

Chemical-Looping Combustion with Fuel Oil in a 10 kW Pilot Plant

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Abstract

A fuel reactor with a fuel-injection system for liquid fuels was designed and built for a chemical-looping reactor system with the nominal fuel input of 10 kW_{th}. The gas velocities in the riser section and at the gas-distribution nozzles of this unit are comparable to those of industrial circulating fluidized-bed boilers. Proof-of-concept experiments were performed with a calcium manganite-based oxygen carrier and a fuel oil with low sulphur content. Fuel conversion was high, but not complete, and most of the fuel carbon was converted to CO₂ in the fuel reactor.

Long-term experiments were performed using an ilmenite oxygen-carrier. The oxygen carrier was exposed to fluidization at hot conditions (more than 600°C) for about 204 h, out of which fuel was injected during a total of 66.6 h. The parameters temperature, fuel flow, steam flow in the fuel reactor, fluidization medium in the fuel reactor and air flow in the air reactor were varied to observe trends in fuel conversion. Most of the experiments were carried out with a fuel flow corresponding to 4 kW_{th} and an oxygen carrier-to-fuel ratio of about 2100 kg/MW_{th}. At 1050°C the fuel could be oxidized to about 87%, and up to 88% of all carbon leaving the fuel reactor was in the form of CO₂. No defluidization or agglomeration problems were experienced over the course of the experimental campaign.

Keywords: chemical-looping combustion (CLC), liquid fuel, fuel oil, ilmenite, calcium manganite, CO₂ capture, carbon capture and storage (CCS)

1. Introduction

1.1. Chemical-Looping Combustion

Chemical-looping combustion (CLC) is a method of burning carbon-based fuels with inherent capture of CO₂. CLC is a so-called CCS (carbon capture and storage) technology and has the purpose of reducing the impact of carbon dioxide from carbon-based fuels on the climate of the Earth. Continued utilization of fossil fuels at a large scale will require implementation of CCS if the UN and EU endorsed temperature limits are to be met.

In CLC a metal oxide-based powder, the oxygen carrier, is alternately exposed to air and fuel. While in air the oxygen carrier takes up oxygen and subsequently passes it to the fuel. This can be achieved by circulating the oxygen-carrier particles continuously between two vessels. The net reaction of this process is the same as for combustion in air, i.e., the heat produced in CLC is the same as in combustion in air. The difference is, however, that in CLC the fuel is never mixed with nitrogen so that the gases from the fuel reactor ideally consist of only carbon dioxide and steam. The latter can be condensed and the capture of CO₂ does not require any input of energy. Recent literature concerning developments, advancements and operational experience in chemical-looping has been published by Fan¹, Adámez et al.² and Lyngfelt³.

1.2. Liquid Fuels in Chemical-Looping Combustion

The use of liquid fuel in stationary combustion processes, as chemical-looping combustion would be, is far less common than the use of coal or gas. Because of their high energy density, liquid fuels are mostly used in transport applications. In an oil refining process, a large variety of end products can be generated, which differ greatly in quality and price. Low-grade heavy-oil products, such as vacuum residues, are upgraded if economically feasible. Such low-grade products, however, could pose an interesting and feasible option for thermal processes, especially if the process is located close to or integrated in a refinery process, where there is a constant need for heat and steam. Difficulties in the use of heavy-oil products are related to handling, because of their high viscosity, and to high amounts of sulfur and other impurities, such as heavy metals.

Research that focuses on employing liquid fuels in chemical-looping combustion is rather limited, which reflects on the number of publications available. Cao et al.⁴ gasified asphalt and bitumen in an upstream process, before burning the product gas in a batch fluidized-bed reactor. Forret et al.⁵ and Hoteit et al.⁶ tested different fuels, namely, *n*-dodecane, fuel oil and heavy fuel oil, in a batch fluidized-bed reactor with direct injection of liquid fuel. Bao et al.⁷ saturated a flow of nitrogen with *n*-heptane, which was used as fuel in a batch fluidized-bed reactor. Chiu et al.⁸ mixed isopropanol with water and used nitrogen as a carrier gas to convey the evaporated fuel into a moving-bed reactor. The only known experiments with continuous operation in a dual fluidized-bed were published by the authors

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of this paper. Prior to the work described in this paper, experiments were performed with different oxygen-carrier materials and sulfurous and sulfur-free kerosene as fuel, which was evaporated, mixed with steam and fed into a bench-scale chemical-looping reactor with continuous circulation of oxygen-carrier particles.^{9–11}

The experiments that are presented here are part of a project that aims at using low-grade heavy liquid fuels in chemical-looping combustion. A fuel reactor with an injection system, which can feed heavier liquid-fuel fractions to the fluidized-bed of the fuel reactor, was designed and constructed. This system has been evaluated using a fuel oil with the calcium-manganite oxygen carrier $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ and the mineral oxygen-carrier ilmenite, FeTiO_3 .

2. Experimental Details

2.1. 10 kW Chemical-Looping Combustion Reactor System

Figure 1 shows a schematic of the reactor system with all major sections shown, including gas and fuel inlets and gas outlets. The unit is based on interconnected fluidized beds and is similar to the design originally presented by Lyngfelt et al.¹². In the riser section there is a fast-fluidized regime, whereas in the loop-seals and the fuel reactor there is a bubbling regime. In the air reactor the fluidization regime is on the transition between bubbling and fast fluidized. The unit is equipped with heating cables, which are wrapped around the riser section, the cyclone, the upper loop-seal and the fuel reactor, and covered with insulation material. Heating cables are needed to compensate for radiation losses at high temperatures that are inherent in small-scale units like the one used here, i.e., such with a high ratio of surface area to volume. Additionally, the air that is fed to the air reactor is preheated to 1000°C. More details about the reactor system can be found elsewhere¹³.

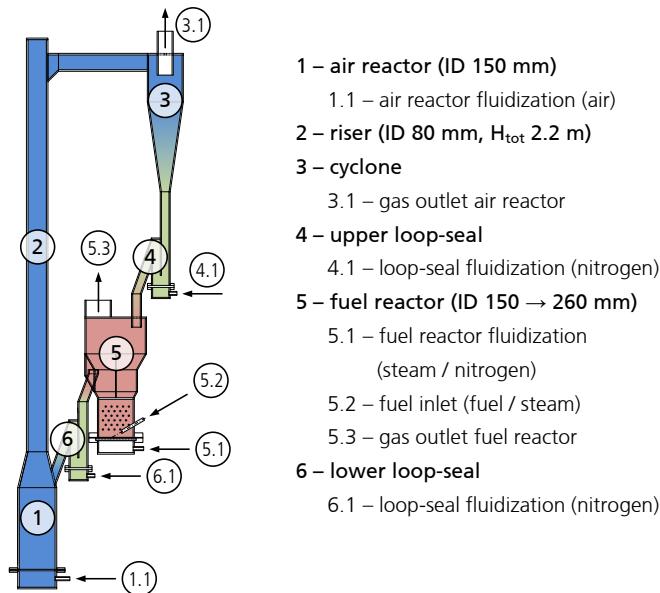


Figure 1: Schematic of the 10 kW chemical-looping combustion reactor

The lower section of the fuel reactor was specifically designed for direct injection of liquid fuel, see Figure 2. The height of this section is about 165 mm and the bed diameter is 150 mm. The total bed height in the fuel reactor is 275 mm. Fuel is injected as a jet close to the center of the fluidized bed and ca. 25 mm above the gas distributor plate. Internals are used to limit the growth of gas bubbles and to reduce the risk of formation of gas channels, which would reduce the fuel-oxygen carrier contact and therefore decrease fuel conversion.

