

Preliminary Assessment of Fluidized bed Sorption-Enhanced Methanation by CaO

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Highlights

- Sorption Enhanced Methanation using Calcium Oxide as sorbent material.
- Development of a Hydration/Deydration Looping Cycle in a Twin Fluidized Bed Reactor.
- Evaluation of H₂O capture capacity of CaO at different temperatures.

1. Introduction

Methane is an important energetic carrier for many sectors such as industry, energy and transportation. The largest source of methane is represented by fossil resources, but the growing debate on the utilization of fossil fuels in the frame of climate changes has stimulated growing interest towards catalytic and biological paths to production of methane [1-3]. In particular, the catalytic methanation ($4\text{H}_2 + \text{CO}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ or $3\text{H}_2 + \text{CO} = \text{CH}_4 + \text{H}_2\text{O}$, 200-300°C), discovered by Sabatier and Senders in 1902 [4], assumes an important role when combined with the concepts of chemical storage, solar fuels and utilization of CO₂. Methane could be considered as the final product for the storage of solar energy, initially converted into hydrogen by water splitting with photochemical and thermochemical processes [5]. Unlike hydrogen, the main advantage of methane is the current existence of a distribution infrastructure in many countries and its utilization in the automotive, furthermore methane benefits from a relatively large public acceptance. In addition, methanation could be considered as process for the utilization of CO₂ coming from fossil fuels in the framework of Carbon Capture and Utilization (CCU) technologies [6]. Conventional Sabatier process typically requires a cascade of adiabatic fixed bed reactors with intermediate cooling steps and recycles [1,7] and high operational pressure to yield a product matching the specification for injection in the natural gas infrastructure. Walspurger et al. [8] studied the possibility to improve the methanation process by the application of the concept of Sorption-Enhanced Methanation (SEM), where the steam generated by the reaction is continuously removed from the gas phase in the catalytic bed by adding a sorbent material. In this preliminary study a novel configuration for Sorption-Enhanced Methanation based on the technology of dual interconnected fluidized beds is investigated. The concept is based on a chemical looping reactor arrangement where the catalytic methanation occurs simultaneously with the hydration of the sorbent in one reactor (the Methanator), so as to drive the equilibrium towards product formation, while the regeneration of the sorbent (Dehydrator) takes place in another reactor. The material used as sorbent was CaO from natural limestone.

2. Methods

The sorbent was CaO obtained by calcination of a natural German limestone named EnBW: the material has been prepared in a lab-scale fluidized bed (40mm-ID) at 850°C with air and a fluidization velocity of 0.5m/s for 20min. The experimental apparatus (called Twin Beds) consists of two identical lab-scale bubbling beds of silica sand, acting as thermal ballast, operated batch-wise and connected by a rapid solids transfer line. This system is an *ad hoc* device to study looping processes and a complete description is reported elsewhere [9]. The two reactors were employed as Methanator/Hydrator and Dehydrator respectively. The experimental campaign was aimed at evaluating the capture and release water capacity of CaO at different temperatures and reaction environments. The investigation on the effect of reaction environments is not reported in this abstract, but will be presented in the full paper. The main operated conditions were: hydration with 10% steam (balance air) and dehydration in nitrogen. A sensitivity analysis on temperature has been carried out first fixing the hydration temperature at 250°C and varying the dehydration temperature at 350, 400 and 450°C (named H25A-D35N, H25A-D40N, H25A-D45N) and subsequently fixing the dehydration temperature at 400°C and varying the hydration one at 200, 250 and 300°C (named H20A-D40N, H25A-D40N, H30A-D40N). Hydration and dehydration reactions have been followed by measuring the

concentration of steam at the outlet by means of a humidity sensor, thus evaluating the absorbing capacity of the material after each cycle by performing 4 complete cycles, while the fluidization velocity was fixed at a value of 0.5m/s.

3. Results and discussion

Figure 1 shows the H₂O capture capacity of CaO, expressed as gram of H₂O captured per gram of initial sorbent, as a function of cycle number at different temperature of dehydration (fig.1A) and hydration (fig.1B). Generally, capture capacity seems to increase with the dehydration temperature after the first cycle, with a maximum identifiable around the 2nd-3rd cycle for H25A-D40N and H25A-D45N, while the value remains nearly constant for H25A-D35N (fig.1A). This behavior may be due to the different dehydration temperatures that could alter the structure of the sorbent (hence the pores) with consequent variation in sorbent capacity. On the contrary, during the first cycles the capture capacity decreases with hydration temperature. This trend is probably due to the increasing role of carbonation by CO₂ present in the air at higher hydration temperatures. Apparently, the effect of the hydration temperature vanishes after 4 cycles.

