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reactor has a higher per-pass conversion because of the higher thermal conductivity and heat capacity of the slurry compared to gas-phase reactors. In addition, superior mixing in a slurry reactor prevents temperature hot spots.

The initial investigations by Air Products were conducted in 316 stainless steel Autoclave reactors equipped with impellers. Physical mixtures of commercially available catalysts were used. The mixtures included a methanol synthesis catalyst with shift activity, and a dehydration catalyst. The slurry concentrations varied between 15 to 30 wt% catalyst. Three types of feed composition were evaluated: recycle case, once-through case, and basic oxygen furnace (BOF) offgas case. An operating temperature range of 240-300 C (464-572 F) and pressure of 5.6 MPa (812 psia) were selected and the range of space velocities was 1000-6000 (liter/kg cat-hr).

For the case of the recycle feed composition, the product selectivity, defined as the ratio of DME rate to the sum of the DME and methanol rate, decreased with increasing space velocity. The catalyst mixture with the greatest amount of dehydration catalyst (64 wt% dehydration and 36 wt% methanol synthesis) gave the highest selectivity to DME. The catalyst mixture with the highest ratio (1.15 on wt-basis) of methanol synthesis to dehydration catalyst gave the best performance, i.e. high productivity and selectivity to DME. It was also observed that the selectivity increased with increasing temperature. Removal of CO_2 from the reactor feed was shown to significantly increase both the selectivity and productivity of DME. This may be due to CO_2 competing for acid sites on the dehydration catalyst, so when removed from the feed more methanol is dehydrated to DME, which in turn stimulates the gross production of methanol. The advantage of using a slurry was demonstrated by noting that the theoretical adiabatic temperature increase for a gas-phase process would have been 350 C (662 F), whereas for the slurry process the corresponding temperature rise was less than 10 C (50 F).

As with the recycle case, the methanol productivity increases (decreasing the selectivity to DME) with increasing space velocity, for the once-through feed case. On the other hand, the DME productivity reaches a maximum at a space velocity of 2000 (liter/kg cat.-hr). The productivity of both methanol and DME drops compared to the recycle case, however the thermodynamics favors a higher selectivity to DME. The decreased productivity is due to a lower rate of methanol formation. The kinetics of methanol synthesis over Cu/ZnO catalysts is known to be linearly proportional to CO partial pressure and the square of H_2 partial pressure. The once-through feed has a higher CO concentration, but lower H_2 concentration compared to the recycle case. Since the H_2 content dominates the kinetics of methanol formation, the drop in productivity is expected. For this type of feed, addition of steam improves productivity by shifting the CO in the feed to H_2.

For the case of BOF off-gas feed which has essentially an H_2 to CO ratio of zero, steam was co-fed to the reactor and shifted to H_2. Methanol and DME productivities were comparable with the once-through configuration.

The laboratory scale studies of DME/methanol synthesis have been followed up by demonstration runs at Air Products' LaPorte Alternative Fuels Development Unit (AFDU). The DME technology was demonstrated in a 2 ft. diameter by 30 ft. tall slurry reactor. Operating conditions of 250 C (482 F) and 5.3 MPa (765 psia) were used. It was found that the preferred dehydration catalyst proportion is between 5 and 25 wt%.

5.0   SLURRY REACTORS FOR OXYGENATES SYNTHESIS

It is clear from a review of the literature that a current trend in the production of alcohols and ethers from synthesis gas has focused on the use of slurry reactors. Extensive work by Air Products and Chemicals has demonstrated the effectiveness of this type of reactor in producing methanol and dimethyl ether. Details of these operations were discussed in the previous sections of this report. Criteria pertinent specifically to the design and operation of a slurry reactor appear here.

5.1   Advantages and Disadvantages

In a slurry reactor the synthesis gas is passed upward into the catalyst-containing reaction vessel. An inert hydrocarbon liquid serves to suspend the fine catalyst particles and to absorb the heat of reaction. The gas provides the turbulence necessary to suspend the catalyst as well as improving gas-liquid contact.

Due to the simplicity of operation, low operating costs (due to reduced compression requirements), and the ease with which temperature can be controlled, slurry reactors have found application in a variety of gas-liquid-solid reaction systems (Ozturk et al., 1988). As a result of the excellent heat removal and hence, reaction temperature control, high per-pass conversions can be achieved. This reduces the recycle gas flow and compression requirements. The heat of reaction may be recovered as high pressure steam. Uniform distribution of the liquid and gas phase across the cross section of the reactor vessel eliminates the need for redistribution along the reactor length (Ozturk et al., 1988), simplifying reactor design. The fine catalyst particle size allows higher reaction rates compared to pellet-sized catalysts.

The rapid internal circulation of the liquid phase in the reactor provides excellent mixing, and thus very uniform concentration and temperature profiles. This has

both advantages and disadvantages (Fox et al., 1990). From a reaction standpoint, the conversion achievable in a given size reactor is limited. However, from a heat dissipation standpoint, the temperatures within the vessel are very uniform and good heat transfer coefficients are obtained.