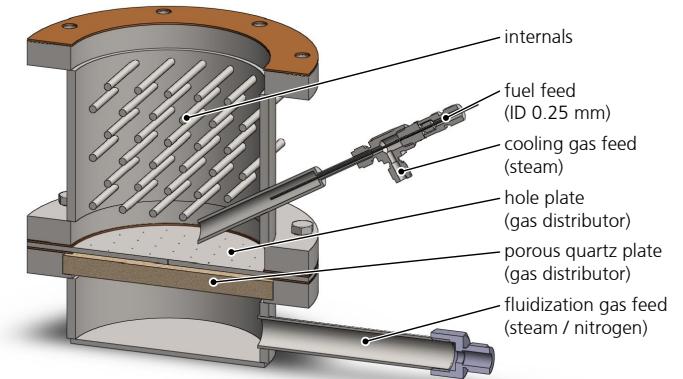


Figure 2: Lower fuel reactor section for direct injection of liquid fuel

The amount of oxygen carrier used in the 10 kW unit depends on the bulk density of the oxygen-carrier particles. In the configuration used for injection of liquid fuel, the bed mass is roughly in the range of 15–25 kg, out of which 5–10 kg are in the fuel reactor.

2.2. Measurements

During the experiments, measurements of pressure, temperature, gas flows and gas concentrations are logged continuously. The fuel flow is logged manually and is based on the measured weight of the fuel tank.

Small streams of the flue gases from air reactor (AR) and fuel reactor (FR), ca. 1 L_n/min on a dry basis, are diverted from the main gas streams, filtered, cooled to about 4°C and fed to gas analyzers. Gas concentrations of O₂ (paramagnetic sensor) and CO, CO₂ and CH₄ (infrared sensors) are measured continuously in the flue gases from both reactor vessels. A fraction of the dried gas stream of the fuel reactor is fed to a micro gas-chromatograph (GC) with two parallel columns (Molsieve MS5Å, 10 m × 0.32 mm and PoraPLOT Q, 10 m × 0.15 mm), which both are equipped with a thermal-conductivity detector. In the gas chromatograph, concentrations of H₂, N₂, O₂, CO, CH₄, CO₂, C₂H_n and C₃H_n¹ are detected and quantified intermittently. Another small stream of the fuel reactor gases is kept above 155°C and analyzed separately and continuously in a flame-ionization detector (FID), which measures the total carbon content in organic compounds, i.e., $\sum(x \cdot C_xH_yO_z)$. A schematic description of the system for gas analysis can be found in Figure 3.

¹C₂H_n and C₃H_n are substitute denominations for hydrocarbons with two and three carbon atoms, respectively. This includes the species C₂H₂, C₂H₄ and C₂H₆ and C₃H₄, C₃H₆ and C₃H₈.

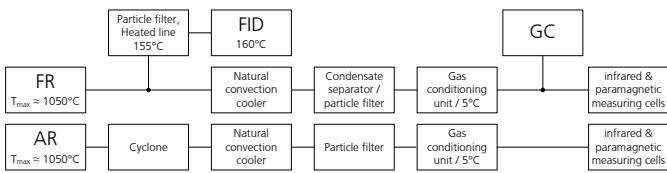


Figure 3: Schematic description of the gas-analysis system

2.3. Oxygen-Carrier Materials

Experiments were carried out with two different oxygen-carrier materials. One material, based on calcium manganite, was used to establish a proof-of-concept. The second material, ilmenite, is based on iron–titanium oxides, has a mineral origin, and was used for long-term testing.

2.3.1. Calcium Manganite

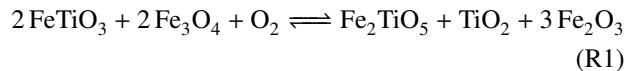
The material based on calcium manganite is of perovskite structure and has the nominal chemical composition $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$. The particles were produced by spray-drying and subsequent calcination at 1300°C for 4 h. This oxygen carrier has so-called CLOU properties (chemical-looping with oxygen uncoupling), which means that it releases gas-phase oxygen in the fuel reactor and allows for a direct reaction of fuel with gaseous oxygen. In regular chemical-looping combustion, fuel reacts with solid oxygen carrier. It is believed that it could be advantageous to use material with CLOU properties, in order to reach high levels of gas conversion. A detailed description of the CLOU concept can be found elsewhere¹⁴.

This oxygen carrier was used prior to the experiments described here for tests in a batch fluidized-bed reactor with methane and syngas as fuel¹⁵ and for an experiment series with a sulfur-free natural gas as fuel^{13,16}. During the latter, fuel was added for 55 h and the particles did not show any signs of chemical degradation. Complete conversion of fuel to CO_2 and H_2O could be achieved. Furthermore, the amount of fines produced was very low, which indicates a long lifetime. On the basis of those positive characteristics, the material was chosen to establish a proof-of-concept with liquid fuel in the 10 kW reactor system.

There are indications from catalysis research that this type of oxygen carrier can be deactivated by sulfur. Current research with calcium manganite-based materials¹⁷ indicates deactivation by sulfur, but also the possibility of regeneration. The mechanisms for deactivation and regeneration, however, are not fully understood.

2.3.2. Ilmenite

Ilmenite is a mineral, which contains iron titanium oxides, the main reduced phase being FeTiO_3 , along with some other minor phases, e.g., iron oxide. When used as an oxygen carrier, the mineral material is ground to a desired particle size and physically beneficiated to increase the fraction of iron-titanium oxides. In a chemical-looping combustion process, ilmenite oxygen-carrier is usually assumed to take the reduced and oxidized forms shown in reaction (R1).



Ilmenite oxygen-carrier is known to undergo changes when used in chemical-looping applications. Typical changes are increase in particle size^{18,19}, decrease in particle density¹⁸, increase in porosity^{20–22} and migration of iron species to the surface of the particle^{11,20,22}. Maybe most important for chemical-looping processes is a clear improvement in reactivity during the initial redox cycles^{11,18,20,22}, which is usually referred to as “activation”. This activation process, together with all other aforementioned changes, is believed to be connected to the phase migration of iron to the surface of the particles. The phase migration in turn is believed to be caused by oxidation of ilmenite at temperatures up to 900°C ²³ and by reduction of ilmenite up to at least 1080°C ²⁴. There are indications that a secondary activation process, observed as a second improvement in fuel conversion, can take place in the presence of sulfur¹¹. The mechanism of this secondary activation by sulfur is still unclear.

