HYSTERESIS STUDIES IN TRICKLE BED REACTORS

By

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Chemical reactors

Dedicated to

... My Dearest Parents

CERTIFICATE

This is to certify that the thesis entitled, **'HYSTERESIS STUDIES IN TRICKLE BED REACTORS'** being submitted by **Mr. Rabindranath Maiti** to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy is a record of bonafide research work carried out by him under our guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology, Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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ABSTRACT

A trickle-bed reactor (TBR) is a reactor in which a gas and a liquid flow cocurrently downward over solid packings. Its use is widespread in petroleum and chemical industries. In general, the reaction occurs between the dissolved gas and liquid phase reactant at the interior surface of the catalyst. The external surfaces of the catalyst happen to be partially or fully covered with liquid for maximum utilization of catalyst based on mass transfer limitation with gas or liquid. The performance of a TBR depends mainly on two hydrodynamic parameters, viz., and pressure drop across the reactor and liquid holdup inside the reactor. The performance of the reactor is mostly predicted by using experimentally developed empirical/semi-empirical correlations for these parameters. Predictions based on these correlations and the actual performances of the TBR differ significantly in many cases and there is no general consensus about the correlations developed so far. One of the major contributors to these differences has been thought to be due to the existence of multiple hydrodynamic states i.e. hysteresis in pressure drop and liquid holdup. The present thesis deals with the various aspects of hysteresis in trickle bed reactors.

A detailed literature survey on hysteresis in trickle bed reactor was carried out. As pointed out above, several authors have reported the phenomena of multiple hydrodynamic states i.e. hysteresis in TBR over decades. Pronounced hysteresis was observed for pressure drop, liquid holdup and wetting efficiency for both porous and nonporous type of packing materials. In all the studies the phenomena of hysteresis was attributed to the difference between advancing and receding contact angle in rivulet and film flow of liquid over the solid packing. From one study it was indicated that several

features of hysteretic behaviors of porous alumina particles are strikingly different than nonporous glass beads. Such features of hysteresis even with the nonporous particle could not also be better explained with prevailing perceptions of hysteresis. Several mathematical approaches have been tried to characterize the history of the process by including several criteria / additional parameters for quantifying hysteresis. The models were able to capture the trend of hysteresis, but with a large deviation between predicted and experimental data. Also such models could not predict different hystersis for several cases such as first cycle of operation and subsequent cycles for porous and nonporous particles, different maximum operating flow range, different startup conditions etc. The models are limited by number of fitting parameters and some have to be generated from prevailing experimental condition. A novel conceptual development of the phenomena of hysteresis is necessary for understanding liquid flow features during hysteresis for both porous and nonporous substrates.

The specific role of pores in hysteresis was examined in details. Experiments were carried out with a model porous substrate with relatively larger pore size. The micro-liter-sized liquid drops were put on porous and nonporous parts of solid substrate have saturated (filled) millimeter-sized pores. The substrate was then rotated in vertical direction and the resulting motion of drops was recorded by a video camera. The analysis of the recorded images revealed that depending on whether the drop edge is moving towards the pore or away from the pore, the pore acts as accelerator or brake for the drop edge. This dual nature of the saturated pores can be ascribed to the attraction between the liquid in the drop and the liquid inside the pore. Qualitative changes in the morphology of the drop as it slides over saturated pores were also presented to highlight the process. This dual effect of pores on liquid spreading is expected to play a major role in different hysteretic behavior of TBR packed with porous particles compared to nonporous particles.

Literature data were critically examined for possible role of pores on hysteresis in trickle bed reactor packed with porous and nonporous particles and various unresolved issues associated with hysteresis were identified. It was also noted that for nonporous particles, no satisfactory explanation of hysteresis is available from earlier studies. A general framework of hysteresis is developed that incorporates the current understanding of fluid flow in TBRs, concepts of participating and nonparticipating particles, and principles of liquid spreading on porous and nonporous substrates. In addition to providing a basis for the general framework within which hysteresis in TBRs should be studied, it provides explanations to specific questions such as (1) the existence of hysteresis in porous packings and its absence in nonporous packings under similar conditions and (2) when to expect open-loop or closed-loop hystersis. The framework is applied to reported experiments and shown to be able to explain the difference in the hysteretic behavior of porous packings and of nonporous packings (with different particle size) under varying startup conditions and numbers of cycles. It was noted during the validation process that the particles used were of different material.

Experiments were performed in a cold flow trickle bed reactor (15cm internal diameter) to study the hysteretic behavior of industrial relevant alumina extrudates with varying pore density (i.e. porous, semi-porous and nonporous), but made of same material e.g. alumina and with identical shape and size in dry and wet bed conditions. Comprehensive pressure drop hysteresis data were generated. In dry bed startup conditions, the first cycle of operation showed open loop hysteresis and the amount of hysteresis also decreased with the increase of pore density of the particles. In wet bed startup conditions first cycle showed marginally open loop hysteresis but amount of hysteresis increased with increase of pore density of the particles. In the subsequent cycles, hysteresis was close loop and increased with increase of pore density of the particles. The new framework of hysteress was found to be able to explain all the different features of hysteresis with particles of varying density of pore.

It is expected that the new framework of hysteresis proposed would be useful to plan the start-up procedures and operating conditions in trickle bed reactors for optimal performance of the reactor. The other likely benefits involve improvement of understanding of hydrodynamic features at particle levels, performance improvement in TBRs both with respect to industrial and pilot plant scale and process intensifications.

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