CONTINUOUS CHEMICAL REACTION CHROMATOGRAPHY

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by

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The research supported by DOE under this Department of Energy grant resulted in the development of continuous flow adsorptive chemical reactors based on chromatographic separations. In particular, the countercurrent moving bed chromatographic reactor and the simulated countercurrent moving bed chromatographic reactor were investigated both theoretically and experimentally. An important contribution was the demonstration that simulated countercurrent moving bed reactors can be successfully used for methane conversion reactions, giving promise of commercial processes for turning natural gas into useful chemical feedstocks and fuels. This work has stimulated interest in the area of reactive adsorption/separation. Publications resulting from this research are listed below.

There has been much recent interest in chemical processing where chemical reaction and separation are carried out simultaneously in combined reactor-separators. Examples of separative reactors are reactive distillation, membrane reactors and adsorptive reactors, in which separation is accomplished by distillation, mass transfer through a porous membrane and selective adsorption on a solid, respectively. When chemical reaction and separation occur in concert, the requirements for downstream processing may be eliminated or greatly reduced, resulting in less complex and less costly chemical plants. A significant advantage of integrated reaction-separation operations is the opportunity for reduction in capital expenditure that is afforded.

The combined separation of reactants and products provides other advantages. Unfavorable chemical equilibria can be shifted to enhance reactant conversions and desired product yields, reducing recycle streams. Unwanted reaction products can be reduced or eliminated because contacting of reactants with products can be minimized. Furthermore, when dealing with reaction networks, it may be possible to optimize the selectivity for a desired, intermediate product. There would not only be economic benefits from realization of these goals, but environmental benefits from reduced waste streams, and lower CO₂ emissions from lessened energy requirements. With the
increasing emphasis upon environmental issues, integrated reaction-separation processes will be of increasing importance. Reactive distillation and membrane reactors are the subject of other chapters in this volume, while adsorptive reactors are discussed in this chapter.

In adsorptive reactors chemical reactions are carried out in the presence of a solid adsorbent capable of selective adsorption of the components of the reaction mixture. Differences in adsorption selectivity cause separation to occur during the course of the reaction. The reaction may be catalyzed by the adsorbent, or by a catalyst that is added to the adsorbent, or the reaction may occur homogeneously in the fluid phase.

There are several ways in which adsorptive reactors have been configured. It has been known for more than three decades that if a chemical reaction occurs in a chromatographic column following pulsed introduction of reactant(s), reaction and separation occur simultaneously in a process called reaction chromatography. Recent developments have extended this concept to continuous flow processing, overcoming the essentially batch nature of reaction chromatography, and the low throughput which is the principle objection to practical applications. Continuous flow reaction chromatography has been demonstrated in rotating cylindrical annulus, countercurrent moving bed and simulated countercurrent moving bed configurations. Reactive separations have also been carried out in pressure swing adsorbers and in a trickle bed reactor.

If equilibrium-limited chemical reactions are carried out in adsorptive reactors, the separation can shift the equilibrium, increasing the conversion of reactant(s). For example, in a reaction of the type $A \leftrightarrow B + C$, separation of B from C suppresses the reverse reaction and the conversion of A can exceed the equilibrium limit that would be the maximum obtainable in a non-separative reactor. Similar conclusions are reached for other reversible reaction types. Under favorable circumstances conversions closely approaching unity can be obtained, and the recycle that would otherwise be necessary can be avoided or greatly reduced. This reduction of process complexity has clear economic implications, both in lower capital costs and in lower energy requirements. Adsorptive separations are less energy intensive than many other types of separations such as distillation.

Adsorptive reactors also provide more flexibility in temperature optimization than do non-separative reactors. For reversible endothermic reactions the increase of equilibrium conversion with increasing temperature means that non-separative reactors should be run at high temperature to avoid or minimize recycle. If equilibrium is circumvented by means of an adsorptive reactor, however, high conversion can be obtained at lower temperature, giving further savings on process energy requirements, and most likely reducing the rate of catalyst deactivation. There will be an optimum temperature depending upon the reaction rate and the separation achieved. In non-separative reactors reversible exothermic reactions should be run at low temperature for high conversion, but attaining adequate reaction rates may dictate higher temperature operation, resulting in lower conversion. Adsorptive reactors permit optimization of the temperature without loss of
conversion, and without need for recycle.

A central issue in adsorptive reactors is adsorbent selection. The adsorbent should be stable, should maintain enough selectivity to accomplish the separation at the reaction temperature, and should preferably have a well-behaved adsorption isotherm. In particular, the distribution of adsorption energies should not be wide. If high energy surface sites are present it will be difficult to regenerate the adsorbent, and reactor performance will be adversely affected: The desired product will contain impurities and conversion will suffer. There is an extensive literature on adsorbents, coming from years of development of commercial adsorptive separations and from analytical gas and liquid chromatography. Conventional solid, porous adsorbents are available in numerous materials ranging from inorganics such as alumina and zeolites to porous polymer beads. Various pore sizes are available for some materials. In addition, there are many liquid stationary phases available for coating on inert solids. These have been utilized mostly in analytical applications, and do not seem to have been much investigated for commercial scale separations. Some zeolites that are shape or size selective have been developed, as well as shape selective zeolite catalysts. With such a wealth of adsorbents, there is considerable scope and flexibility in adsorbent selection for adsorptive reactors.

Publications.


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