2.4. Fuel

The fuel used here is a diesel-type fuel oil with low sulfur content, which is usually used as domestic heating/fuel oil. The fuel’s commercial name is Eo1 E10 and was purchased from a local provider, Preem AB in Gothenburg, Sweden. It meets the requirements for fuel oil defined in the Swedish standard SS 155410²⁵. An elemental analysis was performed and density and heating values were measured, see Table 1. Additionally, a distillation curve was determined according to ASTM standard D 2887-08²⁶, see Figure 4. The fuel contains about 15 vol% aromatic compounds.

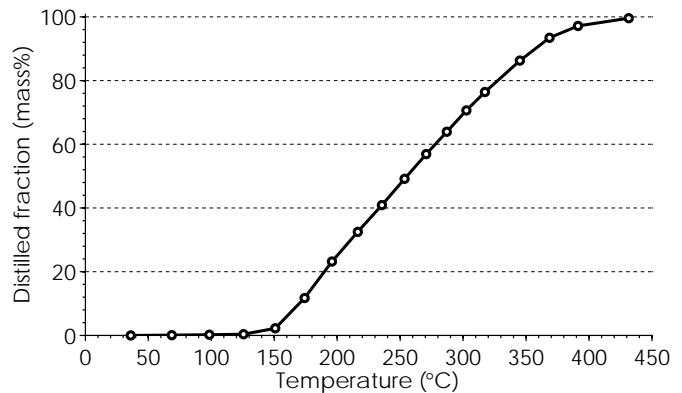


Figure 4: Analysis of fuel oil Eo1 E10 according to ASTM standard D 2887-08

2.5. Parameters Investigated

2.5.1. Proof-of-Concept Study with Calcium Manganite

For the proof-of-concept study, the calcium-manganite oxygen carrier was used. The goal of this study was to check the functionality of the fuel-injection system and to gauge to what extent the fuel is converted in the fuel reactor.

Table 1: Results of the analysis on fuel oil Eo1 E10

Analysis parameter	Unit	Result	Analysis method
Density, 15°C, vacuum	kg/dm ³	0.8321 ± 0.0012	ASTM D 4052
Elementary analysis, carbon	mass%	86.6 ± 0.5	ASTM D 5291
Elementary analysis, hydrogen	mass%	13.7 ± 0.4	ASTM D 5291
Elementary analysis, nitrogen	mass%	< 0.1 ± 0.03	ASTM D 5291
Sulfur	mass%	< 0.05 ± 0.004	ASTM D 1552
Higher heating value	MJ/kg	45.91 ± 0.22	ASTM D 240
Lower heating value	MJ/kg	43.00 ± 0.21	ASTM D 240
Hydrogen-to-carbon ratio	mol/mol	1.885 ± 0.066	–

Two experiments were performed with 38 min and 30 min of fuel injection, respectively. The data evaluation of those experiments is limited, because neither flame-ionization detector (FID) nor gas chromatograph (GC) were online. The fuel-reactor temperature was about 900°C. The fuel flow was estimated based on a calibration of the fuel-injection system at room temperature and atmospheric pressure. The parameters used during this study are summarized in Table 2.

2.5.2. Long-Term Testing with Ilmenite

For the long-term testing, the ilmenite oxygen-carrier was used, as promising results had been obtained previously with ilmenite and kerosene¹¹. The goal during this experimental campaign was to test particle integrity and investigate the effect of important parameters on fuel conversion. Initially, the fuel flow was estimated based on a calibration of the fuel-injection system at room temperature and atmospheric pressure. Later, during the main part of the experiments, the fuel flow was measured based on weight change of the fuel tank over time.

Nine days of experiments with successful fuel injection were performed and a total of 66.6 h with fuel injection was achieved. The total time of hot operation (> 600°C) was about 204 h. The experimental parameters are summarized in Table 2.

3. Data Evaluation

3.1. Oxygen-Carrier Circulation

One way to quantify the circulation of solids in a circulating fluidized-bed (CFB) reactor is through the mass flux of solids, G_s , which expresses the circulation as mass flow per area in kg/m²s. Normally, the cross-sectional area of the riser is used as reference. This allows for comparison of solid circulation of CFB units of different size. It is usually not possible to measure the mass flux of solids directly, which is why it is calculated based on pressure measurements that are extrapolated in order to obtain the bed density at the exit of the riser, ρ_{exit} , see equation (1)²⁷.

$$G_s = \rho_{exit} \cdot (u_0 - u_t) = -\frac{1}{g} \cdot \frac{dp_{exit}}{dh_{exit}} \cdot (u_0 - u_t) \quad (1)$$

For practical reasons equation (1) is simplified and adapted to the 10 kW unit, see equation (2). G'_s in equation (2) is called

the circulation index and is based on a pressure measurement in the middle of the riser. Hence it represents the gross amount of particles, i.e., the sum of particles traveling upward and downward, and gives an overestimation of the true mass flux of solids, G_s . The circulation index is believed to be proportional to the real mass flux.

$$G'_s = -\frac{1}{g} \cdot \frac{\Delta p}{\Delta h} \cdot (u_0 - u_t) \quad (2)$$

The terminal velocity, u_t , is approximated according to Kuri and Levenspiel²⁸.

3.2. Fuel Conversion

A simple and straightforward way to evaluate the conversion of fuel is to compare the amount of oxygen consumed in the air reactor with the stoichiometric amount of oxygen needed for full conversion of fuel to CO₂ and H₂O. Equation (3) shows how the degree of fuel oxidation, η_{fuel} , is calculated.

$$\eta_{fuel} = \frac{\dot{n}_{O2,AR,in} - \dot{n}_{O2,AR,out}}{\dot{n}_{O2,stoich}} \quad (3)$$

The significance of equation (3) strongly depends on the amount of fuel that leaks into the air reactor. If a large amount of fuel leaks into the air reactor, e.g., as coke or reactive gas, oxygen consumption will still be high but at a sacrifice of CO₂ capture efficiency. On the basis of the concentration of CO₂ in the exhaust gases from the air reactor the fraction of fuel carbon that leaks into the air reactor, $f_{C,AR}$, is determined according to equation (4). The flow of CO₂ leaving the air reactor is compensated for the atmospheric concentration of CO₂, which was approximately 400 ppm during the time of the experiments.

$$f_{C,AR} = \frac{\dot{n}_{CO2,AR,out}}{\dot{n}_{C,fuel}} \quad (4)$$

Another way to evaluate the conversion of fuel, which gives more detailed information about the different steps of conversion and selectivity, is to quantify the different species in the exhaust gas of the fuel reactor. The measurement equipment

Table 2: Experimental parameters during proof-of-concept study with calcium manganite and during long-term testing with ilmenite

