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Current Opinion in Chemical Engineering

Continuous flow production of metal-organic frameworks

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While thousands of metal-organic frameworks (MOFs) are known to exist, only a handful are produced commercially. The myriad of potential applications imply that many different MOFs will be required at large scale and versatile production methods could enable this expansion. Continuous flow chemistry is a versatile technique that is compatible with a broad range of laboratory syntheses, with many innovative heating and workup processes, and also with well-established scaled processing methods. With a general synthetic method defined, the state of the art sees a wide and expanding range of MOF materials becoming market-ready in the near future. Key challenges currently lie in increasing processing efficiency, particularly in product work-up.

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Current Opinion in Chemical Engineering 2015, **8**:55–59

This review comes from a themed issue on **Nanotechnology**

Edited by **Hong Yang** and **Hua Chun Zeng**

For a complete overview see the Issue and the Editorial

Available online 13th March 2015

http://dx.doi.org/10.1016/j.coche.2015.02.001

Introduction

Metal-organic frameworks (MOFs) are porous, crystalline materials derived from organic linkers bound periodically by metal coordination centres. MOFs have unprecedented internal surface areas and uniform pores (see Figure 1). Pore size and shape can be tuned by varying the organic linkers, leading to a vast range of possibilities for designing materials with desired functionalities for a raft of potential industrial applications [1–5]. Two decades of research into MOFs has uncovered a large number of high performing materials in gas storage [6–8], automotive components [6,9–11], carbon capture [12], gas separation [13], drug delivery [14], sensing [15], photoelectronics [16] and catalysis [17•].

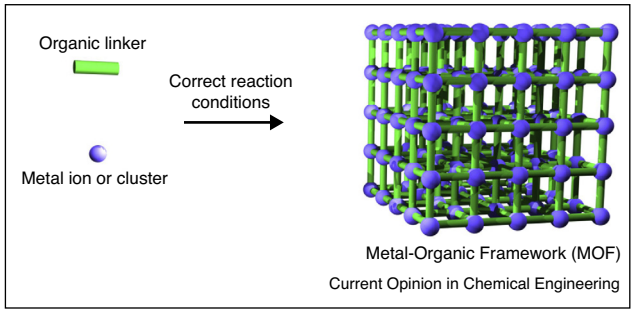
A crucial pre-requisite for accessing the potential applications of MOFs is the ability to routinely synthesise these materials in large quantities (kg scale or higher) with high efficiency. High volume production of MOFs has been slow to develop and whilst more than 4700 MOFs have been reported, only 7 are commercially available [18]. As a consequence, the cost of these materials has remained prohibitively high, and their enormous potential has yet to make a significant impact on prospective markets. Scaled-up production using traditional laboratory routes such as the classical solvothermal synthesis remains challenging due to extended long reaction times and the production of low quality materials. Furthermore, the wide variety of methods for preparing MOFs and the singular nature of some of the preparations provides an inherent risk of inflexibility for any prospective production process. Specifically, switching a bespoke production system to a different MOF material is likely to require significant re-tooling, or indeed a completely new production train.

MOF synthesis chemistry

The classical synthesis of MOFs involves mixing solutions of the metal salt and organic linker, placing the mixed solution in a sealed reaction vessel and heating it to promote the growth of insoluble frameworks that precipitate as fine crystals [19]. This synthesis method is known as *solvothermal synthesis*, the reaction takes place over days or hours. Earlier slow solvent evaporation methods take place over days or weeks, but may still be employed to produce very large single crystals. The sealed solvothermal synthesis systems may be heated to temperatures and pressures above the solvent's boiling point. In this aspect the chemistry resembles hydrothermal Zeolite synthesis. The solvothermal method also includes heating to reflux at ambient pressure [20]. Extensions of solvothermal synthesis employ more efficient heating methods such as microwave or ultrasonic radiation producing a reduction in reaction time — hours to minutes [21].

One of the barriers to scaled MOF synthesis relates to the nucleation of the MOFs at a reaction surface and therefore the size of the reaction vessel becomes a significant parameter. Consequently, reactions that proceed well in small vessels do not readily scale into larger vessels using identical reaction conditions. This factor limits the scaling of MOF chemistry to a small number of MOFs that are

Figure 1



Schematic representation of metal-organic frameworks.