5.2   Heat and Mass Transfer

For the synthesis of oxygenates, an internal heat exchanger would be installed within the slurry reactor to remove the heat released from the highly exothermic reaction. There have been a number of studies of heat transfer from tubes in slurry reactor systems, reported in the literature. The most recent of these is the work by Saxena et al. (1991).

Saxena has performed extensive tests on the hydrodynamics and heat transfer of a slurry reactor, using 10.8 and 30.5 cm i.d. columns. The liquid media used were water and Therminol-66, a high molecular weight, high viscosity hydrocarbon heat transfer fluid. The heat transfer coefficients for the air-water-red iron oxide solid (1.0 and 2.4 micron, up to 30 wt%) decreased with increasing slurry concentrations. The particle size had negligible influence. For tube bundles, the coefficients were appreciably higher than for single tubes. Results with nitrogen-Therminol-red iron oxide system were appreciably different. The coefficients were an order of magnitude smaller than for water. They increased with increasing solids concentration and were smaller than for single tubes. It has also been concluded (Saxena et al., 1991) that existing correlations cannot predict observed results with sufficient accuracy, and should be used with caution for design and evaluation purposes.

As discussed in previous sections, Air Products has performed demonstration tests with a 22 inch i.d. slurry reactor at LaPorte, and evaluated internal heat exchanger performance for high catalyst loading conditions. The slurry side coefficients were

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observed to be 295 to 321 Btu/(hr)(ft^2)(F) and overall coefficients in the range of 44 to 96 Btu/(hr)(ft^2)(F). Furthermore, predicted overall coefficients, using Sieder-Tate and Deckwer correlations, were accurate within the uncertainty range of plant data (LPMEOH PDU Report, Jan. 1991). This is in contrast to Saxena et al. (1991) conclusions.

In a slurry reactor, the reactants must first transfer from the bubbles to the liquid phase and then diffuse through the liquid to the catalyst surface, and finally through the catalyst pores. However, compared to intrinsic reaction rates, only diffusion through the liquid phase is important since it is the slowest step (Akgerman, 1988).

Volumetric mass transfer coefficients for carbon monoxide have been measured in small bubble column reactors (Zaidi et al., 1979). The mass transfer coefficient for CO was determined by using experimentally determined specific gas-liquid interfacial areas, which in turn were obtained from data on gas hold-up and Sauter mean bubble diameters. The coefficients matched fairly well with values predicted by correlations developed by Calderbank and Moo-Young (1961) and Hughmark (1967). Volumetric mass transfer coefficients have been determined for both CO and H$_2$ using stirred tank reactors (Albal et al., 1984; Ledakowicz et al., 1984; and Deimling et al., 1984). Again, these values agree well with predictions from Calderbank and Moo-Young (1961).

5.3   Reactor Design Issues and Scale-Up

Design criteria for the LPMEOH slurry reactor used by Air Products at their LaPorte facility have been discussed by Bonnell and Weimer (1984). Construction of a reactor model requires understanding of the transport and kinetic phenomena for the system. Such understanding would include: 1) correlations for the intrinsic reaction kinetics, 2) models for gas, liquid, and solid distribution and mixing, and 3) correlations for predicting gas/liquid and liquid/solid mass transfer. Integration of this information into a single system constitutes a reactor model.

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In designing a slurry reactor, the goal is to optimize the height and diameter of the reactor vessel for a given capacity. To determine the vessel diameter, the superficial gas velocity, V_G, must be set. If V_G is set too high, excessive gas hold-up results, and if it is set too low, the vessel shape will be uneconomical. Given V_G and the feed gas flow, the reactor cross-sectional area and diameter can be calculated (Bonnell and Weimer, 1984).

The height determination depends on three factors: 1) gas hold-up, 2) slurry loadings, with higher loadings (limited by plugging problems) resulting in lower reactor volume, and 3) space velocity. The choice of space velocity is related to the reactor conversion through mass transfer and kinetics, and this fixes the weight of catalyst in the reactor. The volume of slurry is then determined by the slurry loading. Given the slurry volume and the superficial gas velocity, and the predicted gas holdup, the required reactor volume can be calculated (Bonnell and Weimer, 1984).

Fair approximations for the gas hold-up can be obtained by using the correlations developed by Akita and Yoshida (1973) or Hikita et al. (1980), but considering the importance of gas hold-up to slurry reactor scale-up, measurements of gas hold-up in laboratory scale columns (i.d. > 15 cm) is recommended. Air Products has conducted two-phase gas hold-up studies over a wide range of operating conditions, in their modified slurry reactor at the LaPorte facility (LPMEOH PDU Report, Air Products, Jan. 1991). The reactor hydrodynamics, with an internal heat exchanger, was investigated as a function of pressure, temperature, gas velocity, external liquid circulation rate, and reactor height. Two types of feed gas, nitrogen and CO-rich gas, were tested in Drakeol-10 oil.