Experimental parameter	Unit	Value	
		Proof-of-concept study	Long-term testing
Fuel flow	ml _{liq} /min kW _{th}	≈ 10 ≈ 6	≈ 10 and 6.6–7.6 ≈ 6 and 3.9–4.5
Fuel reactor temperature	°C	≈ 850–900	900, 950, 1000 and 1050
Bed mass in fuel reactor	kg	≈ 7	≈ 8.4
Total bed mass	kg	≤ 20	22–24
Steam flow in fuel reactor	ml _{liq} /min L _n /min	25.5 and 30.5 31.7 and 37.9	4.0, 20.0, 24.0, 34.0 and 38.0 5.0, 24.9, 29.8, 42.3 and 47.2
Nitrogen flow in fuel reactor	L _n /min	0	0 and 22
Air reactor flow	L _n /min	200 and 240	180, 200, 220 and 240
Nitrogen flow in loop-seals (each)	L _n /min	10	3 and 10

used, cf. section 2.2, allows for monitoring the fate of fuel carbon. The different carbon species are distinguished as shown in Table 3 and calculated according to equations (5)–(8).

$$\gamma_{\text{CO}_2} = \frac{\dot{n}_{\text{CO}_2,\text{FR}}}{\dot{n}_{\text{CO}_2,\text{FR}} + \dot{n}_{\text{CO},\text{FR}} + \sum(x \cdot \dot{n}_{\text{C}_x\text{H}_y\text{O}_z,\text{FR}})} \quad (5)$$

$$f_{\text{CO}} = \frac{\dot{n}_{\text{CO},\text{FR}}}{\dot{n}_{\text{CO}_2,\text{FR}} + \dot{n}_{\text{CO},\text{FR}} + \sum(x \cdot \dot{n}_{\text{C}_x\text{H}_y\text{O}_z,\text{FR}})} \quad (6)$$

$$f_{\text{CH}_4} = \frac{\dot{n}_{\text{CH}_4,\text{FR}}}{\dot{n}_{\text{CO}_2,\text{FR}} + \dot{n}_{\text{CO},\text{FR}} + \sum(x \cdot \dot{n}_{\text{C}_x\text{H}_y\text{O}_z,\text{FR}})} \quad (7)$$

$$f_{\text{CHO}} = \frac{\sum(x \cdot \dot{n}_{\text{C}_x\text{H}_y\text{O}_z,\text{FR}}) - \dot{n}_{\text{CH}_4,\text{FR}}}{\dot{n}_{\text{CO}_2,\text{FR}} + \dot{n}_{\text{CO},\text{FR}} + \sum(x \cdot \dot{n}_{\text{C}_x\text{H}_y\text{O}_z,\text{FR}})} \quad (8)$$

Table 3: Groups of carbon fractions as used in evaluation

Carbon species	Symbol	Explanation
CO ₂	γ_{CO_2}	The fraction of CO ₂ of the total carbon in the exhaust gases of the fuel reactor is called the CO ₂ yield. A special denotation, γ instead of f , is chosen to differentiate CO ₂ as desired oxidation product from other carbon species CO, CH ₄ and C _x H _y O _z .
CO	f_{CO}	CO is an intermediate reaction product. It is formed when hydrocarbons are fully reformed but only partially oxidized.
CH ₄	f_{CH_4}	CH ₄ is an intermediate reaction product, which is not necessarily on the direct reaction path from hydrocarbons in fuel to CO ₂ .
C _x H _y O _z	f_{CHO}	Organic compounds, which include hydrocarbons C _m H _n with exception of CH ₄ , originate from fuel molecules that are partially or not at all reformed. Partially reformed molecules can be partially oxidized.

4. Results

4.1. Proof-of-Concept Study with Calcium Manganite

Two experiments using calcium manganite-based oxygen carrier and fuel oil Eo1 E10 were performed. Fuel was injected for a total of 68 min, and most of the fuel carbon was converted to CO₂. Figure 5 shows gas concentrations measured during 30 min of fuel injection during the second experiment. The CO₂ concentration in the fuel reactor on dry-basis was about 40 vol%, CO and CH₄ concentrations were 5 vol% and 3 vol%, respectively. The concentration of oxygen in the fuel reactor is initially about 1 vol% due to the CLOU properties of the oxygen-carrier material but drops sharply down to zero when CO₂, CO and CH₄ occur. The O₂ concentration in the air reactor drops from initially 19 vol% to about 15.5 vol%. Gas-chromatograph measurements were made and indicate the following additional species in the fuel reactor: 36.5 vol% of N₂, 17 vol% of H₂, 2.4 vol% of C₂H_n and 0 vol% of C₃H_n. The nitrogen originates from the lower loop-seal, see Figure 1. Measurements with the flame-ionization detector were not done. On the basis of those concentrations, and under the assumption that no higher organic compounds are present, the degree of oxidation of fuel carbon is estimated to be around 80%.

Average values for oxidation of fuel, estimated mass flux of solids and carbon leakage to air reactor are shown Table 4. The degree of oxidation of fuel for both experiments fluctuated between 60% and 85%, which matches an estimation based on measured concentrations of carbon-containing gases. This suggests that there were no or little organic compounds higher than C₂H_yO_z present. Hence, the carbon species in the flue gases of the fuel reactor were mainly CO₂, CO and CH₄ (in decreasing order). The amount of carbon leakage to the air reactor is very low.

Some problems were experienced with fouling of fuel, which blocked the fuel injector. Fouling of organic fluids is a known problem and happens through three main processes: autoxidation, thermal decomposition and polymerization²⁹. The prob-

Table 4: Average process values of both proof-of-concept experiments. The temperatures in air reactor and fuel reactor are 850–900°C and the fuel flow corresponds roughly to 6 kW_{th}.

Process value	Unit	Experiment 1	Experiment 2
Degree of fuel oxidation, η_{fuel}	%	77	68
Circulation index, G'_s	kg/m ² s	3.0	3.3
Carbon leakage to air reactor, $f_{C,\text{AR}}$	mol%	0.75*	0.52*
Fuel injection time	min	38	30

* On the basis of measurements of CO₂ in the air reactor. The average CO₂ concentrations were 0.09 vol% (including atmospheric CO₂) in both experiments.

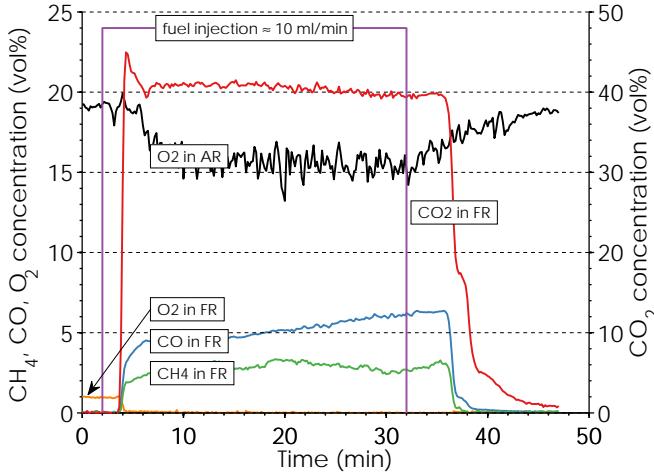


Figure 5: Measured dry-gas concentrations in air reactor (O₂) and fuel reactor (CO₂, CO, CH₄, O₂). The temperatures in the air reactor and the fuel reactor are 850–900°C and the fuel flow corresponds to roughly 6 kW_{th}.

lems experienced were likely caused by thermal decomposition followed by polymerization. The influence of autoxidation is believed to have been negligible. An increase of the steam flow surrounding the injection nozzle in order to increase cooling solved the problem, and the injection system could be used successfully in repeated operation.

