments with sulfurous kerosene *b) After experiments with sulfurous kerosene*

Fig.5: Carbon fractions for 144 W_{th} (0.25 ml_{liq}/min) of sulfur-free kerosene at different temperatures (series 2)

The mechanisms that are discussed in Section 3.1 should also apply when sulfurous kerosene is used, i.e. the trends observed in Fig.4 should be similar to the trends in Fig.6.

However, this does not appear to be the case. The carbon fractions of CO and hydrocarbons, CH_4 and C2…C9, decrease with higher temperatures and the CO_2 yield increases. Even though hydrogen fractions were not calculated, the measured concentrations of H_2 and hydrocarbons were generally low, which indicates a high conversion to H_2O.



a) 144 W_{th} (0.236 ml_{liq}/min) b) 300 W_{th} (0.492 ml_{liq}/min)

Fig.6: Carbon fractions for different flows of sulfurous kerosene and different temperatures (series 2)

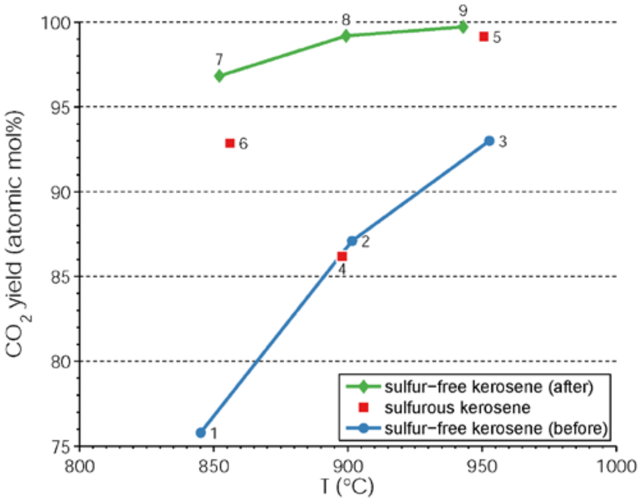


Fig.7: Comparison of experiments with sulfur-free and sulfurous kerosene in series 2. A constant fuel flow equivalent of 144 W_{th} was used. The numbering of the points corresponds to the order in which the experiments were performed, cf. Table 2.

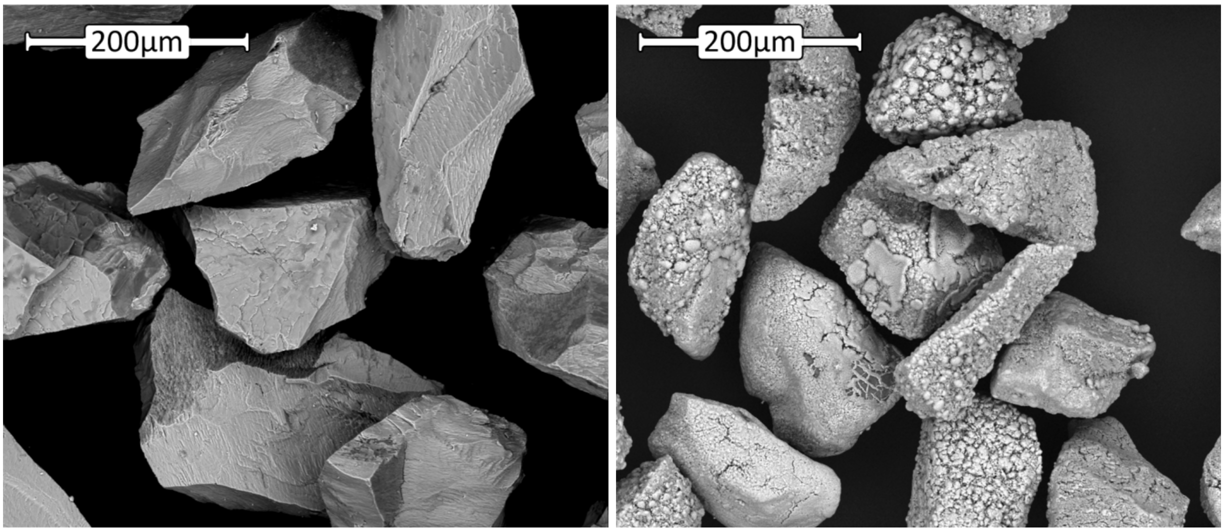
Table 2: Order of experiments in series 2 as indicated in Fig.7

#	Cumulative operation time (h)	Fuel reactor temperature (°C)	Type of kerosene
1	0.5	850	Sulfur-free
2	1.3	900	
3	1.9	950	
4	2.7	900	Sulfurous
5	9.7	950	
6	16.0	850	
7	30.2	850	Sulfur-free
8	31.9	900	
9	33.5	950	

A detailed analysis of the 33 h of operation with and without sulfur was made, clearly indicating that a dramatic increase in reactivity takes place within the first five hours of operation with sulfurous fuel. All periods before these first five hours showed low reactivity, whereas all periods after showed high reactivity, in accordance with the data for 144 W_{th} shown in Fig. 7 and Table 2.

