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A small, well-mixed reactor for high throughput study of commercial catalyst pills

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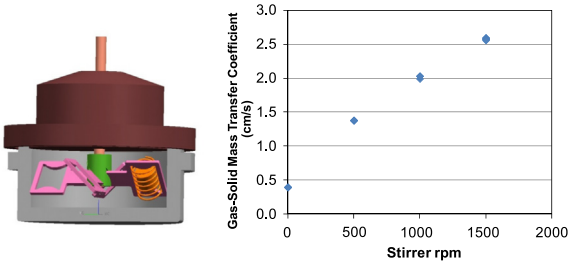
HIGHLIGHTS

- Small CSTR for commercial catalyst pills is well mixed and gives a gas–solid mass transfer coefficient of 2.5 cm/s.
- Small footprint will enable arrays of CSTRs in a laboratory High Throughput system.
- Transport and mixing similar to or better than many common legacy devices.

GRAPHICAL ABSTRACT



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ABSTRACT

Industrial catalyst development is benefiting from the use of high throughput research. This is typically accomplished by running large numbers of experiments in parallel, using common reactant feed manifolds and analytical systems. In order to fit within a reasonable laboratory footprint, high throughput reactors must be small, yet retain mass and heat transfer rates that allow gradientless operation. For heterogeneous catalytic reactions there are a number of high throughput systems available for testing powdered, or granular catalysts in banks of plug flow reactors, but no reports of CSTR systems capable of testing formed catalyst particles used in commercial fixed bed reactors.

We describe the development and engineering characterization of a small prototype CSTR for testing whole catalyst particles. The reactor has inside dimensions of 6.35 cm diameter by 2.8 cm deep and shows well-mixed behavior, based on methane tracer studies. Sublimation of non-porous cylindrical naphthalene cylinders (7.5 mm diameter by 7 mm long) was used to characterize the solid–gas mass transfer coefficient. It was found that the prototype reactor exhibits mass transfer rates similar or higher than reported in the literature for the much larger traditional Carberry and Berty-style reactors. This makes the new device suitable for further development of high throughput arrays of CSTRs for testing commercial catalyst pills.

1. Introduction

Solid-catalyzed gas-phase reactions are among the most important classes of reactions in the petrochemicals industry. These reactions are fraught with complexity, due to the nature of the fundamental catalytic phenomena but also due to the many critical transport phenomena involved. Molecular transport occurs by convective means in the bulk gas phase, by bulk diffusive means in the hydrodynamic boundary layers at reactor walls and catalyst particle surfaces and by the diffusive processes occurring within the catalyst particles. Heat transfer occurs by a number of means that are closely related but not identical to, the mass transfer

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phenomena.

Commercial reactor designs for large-scale, exothermic catalytic processes generally use catalyst particles with equivalent diameters in the range of 3–10 mm and result in particle Reynolds numbers on the order of 500–2000. This allows operation in a regime that is generally controlled by kinetic and/or intraparticle transport phenomena. Refinements in catalyst formulations and the design and construction of new plants for the manufacture of commodity chemicals require ongoing kinetic studies of traditional heterogeneous catalytic processes. In principal, kinetic data can be generated with powders and all intraparticle phenomena, including heat and mass transport could be modeled. However, such modeling is not sufficiently advanced, and commercially produced carriers are not so perfectly uniform or well characterized that the step of testing realistic commercial particles in laboratory reactors can be eliminated. This means that experimental studies with whole pellets of catalyst – the size and shape intended for use in commercial reactors – remain an important part of industrial practice.

In order to accelerate the testing of fully formulated and formed catalyst pellets, we were asked to develop a reactor prototype that could meet the following demands:

- Operate up to at least 2 MPa gauge (7 MPa preferable).
- Produce a transport environment consistent with commercial, multi-tubular reactor systems (i.e., particle Re from 500 to 2000).
- Accommodate at least 4 commercial catalyst pellets of 3–10 mm diameter in any geometry.
- Operate from ambient temperature to 300 °C (preferably 400 °C)
- Be of simple enough design to enable reliability for multi-week operation
- Be small enough that an array of 8–48 reactors can fit the footprint of a typical ventilated enclosure – 1 m by 1.5 m for example.
- Be compatible with existing laboratory equipment and infrastructure for fluid handling, analytical systems, temperature control etc.

