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Intensification of carboxylic acid esterification using a solid catalyst in a mesoscale oscillatory baffled reactor platform

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HIGHLIGHTS

- Clear steady states were obtained at all conditions for the multi-steady states.
- Dynamic screening required 16% less time to run compared to the multi-steady states.
- Least process development time was obtained for multi-dimensional screening.
- Multi-dimensional approach required 30% less resources than multi-steady states.
- Amberlyst™ 70 entirely regained its catalytic activity after water spiking.

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ABSTRACT

Intensified production of carboxylic acid esters has been investigated using a mesoscale oscillatory baffled reactor (meso-OBR), operated in continuous multi-steady states, dynamic and multi-dimensional modes. This study was performed to investigate the suitability of the reactor for solid-liquid reactions, capacity for quality steady states and rapid process development. A heterogeneously catalysed hexanoic acid esterification with methanol was studied in a meso-OBR packed with Amberlyst™ 70 resin as an acid catalyst. The esterification conditions investigated were feed molar ratios in the range of 1.5:1–30:1 and residence times in the range of 1 min–20 min. The meso-OBR was operated at oscillatory conditions of 4.5 Hz frequency and 8 mm amplitude (centre-to-peak) and reaction temperature of 60 °C. Clear steady states were achieved at all the residence times used, with maximum hexanoic acid to methyl hexanoate conversion of 95.4 ± 1.0% obtained at 20 min residence time and 30:1 methanol to acid molar ratio. Methyl ester conversions were 98.5 ± 1.5% at 20 min residence time and 30:1 methanol to acid molar ratio for dynamic screening, and 98.2 ± 1.1% at 14 min residence time and 21:1 methanol to acid molar ratio for the multi-dimensional mode. Use of dynamic screening required 16% less time and reactant compared to the multi-steady states approach. A more significant reduction in the process development time and reactants requirement, approximately 30% compared to the multi-steady states approach, was achieved using the multi-dimensional approach. This demonstrates a substantial reduction in process development time, another major advantage of the meso-OBR platform as the choice reactor in process development for multiphase reactions. The Amberlyst™ 70 entirely regained its catalytic activity after water spiking, and was not permanently deactivated by water.

1. Introduction

The use of heterogeneous catalysts [1,2] and process intensification strategies [3,4] are becoming desirable process design routes for productions of valuable chemicals. Such processes reduce the materials requirement and save costs, and are at the heart of current drive for Green Chemistry processes. Use of heterogeneous catalysts in intensification reactors leads to more efficient utilisation of raw materials, energy efficiency and safer operation through smaller volume of reactors and lower system footprints [5]. The use of heterogeneous catalysts is advantageous due to reductions in the downstream purification stages and the costs of continual catalyst replacement. Acid catalysts are widely used in various chemical production processes such as alkylation, acylation, dehydration, condensation and esterification reactions. The esterification reaction is one of great importance due to its widespread application in the production of millions of tons of

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polyesters yearly, along with a large variety of esters for productions of fine and specialty chemicals used in fragrances, pharmaceuticals, and pesticides [6,7]. Carboxylic acid esterification is also an important reaction in the productions of biodiesel from feedstock that contains high amount of free fatty acids (FFA). This is integral to current biodiesel technologies [8], as it allows for the use of lower quality feedstocks for biodiesel production, as these feedstocks typically contain large quantities of FFA. Another bioenergy related application of acid catalysts is in the areas of pretreatments of bio-oils derived from fast pyrolysis of biomass, through esterification to improve the bio-oil stability through elimination of short chain acids and deoxygenation [9,10].

Esterification is an acid-catalysed reaction of organic acids with alcohol to produce carboxylic acid esters and water as by-product (Fig. 1). This reaction is limited by the equilibrium which determines the conversion of the reactants. The water produced by the reaction should be continuously removed in order to allow for the reaction equilibrium to be driven in favour of the forward reaction. Generally, the esterification rate and ester yields are increased using higher alcohol to FFA molar ratios, catalyst concentration and pressure [11]. Continuous esterification of organic acids with methanol also reduces catalyst poisoning by water and improves the ester yield [2]. Further improvement in the heterogeneous acid-catalysed esterification processes could be achieved through the application of intensified reactors with multiphase mixing capabilities that would overcome the effects of mass transfer in the solid-liquid-liquid reactions, and allow for operations in continuous mode.

