# Apparent kinetics derived from fluidized bed experiments for Norwegian ilmenite as oxygen carrier

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## ARTICLE INFO

## ABSTRACT

Chemical-looping combustion (CLC) is one of the most promising methods for $CO_2$-capture. Regarding the use of solid fuels in CLC, it is assumed that the lifetime of the oxygen carrier material will be lowered preferring low cost and environmental sound materials. In this work apparent kinetics for the reduction of a natural rock ilmenite from Norway are derived from experimental data while utilizing CO, $H_2$ and $CH_4$ as fuel gases. CO, $H_2$ and $CH_4$ are the main combustible gases in solid fuel CLC. The experiments were carried out in a laboratory batch fluidized bed reactor. The reactor was heated to bed temperatures varying from 850 to 950 °C. Different fuel gas concentrations were achieved by diluting the fuel flow with nitrogen. For $H_2$, pulsed reduction experiments have been accomplished to allow the calculation of conversion dependent rates.

The experimental conversion rates were fitted to different model approaches in order to derive the apparent kinetic parameters. Thereby the oxygen carrier conversion was represented by the mass based conversion $\omega$. The results are compared to published data. The reaction order with respect to the gas phase is close to the reported values. Only the reaction order obtained for $CH_4$ with the fitted power law deviated with about 40%, what could indicate a limitation of available surface for the heterogeneous decomposition of $CH_4$. Although the overall agreement between fitted power laws and experimental data was appropriate, their extrapolation outside the experimental data range has to be done with care.

## Introduction

Chemical-looping combustion (CLC) is a promising method to accomplish $CO_2$ capture when converting carbon based fuels [1]. Both economic as well as technical penalties have the potential to be lower than other capture concepts [2].

In general, the denotation "chemical-looping" can be connected to the use of solid oxygen carrier materials, e.g. metal oxides, which provide oxygen through their reduction for the thermochemical conversion of different fuels in the reduction step (Fig. 1). There the net supply of oxygen during reduction may follow different heterogeneous reaction pathways and does not necessarily include gas phase oxygen. For most of the oxygen carrier materials and reaction conditions investigated so far, the reaction pathway does not include gas phase oxygen. In contrast to that, the use of some materials allows the oxygen to be transported via the gas phase under certain conditions, i.e. if the partial pressure of oxygen over the specific oxide is high enough under the reaction conditions. In all cases the reduced oxygen carrier is recharged with oxygen from air in a separate reaction step, i.e. the oxidation. Both the reduction and the oxidation are
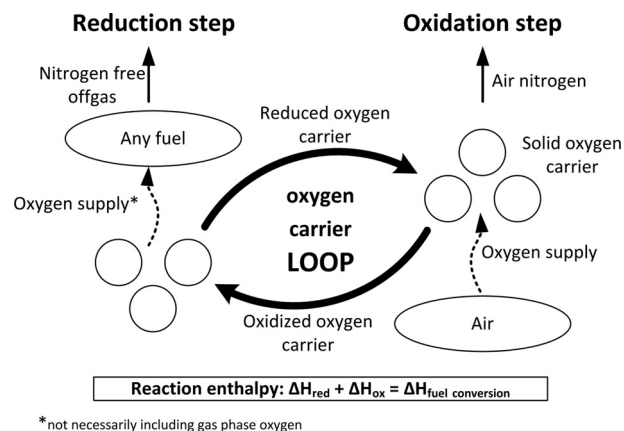


**Fig. 1.** General principle of chemical-looping for thermochemical fuel conversion.

connected via a loop of reduced and oxidized oxygen carrier material.

To carry out these two steps different reactor concepts are under investigation. In the case of conventional chemical-looping combustion, as of interest in the current publication, the reduction and oxidation are carried out in two separate reactors, the air reactor and the

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fuel reactor, respectively. Both reactors are connected by a circulating stream of solid oxygen carrier. While carrying out the reaction steps in two separate reactors, the off gases never mix.

In the air reactor the oxygen carrier is oxidized exothermally by addition of air. The hot excess gas flow from this step can be utilized for power generation. The oxidized oxygen carrier is transferred to the fuel reactor where fuel is added. This principle was proposed in the 1940s [3] to reform methane and it has been patented as an envisaged process for $CO_2$ production from carbonaceous sources [4]. A similar principle was proposed with the goal to lower the irreversibilities of combustion [5,6]. With increasing recognition of the climate change, "chemical-looping-combustion" was investigated to recover $CO_2$ from the exhaust in high concentrations [7,8]. Since then, the capture of $CO_2$ with low energy penalty is the main driving force for the research carried out in that field.

There are two main mechanisms of oxygen transfer from the carrier to the fuel. (I) Gas phase oxygen release from the oxygen carrier and subsequent reaction with the fuel, referred to as CLOU (chemical-looping with oxygen uncoupling [9]) or (II) by heterogeneous reaction between reducing gases like CO and the oxygen carrier particles. If solid fuels are applied directly, the second mechanism requires the gasification of the fuel char which is known to be orders of magnitude slower than its combustion [10] under absence of an oxygen carrier. The rate of gasification increases within CLC due to the consumption of $H_2$ known to inhibit the gasification [11]. However, in CLC the char gasification is still the rate limiting step while solid–solid reactions between oxygen carrier and fuel as found in dedicated experiments with copper based particles [12] are expected to be of low practical relevance.

