

Scaling-out selective hydrogenation reactions: From single capillary reactor to monolith

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Abstract

Selectivity and kinetic studies of the Pd-catalysed hydrogenation of 2-butyne-1,4-diol were performed in a single capillary channel, and monoliths consisting of 1256 capillaries and 5026 capillaries in (I) the pressure range 100–300 kPa (II) the temperature range 298–328 K using a 30% v/v 2-propanol/water solvent. All reactors were operated in downflow mode such that the reaction fluid was in Taylor flow. Transport calculations indicated that liquid–solid transport resistances were low (<5%) and energies of activation were found to be in the range 32–34 kJ mol⁻¹. While the reaction was first order in hydrogen concentration, the order with respect to 2-butyne-1,4-diol changed over the concentration range investigated. A model based upon a Langmuir–Hinshelwood mechanism was applied and found to predict reasonably well the experimental reaction rates. High selectivity values towards the 2-butene-1,4-diol were found in both the single- and multiple-capillary reactors, even at 100% conversion of the alkyne.

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1. Introduction

Three-phase reactors are used to manufacture a large variety of industrial intermediate and consumer end-products. Some examples of application areas are the upgrading and conversion of petroleum feed stocks and intermediates, the manufacture of pharmaceuticals, specialty chemicals and fine chemicals. These processes range from the production of high value-added products with an annual basis of a few kilograms to bulk products with annual production of several thousand metric tons.

For several decades, stirred tanks have been a popular choice of reactor to carry out three-phase catalytic processes, favoured because of their flexibility, relatively easy temperature control and moderate cost. However, these

reactors present some difficulties such as scale-up and mass transport limitations with consequent negative effects on productivity, rate and selectivity [1]. Slurry reactors such as mechanically agitated stirred tanks or bubble columns, also suffer from two significant problems: catalyst separation and catalyst attrition. Although these problems are absent in fixed bed reactors that may alternatively be used for hydrogenation processes, some other difficulties such as temperature control and fluid phase mal-distribution arise, which may give rise to poor performance, hot spots and sintering of the catalyst. To overcome some of these problems, new reactor types have been proposed, including two-phase monolith reactors which are predicted to play an important role in process intensification [2].

Monoliths are structures consisting of parallel, straight and uniform channels. For co-current gas–liquid flow through such channels, several flow regimes can develop and among them Taylor flow is commonly preferred because of the increased radial mass transfer observed.

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This type of flow consists of elongated gas bubbles and liquid slugs flowing successively through the monolith channels. The gas bubble occupies the whole radial distance of the channel so that only a thin liquid layer separates the bubble from the catalyst. In the liquid slug a recirculation pattern has been observed [3] which contributes to increased rate of radial mass transfer. In general, monolith catalysts possess distinct advantages such as low pressure drop, easy scale-up and improved mass transfer resistances [2,4]. The main disadvantages are cost of the monolith and the lack of practical experience.

In principle, scale-up of monolith reactors is very simple [4] and easier than the packed bed. Presumably, when the behaviour of one channel is known then the behaviour of a whole monolith could be predicted. However, this assumption is only found to hold true if an even phase-distribution and flow pattern occurs across the channels in the monolith. If present, mal-distribution of phases may lead to a wide residence time distribution across the radial section of monolith with consequently lower selectivity, ineffective catalyst usage and hot spots in the reactor [5,6]. A non-homogeneous gas–liquid distribution in a monolithic reactor has been evidenced by residence time studies and the distributor was concluded to be the main cause of this phenomenon [6,7].

Different configurations of distributor have been proposed to feed the liquid and gas into the monolith to obtain an even distribution of gas and liquid across the monolith channels and Taylor flow pattern within them. One such method of gas–liquid flow distribution is to place the monolith in a cocurrent downflow contactor (CDC) [8] and the resulting system is called the monolithic CDC reactor. Unlike other monolithic reactors, a stable bubble dispersion is produced above the monolith and driven into it by altering gas and liquid velocities. The occurrence of Taylor flow in the monolith CDC has been observed by Magnetic Resonance technique [9]. The CDC was originally developed for gas–liquid contacting [10]. It has, however, been used as slurry and fixed bed reactor whose mass transfer performance relative to stirred tank has been shown to be superior [11]. The CDC exploits a simple orifice based eductor to create a dense, stable gas–liquid dis-

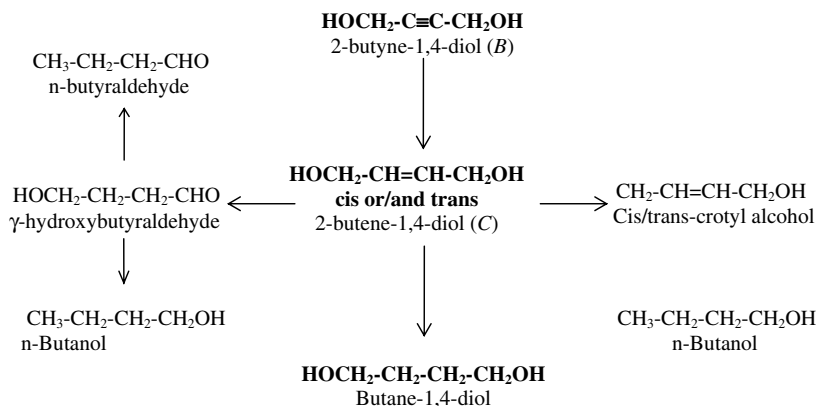
persion. The CDC, either in slurry or fixed bed mode, is a device that can be operated with high gas-hold-up (0.4–0.5) and can give negligible transport resistances (<4%) [12,13] with improved selectivity and is process intensive [8].

This study aims to assess the performance of a monolith CDC and compare it to that of a single capillary reactor to carry out selective hydrogenation reactions. As a model reaction the selective hydrogenation of 2-butyne-1,4-diol (B) to *cis*-2-butene-1,4-diol (C) was chosen (Scheme 1). This reaction has long been studied, usually in stirred tank reactors. The intermediate C is a raw material for the manufacture of endosulfan (insecticide) and vitamins A and B₆. The highest selectivity to 2-butene-1,4-diol has been obtained either by employing a combination of two or more metals or in the presence of organic bases such a pyridine, quinoline or isoquinoline. These systems, however, imply a major drawback that is the consistency of the catalytic activity in subsequent catalyst reuses and the need for the complete removal of the poisons in order to obtain the highest purity of the product for fine chemical and pharmaceutical applications.

2. Experimental methods

2.1. Equipment

Fig. 1 depicts the basic experimental set-up for a single capillary and monolith CDC reactors. In the former, $20 \times 10^{-6} \text{ m}^3$ of reacting solution were contained in a glass flask and circulated through the system by means of a piston pump. Hydrogen was combined with the liquid stream at a T-junction on top of a 0.30 m glass capillary connected to a palladium/alumina wash-coated capillary of the same diameter ($2 \times 10^{-3} \text{ m}$). Liquid flow rate was $0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ and hydrogen was supplied accordingly to obtain Taylor flow, which was visually observed in the glass capillary window placed just before the capillary reactor. This also allowed the determination of the liquid slug length (L_1) by photographic means. Temperature was controlled by an electrical mantle.



Scheme 1. Reaction network for 2-butyne-1,4-diol hydrogenation.

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