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Combining continuous flow oscillatory baffled reactors and microwave heating: Process intensification and accelerated synthesis of metal-organic frameworks

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HIGHLIGHTS

- Continuous flow oscillatory baffled reactor with a homogeneous microwave applicator.
- New chemical production route incorporating principles of process intensification.
- Highest reported space time yield for any metal-organic framework.
- Highest reported surface area production rate for any metal-organic framework.

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ABSTRACT

We have constructed a continuous flow oscillatory baffled reactor (CF-OBR) equipped with a homogeneous and controllable microwave applicator in an entirely novel design. This affords a new route to chemical production incorporating many of the principles of process intensification and allows, for the first time, investigation of the synergistic benefits of microwave heating and CF-OBRs such as; faster and continuous processing; improved product properties and purity; improved control over the processing parameters; and reduced energy consumption. The process is demonstrated by the production of a metal-organic framework (MOF), HKUST-1, a highly porous crystalline material with potential applications in gas storage and separation, catalysis, and sensing. Our reactor enabled the production of HKUST-1 at the 97.42 g/h scale, with a space time yield (STY) of 6.32×10^5 kg/m^3/day and surface area production rate (SAPR) of 1.12×10^{12} m^2/m^3/day. This represents the highest reported STY and fastest reported synthesis (2.2 s) for any MOF produced *via* any method to-date and is an improvement on the current SAPR for HKUST-1 by two orders of magnitude owing to the superior porosity exhibited by HKUST-1 produced using our rig (Langmuir surface area of 1772 compared to 600 m^2/g).

1. Introduction

Microwave heating is an established process intensification method used in industrial sectors such as rubber vulcanizing [1] and for drying food and wood [2]. During microwave heating, energy is delivered instantaneously through interaction of an alternating electromagnetic field with a material rather than by conductive, convective or radiative heat transfer [3]. Microwave heating enables selective and targeted heating to specific components during the reaction; this is particularly attractive for chemical processing as an alternative to conventional heating owing to the following benefits; significantly reduced production times (many hours to minutes), increase in product yield and purity, and enhancement of product properties [4–8].

A continuous flow oscillatory baffled reactor (CF-OBR) is a proven process intensification method in the laboratory for reactions such as biodiesel production [9], bioprocessing [10] and saponification [11], and is increasingly being commercialised [12]. CF-OBRs are tubular reactors containing equally spaced baffles presented transversely to an

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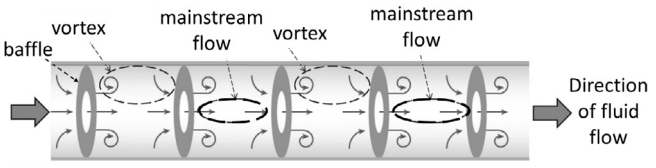

Fig. 1. Schematic representation of fluid flow in an oscillatory baffled reactor (OBR).

oscillatory/pulsed flow, as shown in Fig. 1. Fluid inside the CF-OBR is oscillated by a pump placed at one or both ends of the tube. The baffles disrupt the boundary layer at the tube wall, whilst the oscillation creates vortices, resulting in improved mixing. Superposition of net flow on to the oscillatory motion allows control over mixing and residence times by altering the oscillation conditions, *i.e.* oscillation amplitude and frequency [13]. Unlike a conventional tubular reactor, the degree of mixing in an OBR is independent of the net flow, therefore it is possible to achieve a high level of mixing at low flow rates and what would otherwise be low Reynolds numbers [13]. An advantage of this is the ability to use tubular reactors with a greatly reduced length-to-diameter ratio thus decreasing the size of the process. Size reductions of up to 99.6% compared to continuous stirred tank reactors (CSTRs) with equivalent throughput are possible [14]. Furthermore, OBRs are scalable as the mixing mechanisms do not alter between the laboratory and industrial scale, given geometric and dynamic similarity [13].

As with microwave heating, CF-OBRs offer huge opportunities for intensifying chemical production. The uniform mixing environment and enhanced heat transfer in OBRs enable considerable reduction in processing times (by up to 80%), better temperature control, and consistent product properties (*i.e.* particles with uniform size and morphology) [14].

Microwave heating and CF-OBRs individually show great potential for energy savings, enhanced process control and optimization, and improved product quality compared to other processing methods, such as CSTRs, as a result of reduced solvent and energy usage, faster and continuous processing, smaller processing equipment, and safer implementation of harsh production conditions [13]. Therefore, a production route that combines microwave heating and CF-OBR technology has the potential to deliver synergistic benefits to scalable chemical processing with exceptional process intensification attributes. In particular, the CF-OBR is able to provide plug flow in a compact design whilst uniformly suspending solid particles. The solid particles are suspended by the oscillatory flow mixing structures. They will be in constant motion, hence they will be exposed to the same dose of microwave energy. This is an advantage over packed bed catalytic reactors, for example, where it can be challenging to heat large beds homogeneously using the microwave field. In other designs of laboratory-scale plug flow reactors, such as microchannel reactors, it is difficult to operate with solid particles without blockages, or time-consuming development of catalyst washcoats (carriers to disperse particles).