4.2. Long-Term Testing with Ilmenite

This section consists of two parts. Results attained during 66.6 h of fuel addition are shown and discussed in section 4.2.1. The effects that fluidization under hot conditions, more than 600°C, for about 204 h had on the ilmenite particles are shown in section 4.2.2.

4.2.1. Fuel Conversion

During the first experiments with ilmenite oxygen-carrier, a fuel flow of about 10 ml_{liq}/min (6 kW_{th}) was used. Fuel oxidation was low, i.e., below 45% at 900°C and about 65% at 1000°C, and consequently it was reduced to about 7.2 ml_{liq}/min (4 kW_{th}).

Figure 6 shows the degree of fuel oxidation over the circulation index at different temperatures. The two experiments where nitrogen instead of steam was used to fluidize the particles in the fuel reactor are indicated with “N₂”. Two general trends can

be observed here. First, fuel oxidation increases with increased temperature. Second, increased particle circulation leads almost always to an increased oxidation of fuel. It is not clear whether fluidization with nitrogen has an impact on fuel oxidation. The maximum degree of fuel oxidation is about 87%.

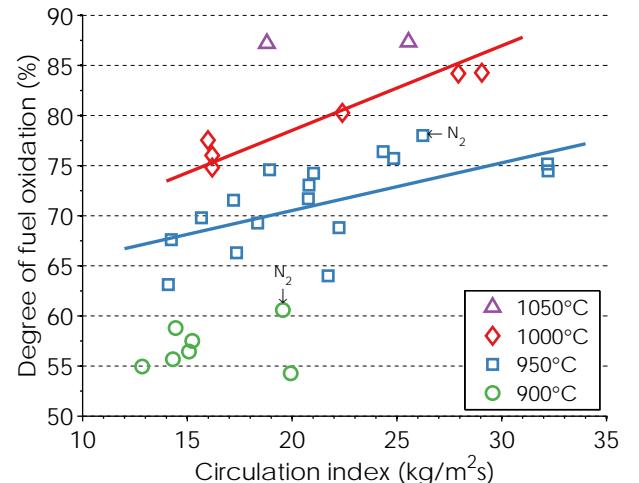


Figure 6: Degree of fuel oxidation with ilmenite oxygen-carrier for different fuel-reactor temperatures. The fuel flow corresponds to about 4 kW_{th}. Each data point represents average values of one experimental setting, which lasted 20–189 min, and 86 min on average.

The effect of variation of fuel flow is shown in Figure 7. Here, the degree of fuel oxidation is shown for fuel flows that correspond to about 4 kW_{th} and 6 kW_{th}. A clear increase in degree of oxidation with both increasing temperature and decreasing fuel flow can be seen. The difference in fuel oxidation between the two fuel flows tested is about 10 %-points. Reasons for that can be one or a combination of the following:

- Decrease in the contact time between gas and solids due to increased gas flow in the fuel reactor.
- Higher bypass of combustible gases through gas channels in the fluidized bed of the fuel reactor.
- Reduced reactivity of the oxygen carrier in the fuel reactor; ilmenite has a decreasing reactivity for conversion of CH₄, CO and H₂ the more its degree of oxidation is reduced.^{22,30,31}

In all experiments the average leakage of fuel carbon to the air reactor was usually below 1 mol% and never above 2 mol%.

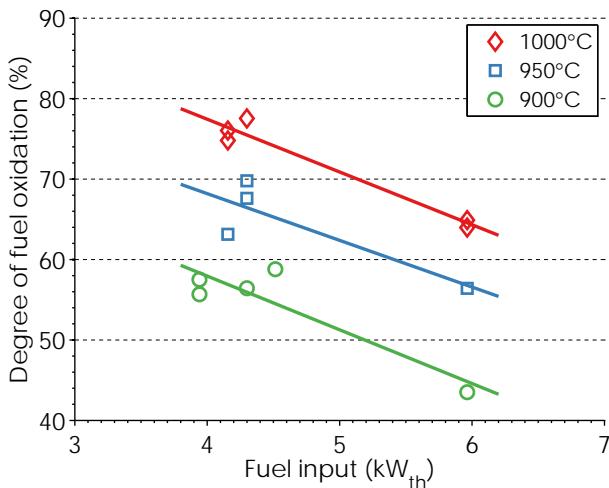


Figure 7: Degree of fuel oxidation with ilmenite oxygen-carrier for different fuel-reactor temperatures and fuel flows. The circulation index for all data points shown was similar and 14–17 kg/m²s.

As was already discussed in section 4.1, the calculated carbon fraction is sensitive to changes in the measured CO₂ concentration. The fact that the CO₂ concentration in the air reactor was very close to the atmospheric concentration of CO₂ as well as the lower detection limit of the gas analyzer adds a certain margin of error to the results. However, it can be said with certainty that carbon leakage to the air reactor is very low, and hence a very high degree of carbon capture was achieved.

Figure 8 shows different carbon fractions in the fuel reactor, i.e., how much of the total carbon in the fuel reactor is in the form of (a) CO₂, (b) CO, (c) CH₄ and (d) organic compounds C_xH_yO_z, not including methane. The two experiments with nitrogen instead of steam as fluidization medium in the fuel reactor are labeled with “N₂”. The following observations can be made in Figure 8:

- The CO₂ yield increases with increased temperature and increased circulation index, see Figure 8a. The maximum CO₂ yield was about 87 mol%.
- The fraction of organic compounds and CH₄ decrease with increased temperature and increased circulation index, see Figure 8c and 8d.
- The carbon fraction of CO increases from 900°C to 950°C and decreases from 1000°C to 1050°C, see Figure 8b. The CO fractions at 950°C and 1000°C are similar as well as those at 900°C and 1050°C. Thus, the carbon fraction of CO seems to reach a maximum between 950°C and 1000°C.
- The use of nitrogen as fluidization medium has a clear benefit on the CO₂ yield (increased), see Figure 8a, and on the organic compounds (decreased), see Figure 8d. The carbon fractions of CO and CH₄ are not distinctly affected.

The measured concentration of hydrogen was generally proportional to the carbon fraction of CO in Figure 8b and varied

between 6 vol% and 16 vol%. The concentration of hydrogen decreases with increasing circulation of solids and seems to peak between 950°C and 1000°C. When steam was used to fluidize the particles in the fuel reactor, the concentration of hydrogen measured was always below, usually about half, the equilibrium concentration predicted by the water–gas shift reaction. This is in agreement with the findings by Schwebel et al.³². However, when nitrogen was used as fluidization medium in the fuel reactor, the measured concentration of hydrogen matched the equilibrium value and hence it could be speculated that metallic Fe-sites promote the water–gas shift reaction, see section 5 below. Naturally, the hydrogen concentration for nitrogen fluidization was much lower than the concentration with steam fluidization and about 2–3 vol%.