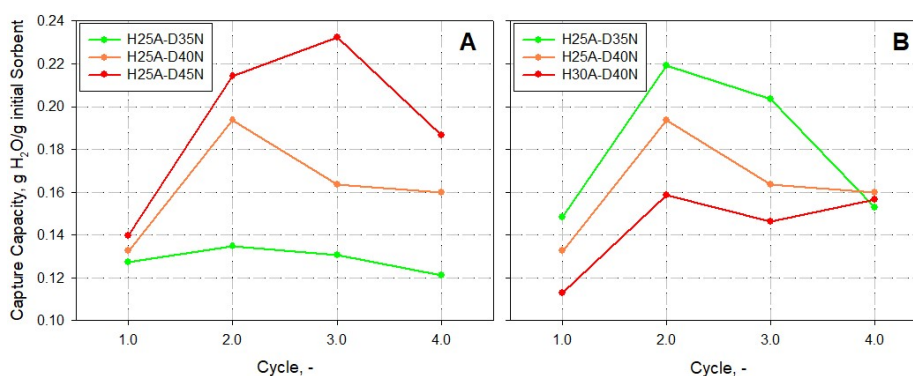


Figure 1. H₂O capture capacity of the sorbent along hydration stages.

4. Conclusions

CaO showed good H₂O capture capacity in the temperature range of interest for catalytic methanation. Moreover, cyclic Hydration/Dehydration tests demonstrated the potential of *in situ* steam uptake in a dual fluidized bed chemical looping reactor. Important results were obtained as to the competition between CO₂ and H₂O for the sorbent, which may negatively impact selective H₂O capture in the presence of CO₂. These results encourage the use of CaO for sorption-enhanced methanation of CO, but encourage the search for alternative sorbents for methanation of CO₂.

References

- [1] A.H. Seifert, S. Rittmann, C. Herwig, Appl. Energy 132 (2014) 155–162.
- [2] M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, et al. Renew. Energy 85 (2015) 1371-1390.
- [3] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, et al., Fuel 166 (2016) 276–296.
- [4] P. Sabatier, J-B. Senderens, Comptes Rendus Des Séances De L'Académie Des Sciences, Section VI – Chimie. Paris: Imprimerie Gauthier-Villars; 1902.
- [5] G.P. Smestad, A. Steinfeld. Ind. Eng. Chem. Res. 51 (2012) 11828–11840.
- [6] R.M. Cuéllar-Franca, A. Azapagic. Journal of CO₂ Utilization 9 (2015) 82–102.
- [7] M.V. Twigg, Catalyst Handbook, second ed., Manson Publishing Ltd., London, 1996.
- [8] S. Walspurger, G.D. Elzinga, J.W. Dijkstra, M. Saric, W.G. Haije. Chem. Eng. J. 242 (2014) 379–386.
- [9] A. Coppola, F. Scala, L. Gargiulo, P. Salatino, Powder Technol. 316 (2017) 585-591.

Keywords

Sorption Enhanced Methanation; Dehydration; Fluidized Bed; Calcium Oxide.

Antonio Coppola: Short CV

Antonio Coppola (AC) was born in Villaricca (Naples, Italy), on January 1st, 1984. He is research fellow at the Istituto di Ricerche sulla Combustione del Consiglio Nazionale delle Ricerche (Naples, Italy). AC obtained his PhD in Chemical Engineering in the Academic year 2012-2013 at the Department of Chemical Engineering of the University of Naples Federico II. His doctoral work, whose title is "Calcium Looping for CCS-ready combustion of solid fuels", deals with the CO₂ capture from flue gas derived from the combustion of fossil fuels. AC obtained his degree in Chemical Engineering (evaluation=110/110 cum laude) in the Academic Year 2008-2009 at the University of Naples Federico II.

His main scientific activities deal with: 1) Chemical processes in fluidized bed reactors; 2) Calcium Looping; 3) Chemical Looping Combustion; 4) Combustion in Fluidized Bed Systems. He is author of about 49 scientific papers, 18 of which appeared on international peer-reviewed Journals and about 31 of which appeared on the proceedings of international peer-reviewed Conferences. His "Hirsch index" is 9 (source: Scopus). His scientific activities have been carried out in collaboration with different public and private partners (such as, e.g., CERTH Greece, Wroclaw University of Technology Poland, University of Stuttgart Germany, Cranfield University UK, ALSTOM, CALCIDRATA Italy, University of Naples Federico II, University of Sannio), and within international and national financed projects (such as, e.g., European Coal and Steel Community, EU Research Fund for Coal and Steel, European Union Framework Programme projects, and Italian project Cattura della CO₂). He obtained the Elsevier prize "Top Cited Papers for 2011 and 2012", for the paper "Fluidized bed calcium looping: the effect of SO₂ on sorbent attrition and CO₂ capture capacity", *Chemical Engineering Journal*, 207-208, 2012, 445-449. He is Reviewer for several international Journals among the most important in the field of Chemical Engineering. He was Session Chairman for: 22nd International Conference on Fluidized Bed Conversion (Turku, Finland, June 14-17, 2015); 4th International Conference on Chemical Looping (Nanjing, China September 26-28, 2016); 40th Meeting of the Italian Section of the Combustion Institute (Roma, Italy, June 7-9, 2017). He was supervisor of about 12 Master Degree Theses in Industrial Chemistry, in Chemical Engineering and in Management Engineering.