While laboratory plug flow reactor systems are convenient and inexpensive to build, reliable in operation, and capable of producing useful kinetic and deactivation information on granular catalyst samples, they are not well suited to the study of formed catalyst pellets. In order to achieve plug flow character, the reactor inside diameter must be several times the pellet diameter, which leads to tube diameters on the order of 2–3 cm or larger for typical catalyst pellets. It is easily shown that for a given space time (τ) the superficial fluid velocity (v) scales with the length (L) of the reactor tube.

$$v = \frac{L}{\tau} \tag{1}$$

This dictates that laboratory-scale plug flow reactors packed with typical whole catalyst pellets cannot concurrently match the space time and transport environments of their commercial counterparts. For strongly exothermic or endothermic reactions, this leads to non-isothermal behavior in the laboratory reactor, and potentially large film temperature and/or concentration gradients. This greatly complicates the interpretation of the resulting data.

While many types of laboratory reactor systems have been proposed for the study of heterogeneous catalytic phenomena, few are suitable for the study of whole catalyst pellets under the conditions of industrial use. Microchannel reactors (Jensen, 2001) provide high area to volume ratios and are potentially capable of providing fine temperature control, even for highly exothermic reactions, but are not intended for the study of catalyst pellets used in existing fixed bed reactor systems. The Transient Analysis of Products (TAP) reactor originally reported by Gleaves et al. (1988) has found ongoing use in the elucidation of details of reaction kinetics and catalyst states (Yablonski et al., 2003) but is not well suited to the study of whole pellet performance at temperatures and pressures used in commercial production. A single pellet reactor described by Harold and Luss (1985) was designed to study bifurcation behavior evidenced by large film temperature gradients. However, its glass construction was not suitable for studying processes operated at elevated pressures, and typical particle Reynolds numbers in this device were 2–3 orders of magnitude lower than what would be encountered in a typical commercial reactor for a partial oxidation process.

Continuous Stirred Tank Reactor (CSTR) systems have long been popular for the laboratory study of catalyst pellets and their use provides important benefits including (i) it allows the space time and the hydrodynamic environment to be decoupled and (ii) it exposes the catalyst sample to a single gas-phase composition, enabling the assumption that the catalyst sample has a single chemical state and extent of deactivation during kinetic studies.

Several styles of CSTRs for the study of catalyst pellets in gas phase chemistries have seen common use in the literature and

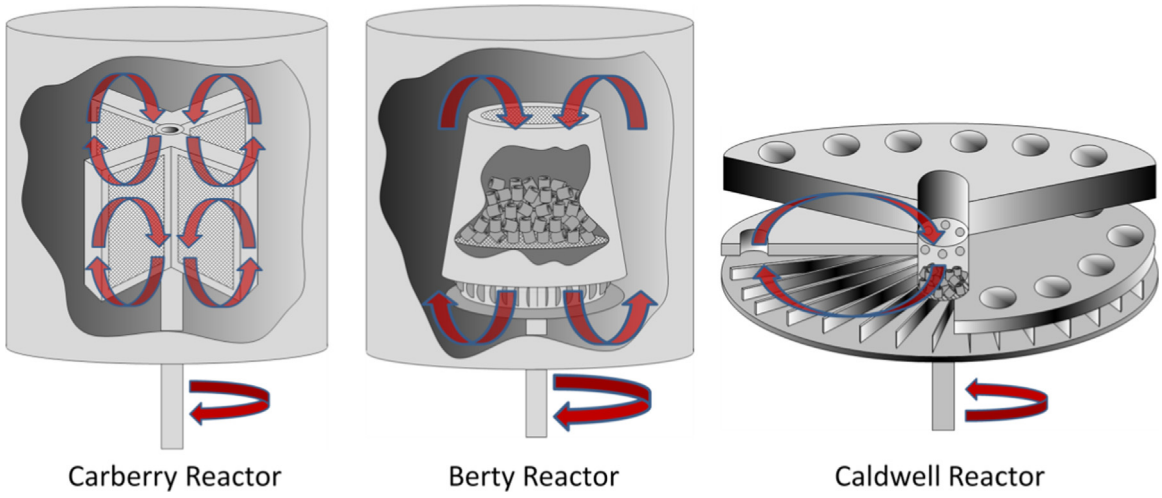

Fig. 1. Schematic of common continuous stirred reactors for the study of heterogeneous catalytic reactions.