A RANKING OF EXPERIMENTS APPROACH FOR THE IDENTIFICATION OF KINETIC MODELS OF ETHYLENE METHOXYCARBONYLATION IN CAPILLARY MICROREACTORS

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Capillary microreactors have proven to be a powerful tool for performing kinetic experiments in multiphase systems, due to the high mass and heat transfer rates they provide, enabling the study of reactions that previously were difficult to be studied in conventional reactors [1-2]. They are more cost effective compared to conventional reactors as the amount of catalyst required is smaller due to the reduced dimensions of the reactor system. Furthermore, flow systems are particularly attractive for kinetic studies as data can be obtained faster and with more precision than in batch systems [3].

Methyl methacrylate (MMA) is an essential building block for acrylic-based products such as resins and adhesives and is used in a wide range of industrial applications. MMA is mainly produced via the acetone cyanhydrin (ACH) route, a route requiring careful management of large quantities of extremely toxic hydrogen cyanide and generating large amounts of acidic ammonium bisulphate waste which has to be recovered by incineration at considerable cost. Conversely, the Alpha Process for the production of MMA is a recent cleaner route based on ethylene methoxycarbonylation involving no by-products and milder operating conditions and requiring around 40% less production costs compared to the ACH route [4]. The goal of the current work is the investigation of reaction kinetics in the first stage of the Alpha Process, related to the synthesis of methyl propionate (MeP) from ethylene, carbon monoxide and methanol over a homogenous Pd catalyst. The gas-liquid catalytic reaction takes place at moderate temperature and pressures (e.g. typical standard conditions are 100^{o}C, 10 bara). Experiments were carried out in a flow

capillary microreactor, where gas-liquid contact led to a slug-annular flow pattern. Selectivity higher than 99.9% was achieved.

After a hydrodynamic study to characterise the two-phase flow and mass transfer characteristics, a number of experiments at variable methanol, CO and ethylene concentration in the feed at temperatures in the range 80-120 °C were carried out to screen out the effect of these experimental design factors on the products. A one-dimensional reactor model was developed using the gPROMS platform to describe the observed reaction kinetics. The model included the description of mass transfer and vapour-liquid equilibrium inside the capillary reactor. A ranking of experiments approach, based on model-based experimental design techniques [5], was then used to select the most informative experimental data for the identification of kinetic parameters. These techniques allowed for a precise estimation of kinetic parameters, in such a way that the proposed model was able to describe the experimentally observed system behaviour in an accurate way.

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