SYNTHOIL HYDRODYNAMICS

FINAL REPORT

H. Brenner, D.C. Prieve, and B. Fitch

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Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

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INTRODUCTION

Synthoil is a process developed by the Pittsburgh Energy Research Center to catalytically liquefy coal. The central unit in the process is a fixed-bed catalytic reactor in which a coal-oil slurry is contacted cocurrently with hydrogen at elevated temperatures and pressures. Hydrodesulfurization and cracking of the coal takes place within the reactor to produce a low-sulfur liquid fuel. After subsequent cleaning steps, the fuel is suitable for direct use in power-generating boilers. Details of the process can be found in a number of publications, including that of Akhtar et al. (Energy Communications, 1:21, 1975).

Due to the extreme conditions within the reactor, it is nearly impossible to study pressure-drop and residence time variations or to observe directly what is happening within the bed. The residence time of the liquid phase is particularly important in controlling the extent of reaction. It is defined as the ratio of the liquid volume held in the bed at any time to the liquid flowrate. The liquid holdup varies significantly with both gas and liquid flowrates as well as with other physical variables. Thus the residence time is not simply related to flowrate and void volume as in reactors containing only one fluid phase. To study the dependence of residence time and pressure-drop upon various physical parameters, "cold-model" experiments were performed by PERC simultaneously with the Synthoil pilot studies. Air and water at ambient temperature and low pressure were used in place of the hot pressurized hydrogen and coal-oil slurry because of the similarity in physical properties of these two systems. With the ambient air-water system it was possible to employ a transparent acrylic column to allow observation of two-phase phenomena and to measure pressure-drop and liquid holdup more easily.

SUMMARY OF OBJECTIVES

Briefly, the objective of the present research is to develop mathematical models to explain and correlate the experimental data concerning two-phase cocurrent upflow through packed beds, as found in the Synthoil reactor and the associated cold-model. Such correlations and understanding will be useful in scale-up as well as optimum design of the reactor.

SUMMARY OF ACTIVITY

Complete details on all items in the following summary are reported in the quarterly technical reports (report numbers COO-0056-001, COO-0056-002, and COO-0056-003).

Pressure-Drop Correlations

Extensive experimental data was collected on the cold-model and analyzed during the first six months. During the same period a survey of the literature was performed which uncovered three separate correlations of pressure-drop and holdup in two-phase, cocurrent upflow through packed beds. Although the mass velocity of the gas is significantly higher in the Synthoil reactor (simulated by the cold-model) than in previous studies, the empirical correlations found in the literature predicted pressure-drops which were consistent with those measured in the cold-model to the extent allowed by uncertainties in the bed porosity.

Liquid Holdup Correlations

However, liquid holdups predicted from previous correlations were consistently much smaller than holdups observed in the cold-model. These deviations could not be explained by uncertainties in bed porosity. Instead it was found that previous correlations were based on measurements of the volume of liquid which drains from the bed, whereas holdup in the cold-model is based on measurements of the total volume of liquid held in the bed at any time. This total liquid volume is greater than the volume which can drain from the bed (when the flows are stopped) by an amount equal to the liquid volume held permanently in the bed by capillary action. The latter quantity represents a significant fraction of the total liquid volume contained in the bed when gas and liquid flow upward cocurrently.

To check this hypothesis, drained volumes and total volumes were simultaneously measured in the cold-model under a range of gas and liquid flowrates. The two volumes differed significantly. Holdups based on the drained volumes were accurately predicted by the previous correlations, confirming the hypothesis.

Regarding the Synthoil reactor, the total liquid holdup (rather than that which drains from the bed) is the dependent variable of greatest interest. Since no correlations of this quantity were located in the literature, one was developed:

$$\ln H_L = -0.603 \left(\frac{D \rho_w V_{wp}}{\mu_w} \right)^{-1/6} \left(\frac{\rho_g V_{gp}^2}{g D \rho_w} \right)^{1/2} \quad (1)$$

where H_L = total liquid holdup

D = size of packing

ρ_w, ρ_g = density of liquid or gas

V_{wp}, V_{gp} = liquid or gas velocity (based on available cross section)

μ_w = viscosity of liquid

g = acceleration of gravity

For cocurrent air-water flows through a 4-inch diameter bed of 1/4-inch or 1/2-inch cylindrical packing, with superficial gas mass velocities in the range 0.07-1.3 lb/ft²-sec, and superficial liquid mass velocities 0.3-2.6 lb/ft²-sec, the above correlation fits the data with an r.m.s. error of $\pm 5\%$.

An attempt was made to extend correlations for two-phase flow in vertical pipes to the packed bed geometry by modelling the packed bed as a bundle of parallel tubes, each having the same hydraulic radius as the packed bed. Reasonable qualitative agreement was found for the dependence

of pressure drop on liquid and gas velocity; however, liquid holdups predicted by the tube-bundle model were consistently low by a factor of three or four. This discrepancy may be a result of extrapolating the correlations to pipe diameters which are smaller than those upon which the pipe correlations were based.

Liquid holdup, as correlated by equation (1), decreases when the gas flowrate is increased and increases when the liquid flowrate is increased. A simple, but completely theoretical model was constructed to explain this behavior. Consider two parallel plates, inclined with respect to the horizon. Further consider that the gas and liquid phases, flowing cocurrently upward between the plates, are separated with the liquid flowing upward as a uniform film on the lower plate. The driving force for the liquid flow is shear stress at the gas-liquid interface, whereas the gas is driven upward by an imposed pressure drop. The shear stress at the gas-liquid interface is proportional to the imposed pressure-drop. An increase in gas flowrate corresponds to an increase in pressure-drop and so an increase in the shear stress. In order to support the larger shear stress, the thickness of the liquid film must shrink. In other words, the model predicts that liquid holdup decreases with gas velocity, which is consistent with equation (1).

