Catalytic Liquid Membrane Reactor:
I. Concept and Preliminary Experiments in Acetaldehyde Synthesis

D. F. OLLIS, J. B. THOMPSON, and E. T. WOLYNIC

Department of Chemical Engineering
Princeton University, Princeton, New Jersey 08540

The ease of catalyst recovery from reaction mixtures has been the traditional advantage of heterogeneous versus homogeneous catalysis. While this feature has motivated recent schemes of catalyst localization (*1* to *7*), the equally traditional problems of mass and heat transfer limitations in heterogeneous systems must be met. Temperature control may be more easily attainable in homogeneous reaction systems, but catalyst recovery often leads to corrosion problems and the production of extraneous byproducts (*8* to *10*).

The present note discusses a new potential catalytic liquid membrane reactor which requires no solid recovery phases, minimizes catalyst handling, and results in partial reactant-product separation in the reactor.

THE REACTOR CONFIGURATION

The heart of the new reaction system derives from a surfactant liquid membrane extraction system due to Li (*11* to *13*). Li's extraction column with a selectively permeable recycled surfactant membrane has been used successfully to separate cyclic from straight chain hydrocarbons (*12* to *14*) and has been examined as a potential blood oxygenator (*15*). Since the membrane-forming solution in his system is handled and recycled in a single vessel without chemical recovery steps, it is logical to dissolve a soluble catalyst in the membrane phase and seek to carry out both reaction and extraction in the same unit.

In a potential system shown in Figure 1 reactants permeate the feed/membrane interface, undergo a catalyzed reaction, $A + B \rightarrow C$, with product C being preferentially extracted into the outer solvent phase. If consideration is restricted to gaseous reactants, aqueous catalyst solutions, and organic solvents, then the relative density requirements of $\rho_{\text{feed}} < \rho_{\text{solvent}} < \rho_{\text{membrane}}$ may be fulfilled for a wide range of components.

Some potential advantages of the system shown in Figure 1 are noted below:

1. The system is a single vessel extraction stage and chemical reactor.
2. Proper reactor design should allow for minimum contacting of the dispersed corrosive catalyst phase with the vessel walls.
3. Small feed droplets may enhance both adsorption of reactants and extraction of products.
4. The thin catalytic membrane would make the liquid-phase diffusional resistance for dissolved gas transfer quite small.
5. The achievement of rapid partial reactant-product separation in the system would allow for high conversion in reactions with small equilibrium constants.
6. Reactant-product separation might also allow for high intermediate product selectivity in series reactions.

Preliminary experiments leading to a feasibility analysis of the proposed system have been conducted using the synthesis of acetaldehyde via ethylene oxidation by palladium chloride-copper chloride catalysts.

PRELIMINARY STUDIES

The synthesis of acetaldehyde via the reaction route (*16, 17*) used in the commercial Wacker process was selected for study as being representative of a large class of useful reactions (*18, 19*). The reaction is highly exothermic and the catalyst phase is highly corrosive towards ferrous alloys.

A potential continuous process utilizing the liquid catalytic membrane is shown schematically in Figure 2. Satisfactory operation clearly depends upon acetaldehyde solubility in the solvent rich phase, appreciable reaction rates in the water rich catalyst phase, and relative ease of raw product recovery in the distillation unit. In these areas,

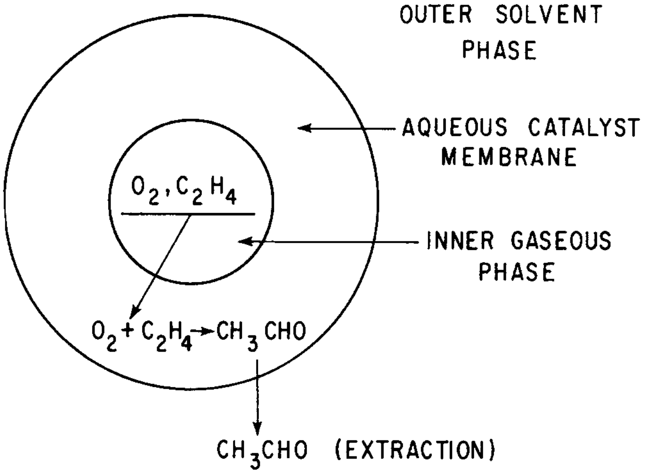

Fig. 1. Schematic diagram of liquid catalytic membrane.

