SIMULTANEOUS REACTION IN SEPARATION

The other papers in this session carefully outline what is already known about separation science. They show that continued improvements will come in an evolutionary way unless we can shift to an entirely new basis. One such basis is chemical manufacture by the simultaneous reaction and separation. In the past, this strategy has been dismissed because the optimal conditions for reaction and for separation are different. Still, this paper will discuss three examples where such processes seem feasible: the dehydrogenation of ethane, the local production of ammonia, and a wearable chemical reactor to avoid dehydration on airplanes. The examples suggest that the possibility of new paradigms combining reaction and separation have the greatest promise for small systems.

BACKGROUND. The earlier papers in this session give accurate and informed descriptions of the current state of separation processes. In particular, in his paper, Wankat argues that distillation will remain the workhorse of chemical separations. He feels that major improvements are unlikely, even though distillation consumes one million barrels of oil per day in the U.S., with an efficiency commonly believed to be about 11 percent. He asserts that this situation won't change much.

I support this assertion. For differential distillation the height of the tower ℓ is given by

$$\ell = HTU \cdot NTU$$

where HTU is the heighth of the transfer unit and NTU is the number of transfer units. The NTU, which is the measure of the difficulty of the separation, will be small when the operating line is far removed from the equilibrium line, that is, when the reflux ratio is big. But a big

reflux ratio means a big heat load in the reboiler, which is a chief cause of process inefficiency. Alternatively, the HTU, which measures the equipment's efficiency, will be small because of structure packing. While this packing will certainly continue to improve a major breakthrough is unlikely.

An alternative way in which separation processes could be significantly improved involves avoiding phase changes, especially phase changes of water, which is the thesis which Prof. Koros advanced. Again, I agree with this goal. Minimizing these phase changes will initially be accomplished mechanically, using presses and screens like those in the paper industry. Further improvements can come from absorption, either by particles or across membranes. Unfortunately, these adsorptive methods may frequently be slower than conventional drying.

Ethane Dehydrogenation. If these strategies fail, we may try to combine reaction and separation. One target example may be the dehydrogenation of ethane, which is run at atmospheric pressure but high temperature, frequently over 800°C. The catalytic reactions which take place under these circumstances are often believed to be limited by equilibrium. Thus the dream is to have some sort of process which removes one product but not the other components. For example, for ethane dehydrogenation, where the reaction is

$$C_2H_6 \text{ É } C_2H_4 + H_2$$

We can imagine a membrane selective for hydrogen, which would continuously remove the hydrogen and hence allow all of the ethane to be converted to ethylene. This type of process has been a dream supported by scattered experiments for at least 20 years. To date, efforts to realize this dream have centered on the flux and the cost of the membrane. Frequently, the target

is a cheap, thin palladium membrane in order to achieve a very high flux. Some progress has been made by alloying the palladium with metals like silver.

I remain concerned that membranes of this sort will be difficult to use in practice. I am unsure what seals can be used at 800°C and whether these seals will be able to stand the start up and shut down without the membrane cracking. While the process is intended to operate at steady state, the inevitable inhomogeneities and upsets may give more strain than the membrane can stand. Still, work on this tipic will almost certainly continue.

Small Scale Ammonia Synthesis. A second example is the dispersed manufacture of ammonia, not in a central location but for an agricultural coop or one large farm. At present ammonia is manufactured from natural gas. The gas is burned in air to produce hydrogen, nitrogen, and carbon oxides. After those oxides and water are carefully separated, the near stoichiometric mixture of hydrogen and nitrogen is fed to the Haber process reactor, which operates at about 400°C and 150 atm. As in the case of ethane dehydrogenation, the high temperature, which is chosen to insure fast kinetics, also prevents the reaction from going to completion. Conversion is normally on the order of 20 percent. As a result, the conventional process must have both elaborate apparatus for removing the carbon oxides and sophisticated recycles for recovering the unreacted hydrogen and nitrogen.

An alternative possibility more suitable for making ammonia locally might be to assume that wind power drives the electrolysis of water to produce hydrogen. After nitrogen is produced using commercially an available membrane process, the hydrogen and nitrogen are fed at high temperature and pressure to a batch reactor containing both the Haber process catalyst, a solid absorbent for ammonia. We have made scattered experiments that show that the conversion in

this batch reactor can exceed 90 percent avoiding both the elaborate separation equipment for preparing the reaction mixture and the elaborate separations and recycles. We pay for this with the batch reactor, operated periodically. The commercial value of this idea is unknown.

Preventing Dehydration. The final example is a still smaller system. I am partially blind in one eye because I have a blood mutant, common to 15 percent of the population, which makes my blood clot more easily than normal. Thus when I became dehydrated on an airplane, I got blood clots which can cause strokes or, in my case, partial blindness. Thus I have wondered about a wearable absorber which would prevent my dehydration. Such adsorbers would imitate the nose of the kangaroo rat, which allows the rat to go for long periods of time in the dessert without sources water liquid. Such a reversible reactive adsorber seems very possible, easily constructed for less than $100. While I know such a gadget must seem bizarre compared to the larger reactors discussed previously, it does suggest that in the future there is a possibility for a changed paradigm for small reaction units, even if none looks likely for large ones.