4.2.2. Particle Analysis

A particle size distribution obtained by sieving shows that the particle diameter has increased during the long-term testing, see Figure 9. It should be mentioned that fines produced during the experiments were elutriated in the cyclone, together with varying amounts of larger particles, and caught in the bag filters of the system. The amount of fines was low but difficult to quantify, as the content of the bag filters was usually refilled back into the system, including fines.

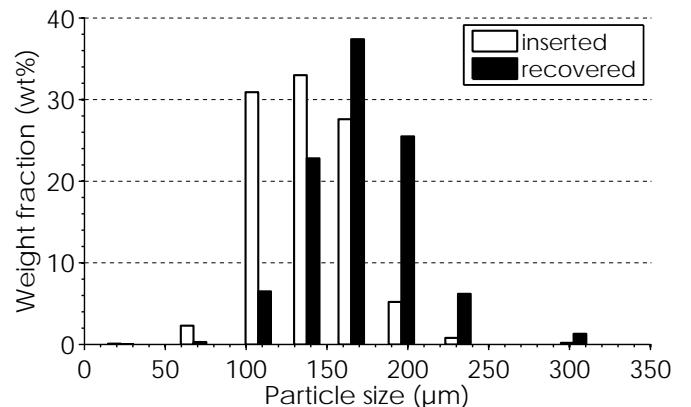


Figure 9: Particle size distribution of ilmenite oxygen-carrier before and after long-term testing with fuel oil Eo1 E10

Light-microscope pictures were taken before and after the long-term testing, see Figure 10. The shape of the particles has become more rounded and the color changed from dark gray to brown. An increase in particle size is also visible. Table 5 shows a summary of the characteristics of ilmenite oxygen-carrier before and after the long-term testing. The physical integrity of the ilmenite oxygen-carrier was experienced to be good and no indications have been found that it is deteriorated during the long-term testing.

5. Discussion

The oxidation of hydrocarbons is complicated. A detailed model for oxidation of iso-octane, for example, includes 3600 elementary reactions with 860 chemical species.³³ This particular model is validated by experiments that cover a wide range

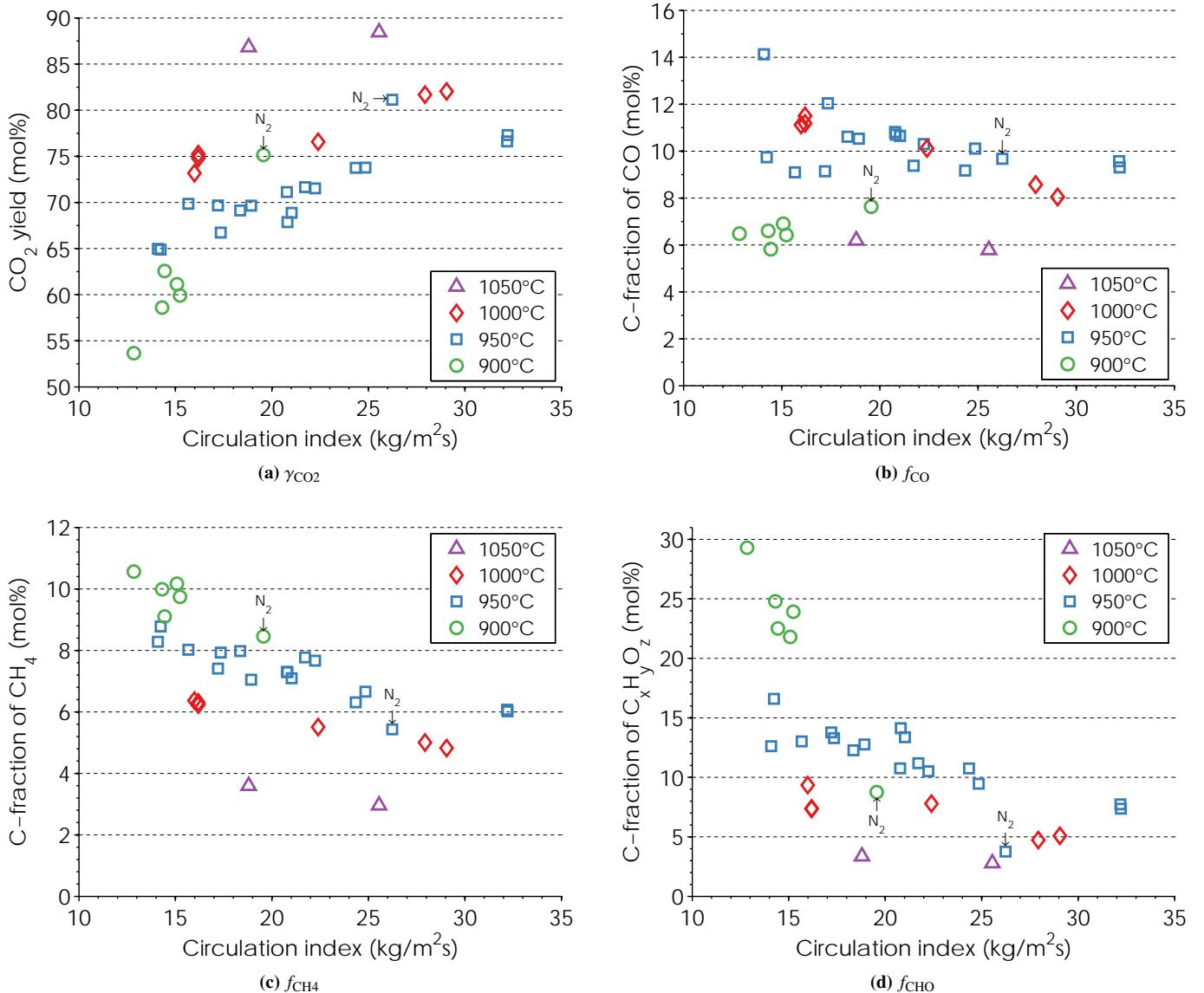


Figure 8: Carbon fractions in the fuel reactor with ilmenite oxygen-carrier. (a) γ_{CO_2} (CO_2), (b) f_{CO} (CO), (c) f_{CH_4} (CH_4) and (d) f_{CHO} (organic compounds without CH_4). The fuel flow corresponds to about 4 kW_{th} .

Table 5: Ilmenite particle characteristics in fresh and used state

	Fresh	Used
Mean particle size (μm)	131	162
Bulk density (kg/m^3)	2575	1740
Colour	Dark gray	Brown
Shape	Irregular with sharp edges	Irregular with rounded-off edges

of physical conditions and practical applications, respectively. Usually hydrocarbons undergo reactions like thermal cracking, so-called β -scission, where carbon–carbon bonds are split, hydrogen-atom abstraction, where hydrogen atoms are transferred from hydrocarbon to a radical, isomerization, partial oxidation and others. The conditions in a fuel reactor in chemical-loop-

ing combustion differ from regular combustion in air. The fuel is normally not surrounded by oxygen in the gas phase, and the main oxygen-transfer mechanism is through noncatalytic gas–solid reaction, although certain metals can have catalytic effects. It is not clear whether the established reaction mechanisms for burning of hydrocarbons, see, e.g., Chakir et al.³⁴, are changed fundamentally. Many reactions are triggered by high temperatures, greater than 850°C , and should be valid in chemical-looping combustion.