Publication List: International peer-reviewed Journals

- 1) A. Coppola, F. Montagnaro, P. Salatino, F. Scala. Attrition of limestone during fluidized bed Calcium Looping Cycles for CO₂ capture. *Combustion Science and Technology* 2012, 184: 7-8, 929-941. DOI: 10.1080/00102202.2012.663986. (2015 Impact Factor: 1.193)
- 2) A. Coppola, F. Montagnaro, P. Salatino, F. Scala. Fluidized bed calcium looping: The effect of SO₂ on sorbent attrition and CO₂ capture capacity. *Chemical Engineering Journal* 2012: 207-208, 445-449. DOI: 10.1016/j.cej.2012.06.149. (2015 Impact Factor: 5.310)
- 3) G. Itskos, P. Grammelis, F. Scala, H. Kruczek, A. Coppola, P. Salatino, E. Kakaras. A comparative characterization study of Ca-looping natural sorbents. *Applied Energy* 108 (2013) 373-382. DOI: 10.1016/j.apenergy.2013.03.009. (2015 Impact Factor: 5.746)
- 4) Coppola, A., Scala, F., Salatino, P., Montagnaro, F. Fluidized bed calcium looping cycles for CO₂ capture under oxy-firing calcination conditions: Part 2. Assessment of dolomite vs. limestone. *Chemical Engineering Journal* (2013) 231, pp. 544-549. DOI: 10.1016/j.cej.2013.07.112. (2015 Impact Factor: 5.310)
- 5) Coppola, A., Scala, F., Salatino, P., Montagnaro, F. Fluidized bed calcium looping cycles for CO₂ capture under oxy-firing calcination conditions: Part 1. Assessment of six limestones. *Chemical Engineering Journal* (2013) 231, pp. 537-543. DOI: 10.1016/j.cej.2013.07.113. (2015 Impact Factor: 5.310)
- 6) Coppola, A., Scala, F., Itskos, G., Grammelis, P., Pawlak-Kruczek, H., Antiohos, S.K., Salatino, P., Montagnaro, F. Performance of natural sorbents during calcium looping cycles: A comparison between fluidized bed and thermo-gravimetric tests. *Energy and Fuels* (2013) 27 (10), pp. 6048-6054. DOI: 10.1021/ef401876q. (2015 Impact Factor: 2.835)
- 7) Coppola, A., Salatino, P., Montagnaro, F., Scala, F. Reactivation by water hydration of the CO₂ capture capacity of a calcium looping sorbent. *Fuel* 127 (2014) 109-115. DOI: 10.1016/j.fuel.2013.09.059. (2015 Impact Factor: 3.661)
- 8) Antonio Coppola, Piero Salatino, Fabio Montagnaro, Fabrizio Scala. Hydration-Induced Reactivation of Spent Sorbents for Fluidized Bed Calcium Looping (Double Looping). *Fuel Processing Technology* 120 (2014) 71-78. DOI:10.1016/j.fuproc.2013.12.004. (2015 Impact Factor: 3.847)