Depending on the oxygen carrier and fuel combination, the reduction step can either be endo- or exothermic [13]. A nitrogen free stream of conversion products, i.e. mainly $CO_2$ and $H_2O$, are released from the fuel reactor. After condensation of the water, almost pure $CO_2$ is ready for further storage. In recent years, the focus of the research has turned to the use of solid fuels. Thereby losses of active material due to possible side reactions of the oxygen carrier and ash as well as due to oxygen carrier material being withdrawn from the reactor with the ash may lead to high expected amounts of oxygen carrier make up [14]. This leads to a demand for abundant, low cost and environmental friendly oxygen carrier materials [15]. Possible materials are natural ores or residues from steel production. Finding promising oxygen carrier materials in extractive or steel industry, also offers the opportunity to insert CLC into the industrial process chain, as proposed, e.g. for hematite or ilmenite in a German patent [16]. Thereby these energy and emission intensive processes could achieve easy $CO_2$ capture by available means. The oxygen carrier investigated in this study is a natural rock ilmenite from Norway. Ilmenite mainly serves as raw material for the pigment industry generating pig iron as by product. Other applications include the production of metallic titanium and to a minor extent the use for refractory maintenance in blast furnaces. A good overview on the production and use of ilmenite ores can be obtained from [17] or [18]. In CLC ilmenite is one of the most investigated oxygen carrier materials with focus on solid fuel application [14,19–32].

A review on the chemical-looping combustion technology can be found in [33,34] or in a more recent work [35].

During modeling, investigation, design and operation of CLC reactor systems, the description of the system requires the time resolved description of the ongoing reactions. The solids inventory per unit fuel power together with the solids circulation rate both presented in [36] are important constituents. The solids inventory is dependent on the integral reaction rate obtained either in the fuel or in the air reactor for chosen process parameters, e.g. temperature, fuel and stoichiometry. The solids circulation rate results from the oxygen carrier conversion achieved in one reactor and is therefore also dependent on a temporal and spatial resolved reaction rate. Thus, a description

of the reaction rate or reactivity of the oxygen carrier in dependence of the temperature and the concentration of reactants is crucial [37].

In general, the reactions for reduction and oxidation of the solid oxygen carrier in chemical-looping combustion are noncatalytic gas–solid reactions in the form of Eq. (1).

$$\nu_1 A_g + \nu_2 B_s \leftrightarrow \nu_3 C_g + \nu_4 D_s \qquad (1)$$

Herein $\nu_i$ is the stoichiometric coefficient of the reactant $i$, $s$ indicates the reactants in solid state and $g$ indicates the reactants in gaseous state. The main difference to catalytic gas–solid reactions is that the solid particle changes throughout the reaction since it takes part in the reaction [38]. Another straight forward example is the combustion of coal. The conversion rates observed for reactions like this do not only results from the chemical reaction kinetics but also from other rate limiting effects, i.e. inner mass transfer. Since the mass transfer ability is dependent on the solids size, structure and composition, its characteristics change throughout the reaction as the solid reactant is converted.

In order to account for the changes within the solid, structural models are used. A review on the different types of models available is found in [39]. During determination of the kinetic parameters from experimental data, the application of structural models helps to determine the effect of the chemical reaction. In CLC research, the application of structural models for kinetic analysis is common. A shrinking unreacted core model was used to interpret the experimental reaction rates obtained from TGA experiments for the oxidation and reduction of NiO/YSZ (yttria-stabilized zirconia) particles [40] and NiO/bentonite particles [41]. In both studies, the oxidation reaction was described including diffusional control. For modeling the reduction of Cu based particles produced by impregnation, a shrinking unreacted core model for plate like geometries with the chemical reaction considered as only resistance was used [42]. The reduction of Norwegian rock ilmenite, like the one used in this study, in a thermo gravimetric analyzer (TGA) was described with a changing grain size model [37].

In [43], the use of empirical models was investigated. A number of sixteen structural models including different resistances have been compared to seven empirical models. The authors fitted all models to the same experimental data taken from the literature. Although the performance of the empirical models was said to be good, the authors state that the use is limited to the area covered by the experimental data, since their structure is made from polynomial and exponential functions. Thus, the presented concept appears interesting since the models are highly flexible.

In the present work reactivity data are gained from laboratory batch fluidized bed experiments. Previously, the solids inventory was derived from a general normalized rate calculated from experimental data obtained at one temperature and one inlet concentration [44]. Therefore, a first order reaction with respect to the fuel gas and negligible resistance between bubble and emulsion phase was assumed. The results obtained give good indications of the performance of different oxygen carriers, and account for the incomplete gas conversion found in the experiments. The validity of this description can be extended if data for different temperatures as well as for different gas concentrations would be included. Furthermore the influence of the solids conversion is not accounted for. Hence, the effective rate constant was found to vary with the conversion of the oxygen carrier [44].

This work aims at a description of the reduction rate depending on the oxygen carrier conversion, reactant gas concentration and temperature. CO, $CH_4$ and $H_2$ have been applied as fuel gases for the reduction of activated Norwegian ilmenite. The operational parameters are chosen close to those used in experiments for the characterization of oxygen carrier particles, i.e. high fuel gas concentration combined with low reduction times [25,32]. The apparent kinetic data were obtained by fitting the equation parameters to experimental values