From the results in this study, there is formation of CH_4 , CO and H_2 at all temperatures, see Figure 8. Hence, it is likely that these are important intermediate compounds in the overall oxidation process. Reaction (R2) is a bulk reaction that contains breakdown and partial oxidation of hydrocarbons to CO and H_2 by the oxygen carrier (MeO_x denotes the oxidized form and MeO_{x-1} denotes a reduced form). Reaction (R3) is a steam-

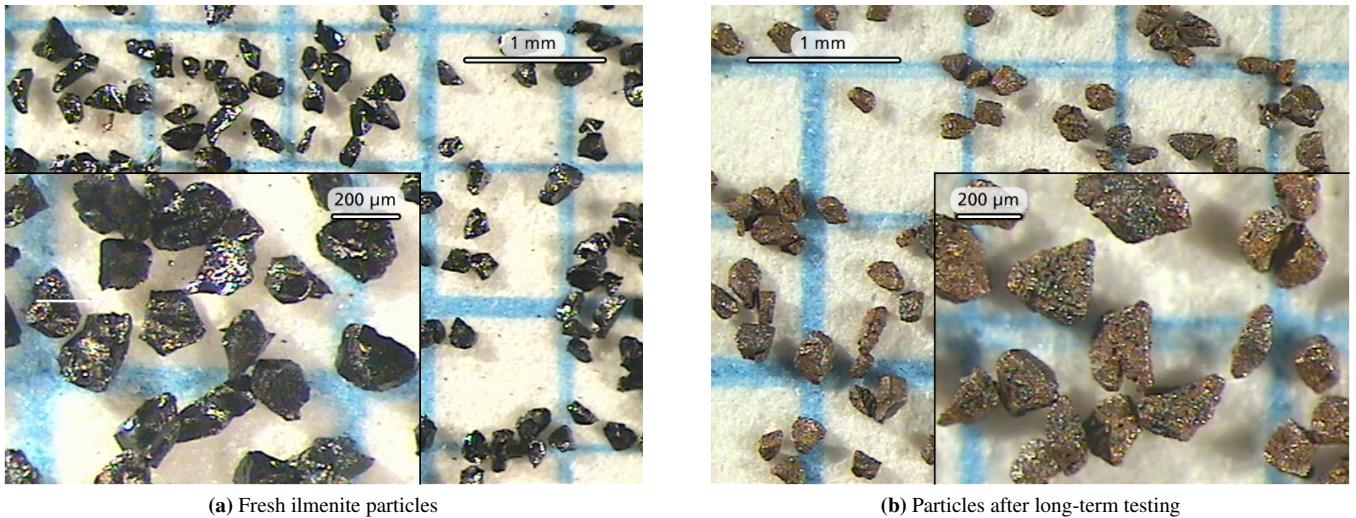
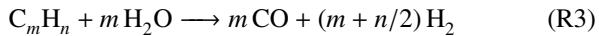
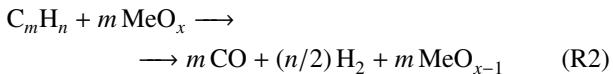
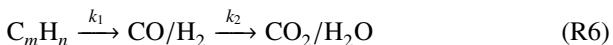


Figure 10: Microscope images of ilmenite particles before and after long-term testing with fuel oil Eo1 E10

reforming reaction and describes another possibility of partially oxidizing fuel to CO and H₂. Reactions (R2) and (R3) represent the vast majority of reactions occurring during the conversion of liquid fuel to CO₂ and H₂O. There is a decrease in the hydrocarbon content as the temperature is increased, but it is not possible to distinguish which reaction is dominating, as the rate of both reactions likely increases as a function of temperature.



Reactions (R4) and (R5) represent the last oxidation step of intermediate products CO and H₂ to CO₂ and H₂O. As was shown by Adámez et al.²⁰ and Jerndal et al.³¹, the reactivity of ilmenite oxygen-carrier with H₂, as in reaction (R5), is much higher than that with CO, as in reaction (R4), and the latter should be the limiting step. The dependence of temperature on the conversion of fuel, as seen in Figure 8, could be explained by the following general reaction sequence:



Below 950°C reactions (R4) and (R5) are faster than reactions (R2) and (R3), i.e., $k_2 > k_1$. Consequently, reactions (R2) and (R3) limit the overall conversion process, and hence there is a rather low fraction of CO. The rates of reactions (R2)–(R5) increase with temperature, but the rate of reactions (R2) and (R3) increase faster than that of reactions (R4) and (R5) in the investigated temperature range. At high temperatures CO, and H₂, is rapidly converted by the ilmenite, which is supported by Berguerand et al.³⁵. It is likely that the actual conversion mechanism is rather complicated, involving the breakdown and partial oxidation of hydrocarbons to other radical and saturated

compounds containing C, H and/or O and the oxidation of radicals to CO₂ and H₂O via CO and H₂.

The fact that the use of nitrogen as fluidization medium in the fuel reactor enhanced the conversion of liquid fuel was surprising. Steam gasification is believed to play an important role in hydrocarbon conversion and replacing steam with nitrogen for fluidization was expected to result in a lower conversion of fuel. It is suspected that the benefits observed are a result of catalytic properties of metallic iron, which can be formed on the oxygen carrier if reduced sufficiently far. Thermodynamic-equilibrium calculations were performed for the conditions in the fuel reactor with steam and nitrogen fluidization. It was found that metallic iron can be theoretically formed when nitrogen is used as a fluidization medium but not when steam is used. The reason for this is that the ratio of H₂ to H₂O has to be below a certain level before metallic iron can be formed. However, this level is not achieved during fluidization with steam. Since the oxygen-carrier particles in the fuel reactor contain much more oxygen than is needed for complete oxidation of fuel, a reduction to metallic iron is restricted to zones with a high fuel-to-oxygen carrier ratio, e.g., in the fuel-injection zone. It is usually not regarded as beneficial to form metallic iron or FeO (wüstite), because those species have poor thermodynamic conversion to CO₂ and H₂O, and are also prone to agglomerate.¹⁸ In an industrial-scale process, the use of nitrogen would not be reasonable, as the purpose of a chemical-looping combustion process is to obtain pure CO₂. The use of recirculated flue gases, which consist mostly of CO₂ and H₂O, as fluidization medium might pose an alternative to the use of pure steam. Using recirculated flue gases, however, is not likely to have a noticeable effect on fuel conversion, as thermodynamic properties of H₂O and CO₂ are similar.

If the process is to be scaled up to an industrial scale, it would be an advantage if fuel conversion is improved in order to avoid costs for reaching full conversion, e.g., through oxygen polishing. Preferably, an improved conversion should also be attained while reducing the oxygen carrier-to-fuel ratio.

During the experiment campaign presented here this ratio was 1400–2100 kg/MW_{th}, which is high. Based on the experience obtained in the experiments performed, some potential areas of improvement of the process are suggested.

