The Water Gas Shift Reaction in a Fluidized Bed Catalytic Reactor
by WILLIAM THOMAS ALUMKAL

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University

Abstract:
Increased uses of fluidized bed reactors have brought about intensive interest in the behavior of fluidized beds. Several physical models of fluidized bed reactors are available in the literature many of them with little or no experimental backing. This research project was designed to investigate these models and determine how well they predict the actual behavior, and if necessary, modify them.

Conversions of carbon monoxide were calculated using the physical models and were compared with the observed values. The two basic models were modified first by introducing one undetermined parameter in each case; namely, cloud size in Rowe's model and the number of transfer units in the models of Davidson and Harrison. In both of these models the emulsion phase was considered under the conditions of plug flow and back-mixing. These two models were further modified by introducing a longitudinal diffusion coefficient in the emulsion phase.

The study involved a 3-inch diameter fluidized bed reactor. Water gas shift /reaction on chromia promoted iron oxide catalyst was used as the reaction system. A pseudo first order reaction was obtained by keeping the concentration of carbon monoxide low in the feed stream.

The results show that considering no undetermined parameters, Rowe's model with plug flow in the emulsion phase yielded a better agreement with the observed values than the models of Davidson and Harrison. Some improvement was obtained by introducing the undetermined parameters into these models.

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ABSTRACT

Increased uses of fluidized bed reactors have brought about intensive interest in the behavior of fluidized beds. Several physical models of fluidized bed reactors are available in the literature, many of them with little or no experimental backing. This research project was designed to investigate these models and determine how well they predict the actual behavior, and if necessary, modify them.

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INTRODUCTION

When gas is forced to flow upwards through a bed of solid particles supported by a porous plate, this causes a pressure drop across the bed. When this pressure drop becomes equivalent to the weight of the bed, this column of solid particles resembles a liquid of high viscosity. At this point, the individual particles are disengaged somewhat from each other. Any further increase in gas flow rate will cause the bed to expand to accommodate this increase. This type of a bed of particles is called a "Fluidized Bed".

History

The first fluidized unit to be operated on a commercial scale was the Winkler Gas Generator (1) for the manufacture of water and producer gas. It was developed in Germany in 1921. The first large scale fluidization application in the United States dates to about 1940 and pertains to the catalytic cracking of oil vapors. The successful operation of fluid cracking units caused a widespread interest in the technique and precipitated a large number of fundamental and applied studies in the field of fluidization. A great deal of work still remains to be done.

If a gas is forced to flow upwards through a bed of solid particles, the pressure drop across the bed increases along the line AB (See Fig. 1), until the flow rate reaches Uo.

Any further increase in flow rate will cause a dip in the pressure drop (BC). At high flow rates the pressure drop across the bed will very nearly be equal to the value at B. U_0 is called the minimum fluidizing velocity and at U_0 the bed is said to be incipiently fluidized.

A fluidized bed, when operated above the minimum fluidizing velocity, consists of two phases -- a dense (emulsion) phase and a dilute (bubble) phase. The emulsion phase is also called continuous or particulate phase and the bubble phase is called a discontinuous phase since the bubbles are discrete. In the emulsion phase, the gas travels at the rate of the minimum fluidizing velocity. The remaining gas passes through the bed at a higher velocity as bubbles. There is gas interchange between the emulsion phase and the bubble phase.

The behavior of the fluidized bed is described by physical models. The early models of fluidized beds considered the bed as a single phase. The relationships developed on this basis were not adequate. All the recent models consider the fluidized bed as composed of two phases, the emulsion phase and the bubble phase.

Shen and Johnstone (2) were the first ones to study the kinetics in a fluidized bed reactor. They studied the catalytic decomposition of nitrous oxide. They considered both perfect mixing and plug flow in the emulsion phase and established rate equations for both cases. Approximate agreement was found between calculated and observed values in the case of both the models. The mass transfer coefficient between the phases was calculated from two simultaneous first order linear differential equations obtained from a material balance in each phase. This mass transfer coefficient was found to be a function of catalyst bed height and the gas flow rate.

Mathis and Watson (3) studied the cracking of cumene in a fluidized bed. Their two phase model assumed plug flow in both the phases. The total feed stream and the total weight of the catalyst were assumed to be distributed between the two phases. Pseudo mass transfer coefficients or interaction coefficients are introduced to compensate for the increased conversion observed in any of the two phases. They tried to apply their data to other models, but without much success.

Lewis, et. al., (4) studied the catalytic hydrogenation of ethylene. They assumed a plug flow in both phases. A fraction of the catalyst is contained in the bubble and therefore reaction takes place in both phases. A pseudo first order reaction was obtained by using a large excess of ethylene. They found that the efficiency of the fluidized bed for carrying out first order irreversible reactions was independent of the bed height. The gas interchange between the two phases was found to be most pronounced at high gas rates. They did not reach any conclusions on backmixing in the emulsion phase.

May (5) postulated a new model where a longitudinal diffusion coefficient was introduced to allow for mixing in the axial direction.

This diffusion coefficient was calculated using radioactive solids tracer in a fluidized bed. Radioactive solids were injected near the top of the bed and the appearance of radioactivity at various points below the injection point was monitored. The diffusion coefficient was calculated under the assumption that it is a constant for the entire cross section of the bed.

