STUDIES ON A SLURRY-FOAM REACTOR FOR CARBONATION OF HYDRATED-LIME SLURRY USING PURE CARBON-DIOXIDE GAS

By

SUSANTA KUMAR JANA

Department of Chemical Engineering

Submitted

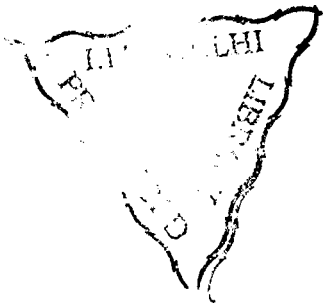
in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

Indian Institute of Technology, Delhi

FEBRUARY 2007

Chemical reactions.



CERTIFICATE

This is to certify that the Thesis entitled, **STUDIES ON A SLURRY-FOAM REACTOR FOR CARBONATION OF HYDRATED-LIME SLURRY USING PURE CARBON-DIOXIDE GAS**, being submitted by **Mr. Susanta Kumar Jana** to the Indian Institute of Technology, Delhi for the award of the degree of **DOCTOR OF PHILOSOPHY** is a record of the bonafide research work carried out by him. Mr. Jana worked under my guidance for the submission of this thesis which to my knowledge has reached the requisite standard.

The thesis or any part of it has not been submitted to any university or institute for the award of any degree or diploma.

February, 2007

Dr. Ashok N. Bhaskarwar
Professor,
Department of Chemical Engineering,
Indian Institute of Technology Delhi,
New Delhi 110016

ACKNOWLEDGEMENTS

With deepest gratitude, I wish to express my indebtedness to my research advisor, Professor Ashok N. Bhaskarwar for suggesting me the research problem on 'Carbonation of hydrated lime slurry in a foam-bed reactor using pure-carbon dioxide gas' which constitute the present thesis. During this long period of association I have received his invaluable advice and sincere guidance.

I am thankful to the administration of Malaviya National Institute of Technology-Jaipur for sponsoring my studies under QIP and specially to Professor R. P. Dahia, the present Director, for permitting me to register as a part-time research scholar in IIT-Delhi, after the stipulated 3-year leave period.

I am thankful to my wife, Monika, for agreeing to my proposal of Ph.D. studies (under QIP) at IIT-Delhi and taking the full responsibility of looking after the children and their education at Jaipur and tolerating long isolation during my occupation with my Ph. D. studies. I perceive that her hardship at Jaipur during my stay at IIT-Delhi and beyond that too, has been far beyond her expectations. I shall remain indebted to my daughters, Anusua and Alivia as their schooling, examinations, and daily life were seriously affected because of my full occupation with my own academic work at IIT-Delhi and at Jaipur too.

I am also thankful to the faculty members of the Department of Chemical Engineering, especially Professor Ashok Kumar Gupta, Professor T. R. Rao, Professor B. K. Guha, Professor S. K. Gupta, Dr. Ratan Mohan, Dr. S. Basu, Dr. Santanu Roy and Professor A. Ramanan of the Department of Chemistry for their help in various ways during the entire period of the present studies. Thanks are also due to the technical staff, Mr. N. K. Gupta and Mr. Vijaypal Singh for their assistance in fabrication of the experimental set-ups.

I wish to thank my colleagues Dr. Arunabha Kundu and Sri Amit Gaikwad for their assistance in preparation of the manuscript of this thesis.

February, 2007

Susanta Kumar Jana

ABSTRACT

In the present investigation new mathematical models have been developed for mass transfer with chemical reaction for semi-batch slurry, slurry-foam, and gas-liquid foam reactors. Some of these models have been validated using experimental data. Carbonation of hydrated lime in slurry using pure carbon-dioxide gas, an industrially important process for the manufacture of precipitated calcium carbonate (PCC), has been chosen for the present study. The performance of a short slurry bubble-column reactor has been compared with that of the slurry-foam reactor using experimental data collected for the above-mentioned reaction.

The models for the **slurry reactor** incorporating sparingly soluble reactive particles have been developed for simultaneous dissolution of particles and reaction with the dissolved gaseous species in the liquid phase. The slurry in the reactor, with gas bubbles rising through it, is assumed to be well mixed. The reaction between hydroxide ions in solution and dissolved carbon-dioxide occurs in accordance with a second-order kinetics (Danckwerts and Sharma, 1966). Further, as the rate of dissolution of particles in liquid depends on its surface area, and because several batches of lime samples having different initial particle-size distributions have been used in the experiments, the particle-size distribution has been incorporated in the model equations for evaluation of the reactor performance.