1. It is expected that the injection of larger fuel flows would mean that more efficient injection nozzles could be employed. Fuel atomization, for example, is believed to increase the contact between fuel and oxygen-carrier particles and thus increase conversion of fuel. A key to reaching high conversion in a larger scale is to distribute the combustible gases over the cross-section with a limited number of fuel feeding locations. A solution for this has been suggested by Lyngfelt et al.³⁶.
2. The fuel reactor could be designed as a circulating fluidized-bed. In a circulating fluidized-bed the contact between gas, i.e., partially converted fuel for applications with liquid fuel, and oxygen carrier is higher than in a bubbling fluidized-bed. Also, circulating fluidized-beds usually allow for a higher throughput of fuel per cross-sectional area of the reactor.
3. The use of an oxygen-carrier material that releases gas-phase oxygen in the fuel reactor, i.e., an oxygen carrier with so called CLOU (chemical-looping with oxygen uncoupling) properties, is expected to improve fuel conversion notably. A more thorough discussion of the advantages of employing oxygen-carrier materials with CLOU properties in chemical-looping combustion can be found in an earlier publication by the authors¹⁰. When comparing the results of the two oxygen carriers tested here, the calcium manganite-based material, which has CLOU properties, achieved a significantly higher degree of fuel oxidation than ilmenite: at 850–900°C the degree of fuel oxidation was 68–77% for the calcium manganite-based oxygen carrier, see Table 4, whereas ilmenite could achieve 65% at 1000°C at comparable fuel flows, see Figure 7. No experiments were conducted at higher temperatures with the calcium-manganite-based material, but this would clearly be of interest. Another possible oxygen-carrier material with CLOU properties is copper oxide. In a previous paper, Moldenhauer et al.¹⁰ used a copper-based oxygen carrier in a smaller CLC reactor with kerosene as fuel, and it was found to have superior fuel conversion compared to regular oxygen-carrier materials such as ilmenite. Other potential materials are combined manganese oxides tolerant to sulphur, such as some of those tested by Arjmand et al.¹⁷. The drawback of these types of material is the much higher cost, compared to natural oxygen carriers, and the stability may be questionable for some materials as well.

One remark should be made concerning the temperature interval that was investigated in the experiments presented here. Current circulating fluidized-bed boilers typically operate at about 850°C, which is considerably lower than 1050°C, i.e., the highest temperature investigated here. The most important factor limiting the temperature upward in conventional CFB

boilers is the high ash content of solid fuels: approaching the melting point of the ash can cause agglomeration of bed material, corrosion, and fouling of heat exchanger surfaces or other equipment. Liquid hydrocarbon fuels have dramatically lower ash content than solid fuels. This might resolve most ash related problems and should make operation at higher temperatures feasible. Also, it is not obvious that oxygen carriers have agglomeration properties similar to those of conventional inert bed materials. Thus, it is of interest to examine if chemical-looping combustion operation at temperatures higher than those of conventional circulating fluidized-bed boilers would be possible, as high temperature typically improves reaction kinetics.

6. Summary and Conclusions

A fuel reactor with an in situ fuel-injection system for fuel oil was designed and constructed for a chemical-looping reactor system with the nominal fuel input of 10 kW_{th}. The riser and nozzle velocities are comparable to those of an industrial circulating fluidized-bed boiler. Proof-of-concept experiments were performed using an oxygen carrier with CLOU properties, which was based on calcium manganite. During the experiments, fuel conversion was high but not complete and most of the fuel carbon was converted to CO₂ in the fuel reactor. Carbon leakage to the air reactor was very low and close to the detection limit. The corresponding fraction of fuel carbon was usually below 1 mol%.

Successful long-term experiments were performed using an ilmenite oxygen-carrier. Fuel addition took place during almost 67 h and the oxygen carrier was fluidized at hot conditions for more than 200 h. A temperature interval of 900–1050°C was tested at a varied circulation of solids. The fuel input was 4 kW_{th} and 6 kW_{th}, which corresponds to an oxygen carrier-to-fuel ratio in the fuel reactor of about 2100 kg/MW_{th} and 1400 kg/MW_{th}, respectively. Fuel oxidation increased with higher temperatures, higher circulation rates of oxygen carrier and lower fuel flows. At 1050°C and a fuel flow corresponding to 4 kW_{th}, the fuel could be oxidized to about 87% and up to 88% of all carbon leaving the fuel reactor was in the form of CO₂. Carbon leakage to the air reactor was very low and close to the detection limit. The corresponding fraction of fuel carbon was usually below 1 mol%.

The following conclusions can be drawn:

- Fuel injection of low-sulphur fuel oil was successful after solving problems regarding fuel fouling in the injection system.
- Stable operation was achieved.
- The integrity of the ilmenite oxygen-carrier was high and no noteworthy problems, such as high formation of fines, agglomeration of bed material or defluidization, were encountered.
- The use of nitrogen as fluidization medium in the fuel reactor seemed to improve the oxidation of fuel. The reason for this is not clear, but the use of nitrogen as fluidization medium in an industrial-scale process is anyway not reasonable.

Nomenclature

dh_{exit}	(m)	height difference of pressure drop dp_{exit}
dp_{exit}	(Pa)	pressure drop at the exit of the riser
$f_{\text{C,AR}}$	(mol%)	carbon fraction of fuel carbon leaking to air reactor
f_{CH_4}	(mol%)	carbon fraction of CH_4 in fuel reactor
f_{CHO}	(mol%)	carbon fraction of $\text{C}_x\text{H}_y\text{O}_z$ without CH_4 in fuel reactor
f_{CO}	(mol%)	carbon fraction of CO in fuel reactor
g	(m/s ²)	gravitational acceleration constant = 9.81 m/s ²
G_s	(kg/m ² s)	mass flux of oxygen carrier
G'_s	(kg/m ² s)	circulation index (gross mass-flux of oxygen carrier)
$\dot{n}_{\text{C,fuel}}$	(mol/s)	molar flow of elemental carbon in the fuel added
$\dot{n}_{\text{CO}_2,\text{AR,out}}$	(mol/s)	molar flow of carbon dioxide leaving the air reactor compensated for atmospheric CO_2 concentration (≈ 400 ppm)
$\dot{n}_{\text{O}_2,\text{AR,in}}$	(mol/s)	molar flow of oxygen entering the air reactor
$\dot{n}_{\text{O}_2,\text{AR,out}}$	(mol/s)	molar flow of oxygen leaving the air reactor
$\dot{n}_{\text{O}_2,\text{stoich}}$	(mol/s)	stoichiometric molar flow of oxygen for combustion of fuel
u_0	(m/s)	superficial gas velocity
u_t	(m/s)	terminal velocity based on average particle size
γ_{CO_2}	(mol%)	CO_2 yield
Δp	(Pa)	pressure drop measured in middle section of the riser
Δh	(m)	height difference of middle section of the riser = 0.678 m
η_{fuel}	(%)	degree of fuel oxidation
ρ_{exit}	(kg/m ³)	(two-phase) bed density at the exit of the riser

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