TOWARDS THE INDUSTRIAL SOLAR PRODUCTION OF LIME

A. Meier, E. Bonaldi (QualiCal AG), G.M. Cella (QualiCal AG), W. Lipinski, R. Palumbo, A. Steinfeld (ETH Zürich and PSI), C. Wieckert, D. Wuillemin

A new industrial concept that aims at the development of the chemical engineering technology for the solar production of lime is being examined. To establish the technical feasibility, a 10 kW solar reactor has been designed, constructed, and experimentally tested at a high-flux solar furnace. The quality of the produced solar lime meets industrial standards.

1 INTRODUCTION

Substituting concentrated solar energy for carbonaceous fuels, as the source of high-temperature process heat for the thermal decomposition of limestone ($CaCO_3$) to produce lime (CaO), is a means to eliminate the dependence on conventional energy resources and to reduce emissions of CO_2 and other pollutants. Solar processing offers a clean and sustainable path for reaching these goals, and the industrial solar lime project with *QualiCal AG* [1] is a pioneering attempt to address this challenge.

The specific purpose of the project is to establish the technical and economic feasibility of a 0.5 MW thermal input solar calcination plant for the production of lime, e.g. as building material in a developing world setting or for high quality applications in the chemical industry.

The current work is based on the experience from previous studies showing that $CaCO_3$ can be calcined with concentrated sunlight and that a high degree of chemical conversion can be achieved [2-5]. Furthermore, an internal study done at PSI along with several leading players in the cement industry concluded that solar calcination is a feasible process [6].

2 EXPERIMENTAL

The raw material used for testing the new concept for the solar calcination process was extremely pure Carrara marble ($CaCO_3$ content close to 98%). We examined different particle size fractions in the range of 1-5 mm that cannot be treated by current industrial technologies for calcination, since they either use grain sizes below 1 mm (flash calciners or fluidised bed reactors), or above about 10 mm (rotary kilns), or even above 40 mm (vertical shaft kilns).

Thermogravimetric measurements were conducted at temperatures up to 1200°C with 400 mg samples for different purge gas compositions (pure air and a mixture of N_2 with varying CO_2 content).

Electric furnace experiments were performed according to the following procedure that was chosen to simulate the conditions in a solar furnace, where the burning temperature is expected to be reached almost instantaneously: (1) the electric furnace is heated to the chosen temperature between 850°C and 1340°C; (2) the cold quartz crucible containing 30 g of limestone material is introduced into the hot furnace without preheating the limestone particles.

In *solar simulator experiments* at ETH Zurich [7], the concentrated radiant energy from a high-pressure argon arc lamp was used to directly irradiate a thin layer of limestone particles (about 10 g of $CaCO_3$) on a SiC plate.

Solar furnace experiments were conducted at PSI to establish the technical feasibility of a 10 kW solar reactor (Figure 1). This novel reactor consists of a horizontal rotary kiln with an innovative particle feeding system for continuous operation (mean CaO production rate 10-30 g min^{-1}). The reaction chamber is lined with a refractory concrete and well insulated with a porous ceramic fibre, both allowing for temperatures up to 1600°C.

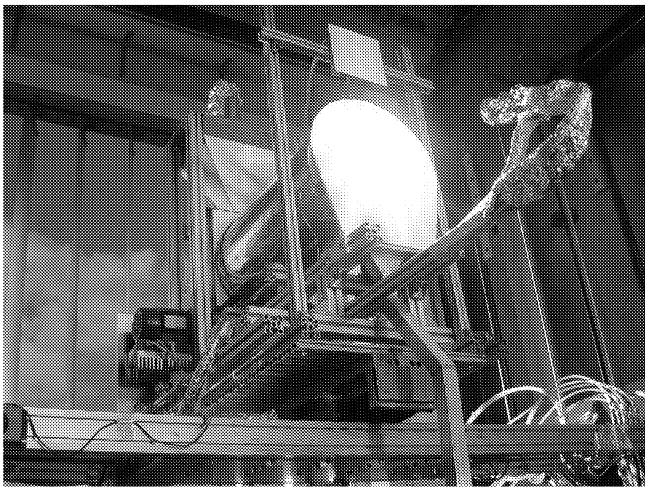

Fig. 1: Test of the 10 kW solar lime prototype reactor in a solar furnace at PSI.

3 RESULTS AND DISCUSSION

Kinetic parameters obtained from thermogravimetric measurements suggest that complete calcination of 2-3 mm limestone particles can be attained within less than 2 minutes at 1050°C and only 4 seconds at 1350°C. The kinetic parameters, however, may be influenced by the sample weight, the shape of the crucibles, and the heating rate [8,9]. For increasing CO_2 content in the gas phase, the calcination proceeds at significantly higher temperatures, thus showing the need for fast CO_2 removal.