The model of a **slurry-foam reactor** has been developed taking into consideration the combined contributions of both the storage and foam sections, especially necessitated by the fast reaction system being investigated in the present work. The entire foam section is assumed to be equivalent to a single stage with an average liquid hold-up (Bhaskarwar and Kumar, 1984). As the dissolved solid species (B) gets consumed by reaction in the liquid phase and its concentration tends to decrease, more solid dissolves into the liquid phase. This necessitated consideration of total loading of B in slurry (both dissolved in solution and that present as particles) in writing the material-balance equations for estimation of conversion with the progress of reaction time. The expressions for evaluation of performance of the slurry-foam reactor remain the same as those used for a slurry reactor, except that in the

former case the total loading of component B and the instantaneous values of particle diameters have to be estimated by considering the conversions in both the sections, i.e. storage and foam simultaneously. For evaluation of performance of the slurry-foam reactor, component A balances in foam and storage sections, component B balance over the storage section, and the volume balance of particles over the storage section are written. Again for writing the component A balance over the storage section, the instantaneous concentration of component A in the liquid stream draining from the foam to the storage section is needed. This concentration is obtained by writing a pseudo-steady state material balance for component A over the foam section. Simultaneous solution of these material-balance equations also needs an expression for the instantaneous volume of particles in the drainage stream from foam section expressed in terms of that in the storage section. For this purpose a mass-balance equation is written assuming that the rate of dissolution of particles in the foam section equals that of reaction in this section, so that the concentration of dissolved calcium hydroxide in the films entering the foam section and that in the drainage stream are the same (pseudo-first order reaction with respect to A).

A separate model has been developed considering the entire gas-liquid interfacial area equivalent to that of a single flat liquid film in contact with gas which may be validated with the experimental data for the reaction undertaken in the present study, but with a lime solution instead of slurry.

In order to validate the models developed, experiments for carbonation of hydrated lime in slurry with pure carbon-dioxide gas were performed in a foam reactor with different types of surfactants, cationic: cetyl trimethyl ammonium bromide, anionic: sodium dodecyl sulphate, and non-ionic: Triton X-100 as the foaming agents as well as in a short slurry bubble column reactor (without any surfactant added to the slurry). Under otherwise identical conditions, after one minute of the reactor operation, a higher conversion, about 40-45 percent higher than that in a slurry reactor, was obtained in the foam reactor using a cationic or an anionic surfactant as the foaming agent. The variables and parameters studied include, nature of surfactant used in generating stable foam, initial loading of hydrated lime in slurry, flow rate of gas, height of foam, volume of slurry charged into the reactor, initial size distribution of

lime particles (with hydrated lime samples from different batches), and the concentration of each of the surfactants mentioned above. Other essential or supplementary experiments performed are (i) chemical analysis of hydrated lime samples from different batches used in the experiments, (ii) particle-size distribution analysis of the different batches of calcium-hydroxide samples used as well as of the product $CaCO_3$ obtained from several different experimental conditions, (iii) Thermo-gravimetric Analysis (TGA) and X-ray diffraction (XRD) studies of calcium hydroxide samples from different batches and of product calcium carbonate obtained after complete carbonation of lime samples, (iv) liquid hold-up measurements in the foam column for all the experimental conditions used in obtaining the different sets of data, (v) measurement of surface-coefficient values of the saturated lime solutions with different types and concentrations of surfactants used, and (vi) measurement of bubble sizes in the foam column.

Chemical analyses of various lime samples have been done for percentage of lime present in it. It varied from 92.28 to 97.75 per cent. The major impurity was $CaCO_3$, (determined by XRD analysis as described below). Particle-size distributions (PSDs) of reactant $Ca(OH)_2$ and product ($CaCO_3$) have been measured using CILAS-940 particle-size analyzer. The PSDs were incorporated in the models as distributions play a significant role in governing the reactor performance. For simulation purposes, the total amount of lime sample taken in an experiment was divided into twelve volume fractions. A higher conversion is obtained with the lime samples having smaller particles than with the sample having larger particles. **Thermo-gravimetric analysis** (TGA) and **X-ray diffraction** (XRD) analysis of the test samples and of the products resulting from complete carbonation of lime were performed to find out the reasons, if any, in addition to the differences in particle sizes, for the different levels of conversions obtained with different batches of lime used in the experiments. It is observed that the lime samples are similar except for the presence of one major impurity identified as calcium carbonate.

Liquid hold-up is an important parameter, governing the performance of a foam-bed reactor under certain conditions. It has been measured at different heights of the foam, for all the experimental conditions used, by suction of foam into an evacuated glass bulb of a known

volume. Liquid hold-up is then estimated from the knowledge of volume of bulb, the extent of vacuum in the bulb, and the volume of slurry obtained from the broken foam.