Metal-organic frameworks (MOFs) are highly porous crystalline materials composed of metal nodes and organic linkers [15]. MOFs have received marked attention from academia and industry owing to their unprecedented porosity (surface areas up to 7000 m^2/g) [16] and diverse structures and functionalities. The properties of MOFs offer immense opportunities for economic and environmental impact in areas such as gas storage and separation [17], catalysis [18], sensing [19], and drug delivery [20]. In particular, the tuneable nature of MOFs could enhance their performance in gas and petrochemical separations compared to other adsorbents, such as activated carbons and zeolites.

MOFs are not currently used in industry owing to the inability to produce these materials at the required quality, purity, quantity and cost for application [6,21]. The main reason for this is the demanding MOF synthesis conditions; *i.e.* use of large amounts of toxic, corrosive and highly flammable chemicals, high temperatures and autogenous pressures (typically above the boiling point of the solvent), long reaction times (hours or days), acidic by-products, high energy requirements, and heterogeneous reaction mixtures that require mixing [6]. Additional challenges include reproducibility between batches and cost and availability of large scale reaction rigs [6]. The development of technologies that address these issues in an efficient and sustainable way is a key enabling step in the transfer of MOFs from the laboratory to industrial application.

As methods for scaling up MOF production evolve, parameters for comparing and assessing their efficiency and practicality and have become important. Two key parameters include production rate (mass of dry MOF product per hour, g/hr) and space time yield (STY, quantity of MOF produced per unit volume of reactor in a 24 h period, $kg/m^3/day$) [6]. Another important factor is the quality of MOF produced; this is dependent upon their intended use. For example, the overall surface area exhibited by MOFs is important for gas capture and storage [6,22] whereas uniformity of size and morphology of the crystals are important for separations [23–25] and controlled drug release [26]. Surface area production rate (SAPR), which is defined as the amount of surface area of MOF produced per unit volume of reactor per day, $m^2/m^3/day$, has recently been developed to indicate the quality of MOF obtained from different production methods [21]. This criterion will be used in this paper to evaluate the production methods discussed and developed herein.

Few examples of combined microwave heating and continuous flow systems for MOF synthesis at the laboratory scale have been reported. These include; a gas liquid segmented flow reactor capable of producing ~90 g/h/L of MOF-74(Ni) with a STY of 2160 $kg/m^3/d$; [27] a plug flow reactor shown to produce three MOFs, namely MIL-53(Al), UiO-66, and HKUST-1 at production rates of 7.1, 14.4 and 79.4 g/h respectively [28]; and a tubular microwave reactor with a high reported STY of up to 400,000 $kg/m^3/d$ for HKUST-1 [21]. In the latter system, a significant decrease in surface area from *ca.* 2100 [29] to 600 m^2/g [21] is observed which would render the MOF with little or no commercial value, highlighting the importance of assessing the quality of MOF produced as well as the production rate. However, these systems do not fully assess the effect of microwave energy on the reaction mixture and rely upon mixing provided by small internal diameters (i.d. < 4.4 mm) [21,27,28] tubes. In order to facilitate developments in continuous flow microwave synthesis of MOFs beyond the laboratory, greater understanding of the effect of microwave and mixing parameters that are essential for scale-up is required. Microwave parameters include; the efficiency of power coupling and distribution of the electric field within the heating cavity; penetration depth and relationship with reactor design and specification; and the required power density distribution (energy per unit volume over the treatment time, see references [7,30] for a more in-depth explanation) to produce MOFs consistently at high quality and at the required production rates and STYs [7]. Mixing parameters include; fluid mechanics, formation and dissipation of vortices, velocity profiles, shear rate distribution, residence times, and scale-up correlations aimed at producing MOFs with a desired particle size distribution and morphology [11]. All of these variables underpin the successful integration of microwave energy with chemical reactor systems capable of delivering the economic large-scale manufacturing processes needed to produce MOFs, consistently at high quality and at the correct cost base and minimal environmental impact.

We have constructed a CF-OBR system equipped with a homogeneous and controllable microwave applicator in an entirely novel design, as CF-OBRs have not been used in conjunction with controllable microwave heating before. This affords a new route to MOF production incorporating many of the principles of process intensification and allows, for the first time, investigation of the synergistic benefits of microwave heating and CF-OBRs. Using our system, herein referred to as the 'MW-CF-OBR' rig (Fig. 2), we have, for the first time, quantified experimentally the amount of microwave energy absorbed by a MOF