THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Investigation of Nickel- and Iron-Based Oxygen Carriers for Chemical-Looping Combustion

ERIK JERNDAL

Department of Chemical and Biological Engineering
Environmental Inorganic Chemistry
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2010

Investigation of Nickel- and Iron-Based Oxygen Carriers for Chemical-Looping Combustion

ERIK JERNDAL

ISBN 978-91-7385-425-2

Doktorsavhandlingar vid Chalmers Tekniska Högskola
Ny Serie Nr 3106
ISSN 0346-718X

Department of Chemical and Biological Engineering
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Phone: +46 (0)31-772 10 00

erik.jerndal@chalmers.se

Chalmers reproservice
Göteborg, Sweden 2010

Investigation of Nickel- and Iron-Based Oxygen Carriers for Chemical-Looping Combustion

Erik Jerndal
Department of Chemical and Biological Engineering, Environmental Inorganic Chemistry, Chalmers University of Technology

ABSTRACT

Carbon capture and storage has the potential of reducing emissions of CO_2, generated by combustion of fossil fuels. Chemical-looping combustion is a method intended to capture CO_2 without an energy consuming gas separation process. Gas separation is avoided by using circulating oxygen carriers to transfer oxygen from an air reactor to a fuel reactor. Thus, the fuel and the combustion air are never mixed.

A thermal analysis of the process identified several oxygen carrier systems with properties suitable for chemical-looping combustion applications. Such properties include high ability to convert different fuels, stability in air and sufficiently high melting temperature. Systems fulfilling these criteria were; metal oxides based on Ni, Cu, Fe, Mn, Co, W and sulphates of Ba, Sr and Ca.

In the experimental part of this work, Ni- and Fe-based particles were analyzed with respect to both chemical and physical properties important for oxygen carriers in chemical-looping combustion, as well as gas conversion in a fluidized bed.

Oxygen carriers of NiO, supported by $NiAl_2O_4$, are suitable for converting gaseous fuels with a high content of CH_4. The main reasons are their high reactivity and high melting temperature. The Ni-based oxygen carriers investigated here were prepared from commercially available raw materials in contrast to the pure chemicals which have generally been used before. Oxygen carriers prepared by spray-drying, a production method suitable for large-scale particle preparation, displayed similar properties as oxygen carriers produced by the small-scale freeze-granulation method. Thus, up-scaling of particle production is not expected to present any difficulties. To reduce the risk of fragmentation and attrition of Ni-based oxygen carriers in a circulating chemical-looping combustion system, the strength can be improved by an addition of $Ca(OH)_2$, by increasing the sintering temperature or by extending the sintering time. Materials with MgO added during particle preparation or with $MgAl_2O_4$ as supporting agent resulted in a considerably increased CH_4 conversion. All oxygen carriers showed high reactivity with CH_4 and O_2 and a for a promising oxygen carrier of $NiO/NiAl_2O_4$, it was concluded that in an ideal reactor without gas solid-phase mass transfer limitations, full CH_4 yield should be reached with a solids inventory in the fuel reactor of less than 10-20 kg/MW at 950°C.

Fe-based oxygen carriers are cheap, abundant and environmentally sound and therefore well suited for chemical-looping combustion with solid fuels, where the expected lifetime of the oxygen carriers is comparatively short. Several industrial iron-based materials and a natural iron ore with properties well suited for chemical-looping combustion with solid fuels were identified. Generally, these materials displayed a high conversion of syngas, the main intermediate when solid fuels are gasified by steam, in combination with a high mechanical strength. The investigation of synthetically produced ilmenites, $FeTiO_3$ in their reduced form, revealed that an increased Fe:Ti ratio generally improves the total conversion of CO although the initial maximum conversion is relatively constant.

Keywords: Carbon Dioxide Capture, Chemical-Looping Combustion, Fluidized Bed, Oxygen Carrier, Nickel Oxide, Iron Oxide, Ilmenite

LIST OF PUBLICATIONS

The thesis is based on the work contained in the following papers, referred to by Roman numbers in the text

Paper I

Jerndal E, Mattisson T, Lyngfelt A, 2006, *Thermal Analysis of Chemical-Looping Combustion.* Chemical Engineering Research and Design, 84(A9), 795-806.

-This Paper was recognized on a shared 1st place in the "Top-75 most cited articles" as published in the IChemE journals 2006-2009.

Paper II

Jerndal E, Mattisson T, Lyngfelt A, 2009, *Investigation of Different $NiO/NiAl_2O_4$ Particles as Oxygen Carriers for Chemical-Looping Combustion.* Energy & Fuels, 23(2), 665–676.