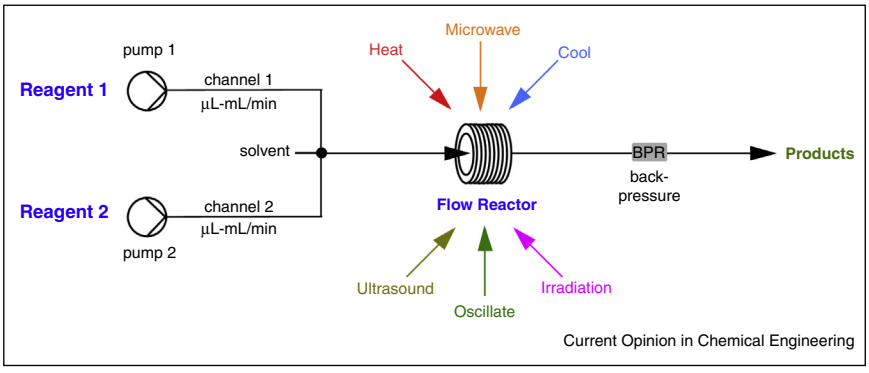
robust in their preparation, each requiring bespoke equipment [8,22–25,26••,27••,28,29••,30,31].

The limitations of the solvothermal method have been overcome by alternative techniques, which have led to successful production of MOFs in commercially useful quantities. Handling large volumes of solvent is not required when MOFs are synthesised mechanochemically, by milling the metal and linker precursors [32]. This results in very efficient production and very high STY (space-time yield — kilograms of product per cubic metre of reaction mixture per day) [8] but results in low surface areas, as the synthesis conditions are not conducive to the formation of the crystalline structures that constitute good quality MOFs. Another commercially viable method produces MOFs by dissolving a metal anode into an electrolytic solution containing the organic linker molecule [8]. Electrochemical systems have a much lower demand for solvent handling and recycling than solvothermal methods and, importantly, can be operated continuously. The main disadvantage of this method is that it can only be used to produce a small number of MOFs and product quality is slightly lower than achieved with solvothermal syntheses [29••,30,33,34]. Another promising alternative that has yet to reach commercial implementation involves injecting metal and organic spacer solutions, similar to those used in solvothermal synthesis, into a spray-drying system [35]. This strategy is continuous and has been demonstrated to work for a number of MOFs. However the technique does use large amounts of complex solvent mixtures, and it is unclear if the process will perform well on a large scale.

Therefore, a method to conveniently expand the scale of a broad number of MOF syntheses whilst minimising the size and cost of the reactor is extremely attractive to those seeking a versatile route to commercial MOF production. Recently continuous flow chemistry has shown great promise for the scalable synthesis of advanced functional materials [36]. Continuous flow technology has been recognised as an attractive alternative to conventional batch processing and this approach may ameliorate the aforementioned challenges associated with the scaled synthesis of MOFs [37–44]. In its simplest form, a continuous flow reactor comprises the continuous pumping of reagents into a tubular reactor and the isolation of products which exit from the reactor (Figure 2).

The advantages of using flow chemistry are derived from the greatly increased surface to volume ratio of the reaction, giving inherent improvements to heat and mass transfer, and leading to rapid syntheses, new synthetic pathways, and greater efficiency [45•]. The technique is also coherent with established large-scale chemical processing techniques, allowing laboratory research and development to dovetail smoothly with process development. Small amounts of MOFs can be made within oil droplets using microfluidic reactors (Figure 3 — Left, Table 1) [25,45•,46••]. While it allows excellent control of the MOF's morphology, microfluidic processing is hampered by low quality of the final products and a low STY. Proof of concept meso- and macroscale flow production has also been reported [26••,27••,29••,47••], and pumped metering of a spacer ligand solution into a stirrer-tank reactor has been described [23,48,49]. Gimeno-Fabra *et al.* showed

Figure 2



A general schematic representation of continuous flow synthesis methodology.