Both electric furnace and solar simulator experiments indicate that the necessary retention time is in the range of 3-7 minutes to ensure complete calcination of the 2-3 mm limestone particles at temperatures above 1100 °C. The retention time for the calcination is strongly related to the burning temperature, the grain size, the void distribution within the sample, and the thickness of the particle bed. Moreover, the elevated CO_2 partial pressure within the closed electric furnace may hamper the $CaCO_3$ decomposition reaction, thus explaining in part the discrepancy to the thermogravimetric measurements.

The results of the solar experimental campaign confirm that lime with a degree of calcination exceeding 98% (Figure 2) and virtually any quality ranging from low to high reactivity can be produced in the solar reactor. The operating temperature and the reactants' residence time are found to be the two most critical parameters. The thermal efficiency, defined as the ratio of process heat used for the chemical reaction to the solar power input, reaches 10-15% for this non-optimised solar reactor prototype, indicating the potential for developing an efficient and cost effective solar industrial calcination process.

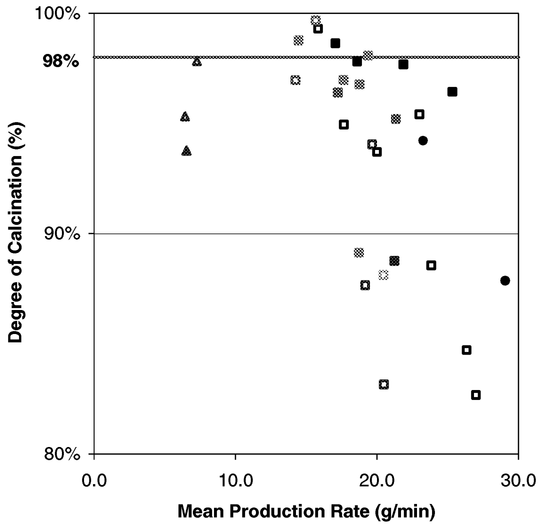

Fig. 2: Degree of calcination for a variety of solar experiments with specific operating conditions depending on temperature, rotational speed of reactor, reactants feeding rate, product discharging system, and particle size (2-3 mm).

4 CONCLUSION AND OUTLOOK

The solar calcination of very pure limestone particles in the range of 2-3 mm has been successfully demonstrated. The quality of the produced solar lime meets industrial standards.

A numerical reactor model is being developed to assist in the modification and optimisation of the current solar reactor and eventually in the conceptual design and economic analysis of a large-scale solar lime plant.

5 ACKNOWLEDGEMENT

We thank the Swiss Federal Office of Energy (BFE) for funding this work.

6 REFERENCES

[1] The Solar Production of Lime, 2000 - 2003 Research Program: www.qualical.com/solar (2001).

[2] G. Flamant, D. Hernandez, C. Bonet, J.-P. Traverse, *Experimental Aspects of the Thermochemical Conversion of Solar Energy; Decarbonation of $CaCO_3$*, Solar Energy **24**, 385 (1980).

[3] J. M. Badie, C. Boner, M. Faure, G. Flamant, R. Foro, D. Hernandez, *Decarbonation of Calcite and Phosphate in Solar Chemical Reactors*, Chem. Eng. Sci. **35**, 413 (1980).

[4] O. A. Salman, N. Kraishi, *Thermal decomposition of limestone and gypsum by solar energy*, Solar Energy **41**, 305 (1988).

[5] A. Steinfeld, A. Imhof, D. Mischler, *Experimental Investigation of an Atmospheric-Open Cyclone Solar Reactor for Solid Gas Thermochemical Reactions*, J. of Solar Energy Eng. **114**, 171 (1992).

[6] A. Imhof, *Internal reports from 3 PSI / Industrial Workshops*, Oct. 1996, June & July 1997.

[7] Professorship in Renewable Energy Carriers at the Institute of Energy Technology, ETH Zurich, Internet address: http://www.pre.ethz.ch (2001).

[8] M. Maciejewski, A. Reller, *How (un)reliable are kinetic data of reversible solid-state decomposition processes ?*, Thermochimica Acta **110**, 145 (1987).

[9] A. Romero Salvador, E. Garcia Calvo, C. Beneitez Aparicio, Effects of sample weight, particle size, purge gas and crystalline structure on the observed kinetic parameters of calcium carbonate decomposition, Thermochimica Acta **143**, 339 (1989).