Paper III

Jerndal E, Mattisson T, Thijs I, Snijkers F, Lyngfelt A, 2010, *Investigation of $NiO/NiAl_2O_4$ Oxygen Carriers for Chemical-Looping Combustion Produced by Spray-Drying.* International Journal of Greenhouse Gas Control, 4(1), 23–35.

Paper IV

Jerndal E, Mattisson T, Thijs I, Snijkers F, Lyngfelt A, 2009, *NiO Particles with Ca and Mg based Additives Produced by Spray-Drying as Oxygen Carriers for Chemical-Looping Combustion.* Energy Procedia, 1, 479-486. (9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), Washington D.C., 16-20 November, 2008.)

Paper V

Mattisson T, Jerndal E, Linderholm C, Lyngfelt A, 2010, Reactivity of a Spray-Dried $NiO/NiAl_2O_4$ Oxygen Carrier for Chemical-Looping Combustion. Submitted for publication.

Paper VI

Azis M M, Jerndal E, Leion H, Mattisson T, Lyngfelt A, 2010, *On the Evaluation of Synthetic and Natural Ilmenite using Syngas as Fuel in Chemical-Looping Combustion (CLC).* Chemical Engineering Research and Design, In Press, available online 27 March 2010.

Paper VII

Jerndal E, Leion H, Axelsson L, Ekvall T, Hedberg M, Johansson K, Källén M, Svensson R, Mattisson T, and Lyngfelt A, 2010, *Using Low-Cost Iron-Based Materials as Oxygen Carriers for Chemical-Looping Combustion.* Submitted to Oil & Gas Science and Technology – Revue de l'IFP. To be published in a Special Issue: 1st International Conference on Chemical Looping.

My contribution to the attended papers

Paper I; all calculations and writing
Paper II; all experimental work except preparation of oxygen carriers, all evaluation of experiments and writing
Paper III & IV; all experimental work, evaluation of experiments and writing except the parts concerning preparation of oxygen carriers
Paper V; part of the experimental work, evaluation of experiments and modelling
Paper VI; part of the experimental work, evaluation of experiments and writing
Paper VII; part of the experimental work, evaluation of experiments and all writing

Related papers not included in the thesis

Mattisson T, Johansson M, Jerndal E, Lyngfelt A, 2008, *The Reaction of NiO/*$NiAl_2O_4$ *Particles with Alternating Methane and Oxygen.* Canadian Journal of Chemical Engineering, 86(4), 756-767.

Leion H, Lyngfelt A, Johansson M, Jerndal E, Mattisson T, 2008, *The Use of Ilmenite as an Oxygen Carrier in Chemical-Looping Combustion.* Chemical Engineering Research and Design, 86(9), 1017-1026.

Leion H, Jerndal E, Steenari B-M, Hermansson S, Israelsson M, Jansson E, Johnsson M, Thunberg R, Vadenbo A, Mattisson T, Lyngfelt A, 2009, *Solid Fuels in Chemical-Looping Combustion using Oxide Scale and Unprocessed Iron Ore as Oxygen Carriers.* Fuel, 88(10), 1945-1954.

Linderholm C, Lyngfelt A, Béal C, Trikkel A, Kuusik R, Jerndal E, Mattisson T, *Chemical-Looping Combustion with Natural Gas using Spray-Dried NiO-Based Oxygen Carriers.* In “Carbon Dioxide Capture for Storage in Deep Geological Formations”, Volume 3, Advances in CO_2 Capture and Storage Technology (2004-2009) L I Eide (Ed.), October 2009, 67-74.

Linderholm C, Jerndal E, Mattisson, T, Lyngfelt, A, 2010, *Investigation of Ni-Based Mixed Oxides in a 300 W Chemical-Looping Combustor.* Chemical Engineering Research and Design, 88(5-6) 661-672.

Snijkers F, Jerndal E, Thijs T, Mattisson T, Lyngfelt A, *Preparation of Oxygen Carriers for Chemical Looping Combustion by Industrial Spray Drying Method.* 1st International Conference on Chemical Looping**,** Lyon, 17-19 March 2010.

Jerndal E, Leion H, Mattison T, Lyngfelt A. *Using Low-Cost Iron-Based Materials as Oxygen Carriers for Chemical-Looping Combustion.* 1st International Conference on Chemical Looping, Lyon, 17-19 March 2010.

-This Paper is an “extended abstract” and a shorter version of Paper VII.