A quantitative description, based on this model, assuming laminar flow of the liquid film, lead to an explicit relationship among pressure-drop, liquid holdup and liquid velocity. Gas velocity does not explicitly appear. This suggested cross-correlation of holdup with pressure-drop, using liquid flowrate as the parameter. The model was found to correctly predict the dependence of holdup on pressure-drop, but the dependence on liquid velocity was considerably overestimated. Of particular interest was the observation that, for low pressure-drop, the model predicts two values of the

liquid holdup corresponding to the same pressure drop. This suggests a mechanism for instability in the flow, which was pursued below using another model.

Radial Distribution of Gas and Liquid

To explain the observed nonuniform radial distributions of liquid, it was postulated, on an intuitive basis, that the liquid distributes radially in a fashion which leads to the lowest pressure drop per unit length. In other words, the fluid selects the path of least resistance. Application of this postulate to determine the radial distribution in a packed bed is a complex mathematical problem. Before tackling this problem, the postulate was first tested on a simpler case: suppose gas and liquid flow simultaneously through a vertical pipe (without packing) which splits into two identical tubes that run parallel for some length before joining together to form a single tube again. If there is no difference between the two tubes, will the gas and liquid split uniformly?

In calculations of pressure drop and holdup as a function of the assumed gas split, using this two-parallel-tube model, the liquid split was determined so that the pressure drop per unit length was identical for both tubes. This pressure matching is necessary, since the tubes are joined to a common manifold at either end. These calculations indicated that, for low liquid flowrates, a uniform split gives the lowest pressure drop; whereas for high liquid flows, nonuniform splits give lower pressure drop. In the latter case, the liquid holdup in the two tubes is substantially different at the split giving the lowest pressure drop. Hence, by extrapolation, high liquid flowrates may favor maldistribution of liquid in the Synthoil

reactor. On the other hand, gas flowrate seemed to have little effect on the computed distribution. Since porosity affects the hydraulic radius of the bed, radial variations in bed porosity can be modelled by taking the two tubes to have different radii. This leads to substantially nonuniform splits and different holdups in the two tubes, as might be expected. Of course, all the predictions of this model are highly speculative and should be further investigated.

Thermal Profiles Without Internal Heat Generation

James Bachelor's memo of March 17, 1976 caused a shift in emphasis from the Synthoil reactor, where the temperature is nearly constant, to the Synthoil preheater, where large changes in temperature occur. Bachelor requested an estimate of time which the liquid spends in the preheater at the reaction temperature. Besides the difference in temperature, the preheater used in runs FB-39 is of much larger diameter and contains much larger packing than the reactor. Consequently, the gas and liquid fluxes are much smaller than any used in the correlations developed from the cold model. Furthermore, the liquid viscosity increases by orders of magnitude at lower temperature. Hence either extrapolation of previous correlations of holdup or more cold model experiments were needed. Effect of liquid viscosity is discussed below.

Independent of the liquid holdup estimate is the determination of the temperature profile within the preheater. This is needed to obtain the reactor volume which is at the reaction temperature. A few measurements of temperature along the length of the preheater were made in runs FB-39 and FB-53.

The number of temperature measurements made was insufficient to support direct correlation of the many variables involved. Therefore, two simplified models were considered in which the reactor wall is jacketed and heated to some temperature. The first model assumes the heat transfer is determined by the wall resistance and in the second model the transfer is determined by the resistance in the packing. Assuming the flowrate per unit area is constant, the first model suggests that the length of preheater needed to heat the inlet stream to a given temperature is proportional to the radius of the preheater, while the second suggests the length is proportional to the square of the radius. Unfortunately, the experimental data are not wholly consistent with either model. Apparently a more complex model is needed, but the amount of available data are insufficient to suggest what additional effects should be introduced.

Effect of Temperature on Holdup

Within the preheater, temperatures will vary between 100°C and 450°C . In this range the viscosity of the coal/oil slurry varies between 1 and 3200 cp and the gas density is halved. The effect these property changes have upon the liquid holdup fraction was estimated using the extensive correlations available in the literature for vertical, two-phase flows in pipes. The results showed that the effect is not monotonic, partly because changes in gas density and liquid viscosity have opposing effects and partly because the oil viscosity does not vary monotonically with temperature. For the specific set of conditions studied the calculated holdup varied from 0.920 at 100°C to 0.592 at 235°C (where the viscosity has a sharp maximum) and back up to 0.833 at 450°C . Considering the enormity of the viscosity change, the computed holdup changes are unexpectedly small, but certainly not insignificant.

Thermal Stability of the Reactor

Reactions occurring in the Synthoil reactor are exothermic. This heat must be removed, perhaps by an external cooling jacket, to keep the temperature within safe operating limits. If a jacket is employed, heat will be transferred radially from a hot center to a cooler wall. Of course, the rate of the reaction increases rapidly with increasing temperature. Unless the heat of reaction can be removed quickly by radial transport, local temperatures in the reactor will rise, increasing the rate of reaction and rate of heat generation, which in turn causes further increases in local temperature, etc. A thermal runaway may occur.

A critique was made of George Quarderer's (Dow Chemical Co.) analysis of this problem. Taking reasonable values for activation energy, thermal conductivities and reaction rates, Quarderer estimates that the largest stable reactor has a diameter of six inches. Although we bring forth several minor criticisms of his analysis, we agree with his principal conclusion: there is ample reason for concern that a six-inch reactor may require some mode of heat removal in addition to an external jacket.