3.3 Oxygen Carrier Analysis

The XRD analysis of the ilmenite oxygen carrier after series 1 indicated the presence of Fe_2TiO_5 (pseudobrookite), TiO_2 (rutile) and Fe_2O_3 (hematite). This matches earlier findings when syngas was used as fuel [27]. SEM pictures suggest that the phases are not evenly distributed, see Fig.8b, as many particles have elevated spots on their surface. In an EDX analysis of the surface it was found that the spots consist mostly of iron and oxygen, possibly Fe_2O_3, and the space in between the spots consists of iron, titanium and oxygen, which could be Fe_2TiO_5 and TiO_2. This differs from the findings made by Adánez et al. [25], where iron oxide formed a continuous shell around a core enriched with titanium. It is not clear whether those patches are just an intermediate step, which would eventually lead to an enclosing iron shell if the experiments had been continued longer.



a) Fresh and not calcined *b) After experiments*

Fig.8: SEM images of ilmenite particles, (a) before, and (b) after experiments with sulfur-free kerosene

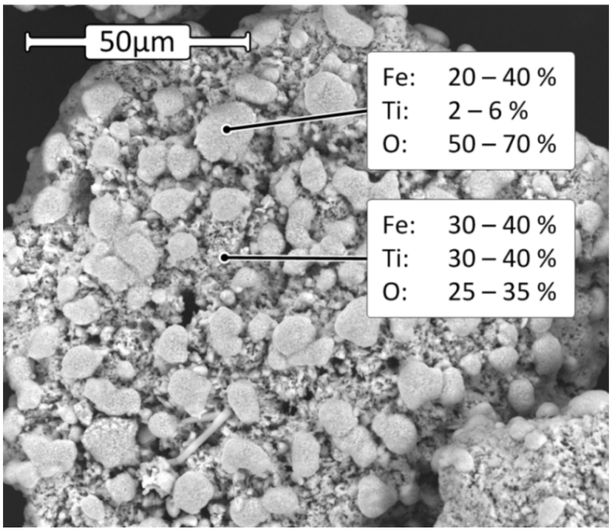


Fig.9: SEM image and results of EDX analysis of ilmenite oxygen carrier after experiments with sulfur-free kerosene (series 1). The indicated phases are shown in molar percent.

After the last experiment of series 2, the oxygen carrier was continuously oxidized and reduced with 400 W_{th} of sulfurous kerosene for about 3 h. The fuel was then replaced with argon, the circulation between air reactor and fuel reactor was stopped and the furnace was switched off. When the reactor had cooled down some of the bed material in fuel reactor was extracted and analyzed with XRD and EDX. Neither analysis showed the presence of sulfur.

4 Conclusions

- A total of 80 h of fuel operation were performed with sulfurous and sulfur-free kerosene and ilmenite oxygen carrier in a 300W CLC reactor with continuous circulation of oxygen carrier particles.
- With both types of kerosene CO_2 yields above 99% were reached at 950°C and fuel flows equivalent to 144 W_{th}.
- The presence of sulfur seems to have a positive effect on the reactivity of ilmenite oxygen carrier. Reactivity increased when sulfurous kerosene was used and stayed on a higher level even when sulfur-free kerosene was used thereafter.
- No evidence was found for sulfur poisoning or deactivation of the ilmenite oxygen carrier. Even though possible, it seems unlikely that this should be different for higher concentrations of sulfur.
- Ilmenite oxygen carrier can be used with sulfurous fuels, both being potentially cheap.

Acknowledgments

The study is carried out under the project “Chemical-looping with liquid hydrocarbon fuels” financed by Saudi Aramco. The authors would also like to thank Harald Jeppsson from Preem AB for providing the kerosene. A special thanks to Sven-Ingvar Andersson for conducting fuel analysis and helping with his expertise.

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