Surface coefficient of the reactant mixture is another important parameter necessarily incorporated in the slurry-foam reactor model, because the system involves gas absorption with a fast chemical reaction. Surface coefficients of saturated lime solutions containing different surfactants (Sodium Lauryl Sulphate, Cetyl Trimethyl Ammonium Bromide, and Triton X-100) were measured for the later use in the numerical solution of the mathematical equations. A manometric apparatus, similar to the one used by Blank and Roughton (1960), was used for this purpose. An analytical expression was derived for the estimation of volumes of gas absorbed from the experimental manometer readings. The surface coefficient was then calculated following the analysis by Blank and Roughton (1960). Photographs of foam bubbles at different heights and times for some of the experiments performed earlier were taken separately under the same conditions.

A **comparison** of the conversions obtained **in** the **slurry-foam reactor** with different surfactants (cationic and anionic) with those in a conventional short **slurry bubble-column reactor** showed that after one minute of the reactor operation, about 40-45 per cent higher conversions were obtained in a foam reactor. The higher conversions obtained when ionic surfactants were used as the foaming agents over those with a non-ionic surfactant have been attributed to the higher gas-liquid interfacial areas and liquid hold-up values obtained experimentally. The effect of **initial solids loading** was studied keeping all other parameters constant. Increased solids loading causes an increased solid-liquid interfacial area and the higher total rate of dissolution of solids leads to a higher observed rate of reaction. The effect of **gas-flow rate** on conversion of lime is quite distinct. Increase in gas-flow rate causes a higher liquid hold-up and a higher drainage rate within the foam column, and also an increased turbulence intensity in the storage section. These result in higher rates of mass transfer and of conversion of the two reactants. With an increase in **foam height,** the total gas-liquid interfacial area for gas absorption in the foam section, gas-liquid contact time, and the total amount of liquid in the foam section (in the reactor part of larger interfacial area) increase. These factors together cause an increase in the conversion of lime. As the **volume of**

slurry is increased, keeping at constant values all other parameters including the solids loading, the conversion of lime reduces. With an increase in the volume of slurry, at constant gas-flow rate and other parameters, the intensity of agitation in the storage section reduces with the consequent reduction in the mass-transfer coefficient. The rates of dissolution of solids and of absorption of gas in the liquid reduce. Besides, solids loading being constant, the total amount of solids present is more in a larger volume of slurry, and the calculated conversion reduces due to the definition of conversion used. With an **increase in the concentration of surfactants**, viz. sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB), maintaining all other parameters constant, the conversion of lime is seen first to increase and then to reduce at still higher concentrations. The liquid hold-up in the foam column increases, possibly due to the increased stability of foam, with an increase in the surfactant concentration. The total volume of liquid in the storage section reduces with the consequent increase in turbulence. These beneficial effects, along with the larger interfacial area in the foam section for the reasons cited earlier, off set any retarding effect the surface resistance may have on gas absorption, and a small increase in the conversion is thus obtained. However, at higher concentration levels of the surfactant, the surface resistance becomes appreciable and the particle surfaces also get appreciably covered with the surfactant molecules, reducing the solid-liquid mass-transfer coefficient too. These phenomena cause a decrease in the conversion of lime at higher surfactant concentrations. With the non-ionic surfactant (octyl phenoxy polyethoxyethanol) also, the conversion was found to increase up to the maximum concentration used in the experiments possibly due to the same reasons, viz. increased foam stability, higher gas-liquid interfacial area and liquid hold up, cited above. **Effect of initial particle-size distribution** on conversion of lime has also been studied maintaining all other parameters at constant values. For a given solids loading, the solids sample having a larger population of finer particles would have a larger interfacial area. The dissolution rate of finer particles is higher resulting in the higher conversion of lime. The model also predicts the effect.

The semi-theoretically determined values of the solid-liquid mass-transfer coefficient, one of the parameters in the model, agree well with the values reported in the literature.

Design of a slurry-foam reactor system has been presented for production of 50 tons per day of precipitated calcium carbonate (PCC), using hydrated lime and pure carbon-dioxide gas, in a series of continuously operated reactors. Volumetric flow rate of reactant slurry being sufficiently high, conversion obtainable in a single reactor is likely to be small. This necessitates the use of multiple foam reactors in series or in parallel. Reactors in series will be more convenient as the need for recirculation of slurry for desired conversion can be avoided. Design charts and detailed methodology have been presented. One can choose a suitable aspect ratio and find, using the chart, the minimum number of reactors required for the desired operating conditions.

ONTENTS