- 9) Antonio Coppola, Roberto Solimene, Piero Bareschino, Piero Salatino. *Mathematical modeling of a two-stage fuel reactor for chemical looping combustion with oxygen uncoupling of solid fuels.* *Appl Energy* (2015), DOI:10.1016/j.apenergy.2015.04.052. (2015 Impact Factor: 5.746)
- 10) Antonio Coppola, Lucia Palladino, Fabio Montagnaro, Fabrizio Scala and Piero Salatino. *Reactivation by Steam Hydration of Sorbents for Fluidized-Bed Calcium Looping.* *Energy Fuels* (2015), DOI:10.1021/acs.energyfuels.5b00413. (2015 Impact Factor: 2.835)
- 11) Chinnathan Areeprasert, Antonio Coppola, Massimo Urciuolo, Riccardo Chirone, Kunio Yoshikawa and Fabrizio Scala. *The effect of hydrothermal treatment on attrition during the fluidized bed combustion of paper sludge.* *Fuel Processing Technology* (2015), DOI: 10.1016/j.fuproc.2015.08.013. (2015 Impact Factor: 3.847)
- 12) Chinnathan Areeprasert, Fabrizio Scala, Antonio Coppola, Massimo Urciuolo, Riccardo Chirone, Prut Chanyavanich, Kunio Yoshikawa. *Fluidized bed co-combustion of hydrothermally treated paper sludge with two coals of different rank.* *Fuel Processing Technology* (2016), <http://dx.doi.org/10.1016/j.fuproc.2015.12.033>. (2015 Impact Factor: 3.847)
- 13) María Erans, Francesca Cerciello, Antonio Coppola, Osvalda Senneca, Fabrizio Scala, Vasilije Manovic, Edward J. Anthony. *Fragmentation of biomass-templated CaO-based pellets.* *Fuel* 187 (2017) 388–397. <http://dx.doi.org/10.1016/j.fuel.2016.09.061>. (2015 Impact Factor: 3.611).
- 14) Antonio Coppola, Eduardo Gais, Gabriella Mancino, Fabio Montagnaro, Fabrizio Scala, Piero Salatino. *Effect of steam on the performance of Ca-based sorbents in calcium looping processes.* *Powder Technol.* 316 (2017) 578-584. <http://dx.doi.org/10.1016/j.powtec.2016.11.062> (2015 Impact Factor: 2.759).
- 15) Antonio Coppola, Fabrizio Scala, Liberato Gargiulo, Piero Salatino. *A twin-bed test reactor for characterization of calcium looping sorbents.* *Powder Technol.* 316 (2017) 585-591. <http://dx.doi.org/10.1016/j.powtec.2016.11.067> (2015 Impact Factor: 2.759).
- 16) Antonio Coppola, Fabrizio Scala, Liberato Gargiulo, Piero Salatino. *An innovative lab-scale apparatus for the characterization of calcium looping sorbents.* *Advanced Science Letters* 23 (6), pp. 5923-5926. DOI: 10.1166/asl.2017.9070
- 17) Antonio Coppola, Fabio Montagnaro, Fabrizio Scala, Piero Salatino. *Performance of ca-based sorbents for calcium looping processes: Role of steam.* *Advanced Science Letters* 23 (6), pp. 5920-5922. DOI: 10.1166/asl.2017.9069
- 18) Antonio Coppola, Michele Allocca, Fabio Montagnaro, Fabrizio Scala, Piero Salatino. *The effect of steam on CO₂ uptake and sorbent attrition in fluidised bed calcium looping: The influence of process conditions and sorbent properties.* *Separation and Purification Technology* 189, pp. 101-107. DOI: 10.1016/j.seppur.2017.08.001 (2016 Impact Factor: 3.359)

Selection of the most significant talks/lectures, awards and honours

Speaker at 9th Mediterranean Combustion Symposium, 7 – 11 JUNE 2015 Rhodes, Greece, presenting the research activity: *REACTIVATION OF FLUIDIZED BED CALCIUM LOOPING SORBENTS BY STEAM HYDRATION*, by Antonio Coppola, Lucia Palladino, Fabio Montagnaro, Fabrizio Scala and Piero Salatino.

Speaker at VI Workshop on Oxide-based Materials Perspectives in Material Science and Technological Applications Joined with AIZ DAY 2016 – Annual Meeting of Italian Zeolite Association 21- 24 of September 2016, Napoli – Italy, presenting the research activity: *PERFORMANCE OF CA-BASED SORBENTS FOR CALCIUM LOOPING PROCESSES: ROLE OF STEAM*, by Antonio Coppola, Fabio Montagnaro, Fabrizio Scala, Piero Salatino.

Speaker at 4th International Conference on Chemical Looping, September 26-28, 2016, Nanjing, China, presenting the research activity: *Characterization of the Calcium Looping Performance of a Limestone in a Novel Twin-Bed Test Reactor*, by Antonio Coppola, Liberato Gargiulo, Fabrizio Scala, Piero Salatino.

Speaker at 12th International Conference on Fluidized Bed Technology CFB-12, Kraków, Poland, 23-26 May, 2017, presenting the research activity: *ASSESSMENT OF THE CARBON LOOPING (CARBOLOOP) CONCEPT IN A NOVEL TWIN FLUIDIZED BED REACTOR* by Antonio Coppola, Osvalda Senneca, Piero Salatino.

Elsevier prize "Top Cited Papers for 2011 and 2012", for the paper "Fluidized bed calcium looping: the effect of SO₂ on sorbent attrition and CO₂ capture capacity", *Chemical Engineering Journal*, 207-208, 2012, 445-449.