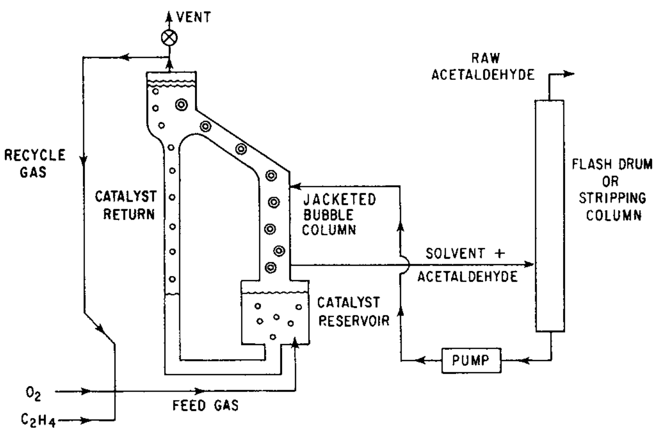

Fig. 2. Flow diagram for multiphase reactor and product recovery.

TABLE 1. RELATIVE RATE OF ACETALDEHYDE PRODUCTION IN WATER ($R = 1.0$) AND IN SOLVENT-SATURATED AQUEOUS PHASES[a]

Added solvent	Reactor solution[b]	Relative rate at steady conditions
—[c]	0:10:90	1.0
ethyl acetate	8.7:1.3:90	0.88
3-pentanone	4.1:5.9:90	0.76
2-pentanone	7.3:2.7:90	0.74
3-heptanone	0.5:9.5:90	0.61
n-butanol	9.5:0.5:90	0.47

[a] $O_2:C_2H_4$ ratio = 2.0, T = 50°C., total gas flow = 2.44 cm^3/s.

[b] Volume solvent: volume de-ionized water: volume catalyst solution: 0.0033 *M* $PdCl_2$, 0.558 *M* $CuCl_2$, reactor volume = constant = 100 cu. cm.

[c] Pure de-ionized water.

Reactor: Low conversion bubble reactor, height = 3.8 cm.

preliminary experiments were conducted using a range of solvents.

The relative steady state differential rates of ethylene conversion to acetaldehyde were measured in a 3.8 cm column of catalyst solution saturated with solvent. Pertinent reaction conditions and the resulting rates of reaction are summarized in Table 1. Analysis was performed with a Perkin Elmer 810/820 V.P.G.C. using a 3.0 m. 15% Carbowax 400 column.

A simple distillation study was also carried out using an insulated, 250 $cm.^3$ preheated still which was charged with 100 $cm.^3$ of solvent which was saturated with water and contained 0.01 mole fraction acetaldehyde. The vapor line from the still to a flowmeter and on to the V.P.G.C. was maintained above the still temperature to avoid any refluxing action. The distillation runs were analyzed in plots of mole fraction acetaldehyde in the instantaneous vapor distillate versus weight % of the original acetaldehyde charge distilled.

DISCUSSION

The reaction rate data of Table 1 indicates that with the solvents used the relative rates are not significantly changed from that of the reference aqueous catalyst solution, varying from 88% of the reference rate when 8.7 vol. % of ethyl acetate is present to 47% of the reference rate when 0.5 vol. % of *n*-butanol is present. All runs appeared physically reproducible in that bubble sizes did not appear to change with varying solvents. Thus, rate differences cannot be explained by varying available reaction surface areas. The measured reaction rates should be representative of those expected in the proposed liquid membrane reactor. Since the slowest measured rate was only about half of the reference rate, an obviously superior solvent choice was not indicated by these rate experiments.

In all runs, the characteristic green color of the catalyst solution was maintained indicating no palladium metal precipitation due to oxygen depletion in the catalyst phase. Thus, solvent presence in the catalyst phase did not appear to greatly diminish its oxygen solubility characteristics.

The distillation results indicate that product recovery is easiest with the solvents 2- and 3-pentanone and 3-heptanone. In the latter case, the one stage overhead acetaldehyde composition is essentially unity up to 73 weight % recovery of the original acetaldehyde charged. However, the product is significantly less volatile in the ternary mixtures containing the solvents *n*-butanol or methyl isobutyl ketone. The qualitative trend of increased difficulty of acetaldehyde separation with increased solubility of solvent in the catalyst phase is seen from this data. Increasing water solubility in the solvent phase may result in an undesirable increase of catalyst concentration in the solvent phase with its corresponding decrease in the aqueous catalyst phase. The above two considerations indicate that the prime criterion for solvent selection in this system would be solvent-water incompatibility.

Operation of the complete unit to ascertain membrane stability, degree of reactant-product separation, catalyst concentration in the solvent phase, and solvent loss in the product recovery section will be reported in a subsequent paper.

CONCLUSION

The principle of a novel reaction-separation device, a catalytic liquid membrane reactor, has been discussed and several potential advantages pointed out. Preliminary data on the system has been obtained using the homogeneously catalyzed oxidation of ethylene to acetaldehyde. These data indicate a minimal reaction rate inhibition in the mixed solvent-water catalyst phase investigated, with a reasonable product recovery via simple distillation with appropriate solvent choice.

This new reaction-separation system appears to be applicable to a fairly large number of homogeneously catalyzed processes, and in particular, appears to offer an attractive alternative to recent localization schemes for transition metal catalysts.

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