Operating ranges for the Air Products tests covered 0.66-6.3 MPa (95-915 psia), 77-250 C (170-482 F), and 0-198 gpm of external liquid circulation. As expected, the gas hold-up increases with increasing superficial gas velocity. Little difference was observed between the gas hold-up generated with nitrogen compared to that of CO-rich gas. The liquid superficial velocity has no significant impact on the gas

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hold-up at gas velocities of 0.04 ft/sec, however above gas velocities of 0.1 ft/sec, the gas hold-up decreases as superficial liquid velocity is increased. At both high and low liquid velocities, the gas hold-up increases with an increase in pressure at gas velocities greater than 0.1 ft/sec. This is predicted well by Tarmy et al. (1984) and Idozawa et al. (1987). It is not clear whether the change in the gas hold-up is caused by the gas density change or a change in the oil physical properties. No pressure effect was observed above 5.3 MPa (765 psia). Increase of temperature was seen to increase the gas hold-up with no liquid circulation flow. With a liquid velocity of 0.2 ft/sec, the trend was reversed. This does not follow any expected trend and was attributed to scatter in the data. The gas hold-up was uniform over the reactor height (especially at low gas velocities) over a range of liquid velocities. A comprehensive discussion of the gas hold-up runs, including the conditions tested, can be found in the Air Products report (LPMEOH PDU Report, Jan. 1991).

Based on Air Products experience with methanol catalyst slurries, non-Newtonian behavior can be expected. The slurry characteristics can depend on: 1) catalyst formulation and treatment, 2) method of mixing the slurry, and 3) weight fraction of catalyst loading. The design should give consideration to the tendency of fine catalyst particles to adhere to each other as well as the vessel. The internal agitation, determined by the sparger design, must be sufficient to keep the catalyst from settling.

Studies of mass transfer and kinetics in a slurry reactor system were not made in the LPMEOH facility, however earlier work by Air Products indicates that the mass transfer coefficients can be correlated well by using the Akita and Yoshida correlation (1974). For scale-up purposes, it has been suggested that the mass transfer coefficient can be assumed to be a function of gas hold-up only, and not reactor length or diameter. This is a good assumption for reactors with diameters greater than a few inches.

A simplified, empirical model has been proposed (Bonnell and Weimer, 1984) for scale-up studies of slurry reactor systems used for methanol synthesis. This model is built on several assumptions:

- Methanol synthesis reactions can be predicted by means of approach to equilibrium, expressed as a percentage of equilibrium conversion.

- Approach to equilibrium is a function of synthesis gas composition, temperature, and space velocity.

- Gas/liquid and liquid/solid mass transfer coefficients will be as high (or higher) in large-scale reactors as in the autoclave.

- Catalyst particle sizes are small enough so that effectiveness factors equal unity.

Although the model has been developed for methanol synthesis, there is no reason not to extend it to the synthesis of higher alcohols and ethers. Air Products' results suggest that mass transfer resistances in a slurry system are insignificant compared to equilibrium and kinetic limitations.

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6.0 RECOMMENDATIONS

The previous sections have covered a range of processes, both commercial and developing, for the production of alcohols and ethers. Most importantly, catalyst compositions and ranges of operating conditions have been included for the majority of these processes. The use of gas-phase fixed-bed reactors for producing methanol and higher alcohols has been covered in Sections 2.0 and 3.0. Review of current literature indicates that the most promising improvement in oxygenates synthesis technology, is the development of the liquid-phase slurry reactor. A key factor favoring the use of slurry reactors versus the fixed-bed technology is the considerable improvement in temperature control and heat dissipation. This translates into greater production rates as a result of increased per-pass conversion. It is therefore recommended that the fixed-bed reactor technology for oxygenates synthesis not be pursued.

The liquid-phase synthesis of methanol demonstrated by Air Products in their slurry reactor at the LaPorte facility holds great potential for improving the economics of methanol production. It is advisable to follow the design and operating conditions of this LPMEOH unit closely, in determining the design for the oxygenates section of the pilot plant. This means operation in the 235-270 C (428-518 F) and 3.55-6.31 MPa (515-915 psia) range. Special attention should be paid to the internal recirculation and heat exchange mode of operation, for it holds the potential of greater simplicity of operation and process reliability.

More recent work by Air Products has demonstrated the successful synthesis of DME and methanol mixtures, using the liquid-phase technology. Demonstration runs at the LPDME unit at LaPorte have operated at 250 C (482 F) and 5.28 MPa (765 psia). Commercially available mixtures of methanol synthesis catalyst and dehydration catalyst have been used by Air Products. To insure the ether production capability of DOE pilot plant's oxygenates slurry reactor, the

operation of the LPDME unit should be closely. Air Products has also scheduled
runs for the early part of 1992, to produce isobutanol using their liquid-phase
(slurry) process. Their work should be followed closely to determine the
conditions selected to perform these runs.

Based on the information available in the literature, the following conditions are
recommended for operation and design of the oxygenates synthesis slurry reactor:

Conditions	Operating Range	Design Condition
Temperature, C	150-380	250
Inlet Pressure, psig	750-1700	750
Space Velocity, sl/hr-kg cat.	2000-17500	10000
Catalyst Loading, wt%	30.0-50.0	35.0
Superficial Gas Velocity, cm/s	3.0-30.0	15.0

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