Many process intensification strategies have been considered for continuous esterification, such as reactive distillation [3,12,13], microchannel-flow reactors [14], fixed bed processes for fatty acids [15,16], pervaporation methods [3,17], and the use of meso-OBR [2]. The intensified continuous esterification reactors are designed to allow for utilisation of solid catalysts, ensure reduced reactor size and plug flow characteristics, and to achieve products of uniform composition at lower capital and running costs. The meso-OBR overcomes these problems through good multiphase mixing capability and plug flow behaviour arising from oscillating the reaction fluid through the orifices of equally spaced baffles [4]. Oscillatory baffled reactors have been widely investigated for application in multi-phase fluid mixing, and their capacity for enhanced heat and mass transport and particle suspension [4,18–22]. Net fluid flow in the OBR is decoupled from the oscillatory flow, which provides for independent control of the mixing intensity and residence time of the reaction [22]. This makes the reactors suitable for screening reactions that have long residence times, using reactors of greatly reduced length-to-diameter ratio. A mesoscale OBR is a millimetre scale version of the conventional OBR, typically consists of a 5 mm inner diameter tube with equally spaced baffles. The meso-OBR has been designed particularly for screening of reactions because of their small volume [23]. It has a small volume which allows for operation at low flow rates and reductions in the amount of reagent used and also the waste [24,25]. Previous studies [2,26,27] have shown that the formation and cessations of vortices in the OBR is an effective and controllable method of uniform suspension of solid particles such as catalysts. These characteristics of OBRs makes them ideal for screening of multi-phase reactions, as well for suspension and screening of solid catalysts. Operation with solids is also very challenging for flow chemistry platforms based on microchannels, for the simple reason that representative catalyst particles do not fit in the channels. This work investigated the applications of the OBR as a reactor platform for rapid process development in solid-liquid reactions. Process parameters for heterogeneously catalysed carboxylic acid esterification with the Amberlyst™ 70 resin catalyst were screened in continuous multi-steady states, dynamic and multidimensional modes. Carboxylic acid esterification was selected for this study due to the importance of the process in industrial productions of fine chemicals and biofuels.

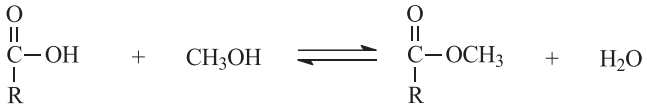

Fig. 1. Carboxylic acid esterification.

2. Materials and methods

2.1. Materials

Materials used in the experiments were hexanoic acid (99%, Sigma-Aldrich), anhydrous methanol (99.8%, Sigma-Aldrich), methyl octanoate analytical standard (99.8%, Sigma-Aldrich), methyl hexanoate analytical standard (99.8%, Sigma-Aldrich), and Amberlyst™ 70 resin catalyst – consisting of sulphonic acid functionalised divinylbenzene/styrene copolymer. The Amberlyst™ 70 resin was supplied by Dow Chemical Company, Netherland. Physical and chemical properties of the Amberlyst™ 70 resin could be found in the chemical datasheet and in existing studies [28–30].

2.2. Experimental procedures

The Amberlyst™ 70 resin was screened for catalysis of hexanoic acid esterification using the meso-OBR platform. The reactor was a jacketed integrally baffled glass tube of about 770 mm length, 8 mm outer diameter, 5 mm inner diameter and periodic constrictions of 2.5 mm diameter along the length of the tube at 7.5 mm spacing (Fig. 2). The baffled tube was fully packed with 400–500 μm beads of the Amberlyst™ 70 resin which had been conditioned by washing it several times using methanol.

The base and top of the packed baffled tube were sealed with 5 mm discs of stainless steel wire mesh (#60) of 160 μm wire diameter and 263 μm apertures to constrain the catalyst beads from leaving the reactor. The reactor was then assembled with the base, connected through Swagelok fittings to three Confluent syringe pumps (Eurodyne Ltd). One of these pumps was used to provide the oscillations at 2 Hz–4.5 Hz frequency and 4 mm–8 mm amplitude, and the other two to provide the net flows of hexanoic acid and methanol (Fig. 2b). The syringe pump used for oscillation was connected to the base of the reactor, and the fluid mixing inside the reactor provided by adjusting the speed of the piston movement (frequency) and the oscillation amplitude (centre-to-peak) of the pump [31]. The syringe pumps were controlled via a PC interface. Prior to each experiment, the pumps were initialised, and set at the required mixing intensity (amplitude and frequency) and reactants net flow rates.

The volume of the reactor after packing with 9 g of Amberlyst™ 70 resin was 8.3 mL, and the volume of the reactor without packing was 15.2 mL. The reaction temperature was maintained by the circulation of heated water through the jacket of the meso-OBR using a temperature-control water bath (Ecoline, LUADA E100). Hexanoic acid and methanol feed were dispensed from reservoirs maintained at the reaction temperatures inside the water bath. Prior to each experiment, continuous circulation of methanol over the Amberlyst™ 70 resin packed bed was carried out to swell the resins and make the pores accessible to the reactants [32,33]. The reactor was operated at atmospheric pressure for all the experiments.

The effect of oscillation conditions was investigated at 4 mm–8 mm amplitude and 2 Hz–4.5 Hz to ensure that the meso-OBR