The cross-flow ratio, which is the total rate of exchange of gas between the bubble and the particulate phase, was determined by a time of contact experiment. A small amount of tracer gas, helium, was added to the fluidizing air and the unit was run until equilibrium was established. The tracer gas was then cut off and its concentration in the exit gas was monitored. The cross flow rate is related to the slope of the residence time distribution.

Although May showed results of his tracer studies, no experimental results were given for the study of first order reaction system in a fluidized bed, which he also considered.

The model of May was applied to gas mixing experiments by Van Deemter (6) to determine both dense phase gas vertical diffusivity and the gas interchange between the two phases without using the assumption of equal diffusivity of solids and dense phase gas. For the case of first order irreversible chemical reaction, he concluded that axial diffusion is important only at high conversions. No experimental work was reported in this case, either.

Lanneau (7) used a capacitance probe to investigate the gas flow in a fluidized bed by means of density measurements. From the results of his experiments, conclusions were drawn about the distribution of solids between the bubble and emulsion phases, the gas backmixing, and the interchange between the two phases. Based on this, he postulated a two phase model to describe a first order irreversible reaction in a fluidized bed. Lanneau also developed curves showing the effect of reaction rate and interchange between the phases on conversion, but no experimental results of this were given.

Orcutt, et. al., (8) studied the decomposition of ozone over iron oxide catalyst in a fluidized bed. They assumed the bubble phase to be discrete and well mixed and to contain no solid particles. The emulsion phase is considered under the conditions of both plug flow and complete mixing. The interchange of reactants between the two phases is assumed to take place by bulk flow and diffusion. Their experimental conversions ranged from 10% to 95%. The main variable in this study was temperature. Flow rate, bed diameter, and the amount of catalyst were also taken as variables (parameters). The calculated values using both the models showed reasonable agreement with the experimental results. The experimental values tended to lie between those obtained from the two models.

Heidel, et. al., (9) studied the influence of mixing and/or segregation processes on chemical reaction existing in fluidized beds using hydrogenation of ethylene on copper catalyst. They used three different models to analyze their results. Two of them were the diffusion model and the two-phase model, which are similar to those described earlier. The third one was the two zone model based on the work of De Maria, et. al., (10). De Maria and co-workers found that, in fluidized beds, the intensity of mixing was different at various radial positions. The central core of the fluidized bed was found to be mixed much better than the region near the wall. Based on this, the two zone model of Heidel, et. al., divided the fluidized bed into a wall zone and a central zone, each characterized by an average residence time and a mixing coefficient of its own. The proportion between the wall zone and the central zone can be determined by taking the ratio of the areas under the residence time curves for the two zones. The conversion values calcalated using this model were found to be higher than the observed results. This model was found to be valid only for shallow beds where the average residence times of the two zones show appreciable difference. When 4L/D is greater than 6.9, the effect of radial mixing becomes great and the two zone model will be the same as a diffusion model.

Davidson and Harrison (11) described two models for two phase fluidization which are essentially the same as that used by Orcutt, et. al. Here, also, the bubbles were assumed to be of spherical shape containing no solid particles in them. The interchange of reactants between the two phases is considered to take place by bulk flow and diffusion. The difference between their two models is that, in one case, the particulate phase was taken to be perfectly mixed, and in the other case, piston flow is assumed.

Rowe (12) also considered the fluidized bed to be composed of two phases. Rowe's model is based on recent studies done on the nature of the gas solid contacting in fluidized beds. This model considered the bubbles to be spherical but have an indented base of one-third the complete sphere volume. This lowest one-third is the wake of particles which travels with the bubble. Also, a cloud of gas is present around each bubble which exchanges the gas with the bubble freely. Thus Rowe's model considered the fluidized bed to be composed of (a) an emulsion phase through which gas travels at approximately the minimum fluidizing velocity, and (b) bubbles along with their wake and the gas cloud travelling through the fluidized bed at the velocity of the bubbles.

Mamuro and Muchi (13) postulated a partitioned model in which the fluidized bed is divided into a number of cells of height equal to the diameter of the gas bubbles. Each cell is composed of two phases, the bubble phase and the emulsion phase. Gas backmixing is present in the emulsion phase of each cell and its effects are carried over only to the adjacent cells. The bubble phase was assumed to contain no solids and gas is interchanged between the two phases.

The models of Harrison and Davidson, Rowe, and Mamuro and Muchi are described in detail in the later part of the text. These four models were used to analyze the experimental data obtained in this investigation.

RESEARCH OBJECTIVES

This research was conducted to improve the understanding of first order chemical reactions taking place in a fluidized bed. Various physical models have been postulated by previous investigators, many of them without experimental backing. Conversions of reactants calculated using these models for the experimental conditions were to be compared with the observed values to determine which of these models described the actual behavior of fluidized beds, and if necessary, a new model was to be developed.

A pseudo first order irreversible gaseous reaction was to be used for this study where the reaction took place at the surface of the catalyst. The system chosen for this study was the reaction of carbon monoxide and steam over iron oxide catalyst yielding carbon dioxide and hydrogen. The limiting reactant was carbon monoxide.

The specific conclusions to be drawn from this study were:

A. The effect of particle size, bed height, and temperature on the conversion in a fluidized bed.

B. The effect of backmixing in the emulsion phase on the conversion.

C. The extent of interaction between the emulsion phase and the bubble phase.