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PII: S1385-8947(18)31720-0
DOI: https://doi.org/10.1016/j.cej.2018.09.011
Reference: CEJ 19850

To appear in: *Chemical Engineering Journal*

Received Date: 29 May 2018
Revised Date: 10 August 2018
Accepted Date: 2 September 2018

Please cite this article as: A. Laybourn, A.M. López-Fernández, I. Thomas-Hillman, J. Katrib, W. Lewis, C. Dodds, A.P. Harvey, S.W. Kingman, Combining continuous flow oscillatory baffled reactors and microwave heating: process intensification and accelerated synthesis of metal-organic frameworks, *Chemical Engineering Journal* (2018), doi: https://doi.org/10.1016/j.cej.2018.09.011

Research article

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

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Keywords: Metal-organic framework, microwave, oscillatory baffled reactor, process intensification, ultra-fast synthesis, continuous flow.

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 seconds) 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).

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 oscillatory/pulsed flow, as shown in **Figure 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]

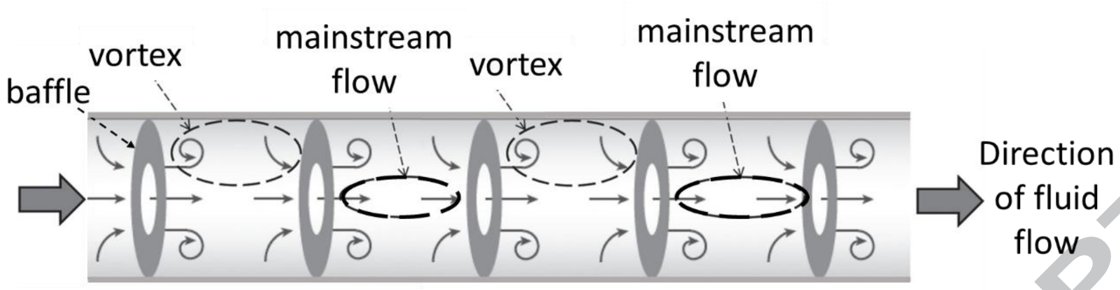


Figure 1: Schematic representation of fluid flow in an oscillatory baffled reactor (OBR).

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 hour 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 (**Figure 2**), we have, for the first time, quantified experimentally the amount of microwave energy absorbed by a MOF reaction mixture in continuous flow thus allowing investigation of the effect of mixing and microwave heating on continuous MOF production. We report the effect of flow rate and baffle material on the production rate, STY and quality (SAPR, porosity, crystallinity, particle size and morphology) of an archetypal MOF, HKUST-1[31]. This particular MOF was chosen to enable comparison with other production routes. Using our MW-CF-OBR rig we have produced HKUST-1 at the 97.42 g/h scale and with a space time yield (STY) of 6.32×10^5 kg/m^3/day. This is more than 50 % higher than the previously reported STY[21] and represents the highest reported STY for any MOF produced *via* any method to-date. Additionally, all the HKUST-1 materials produced were highly porous and exhibited Brunauer–Emmett–Teller surface areas (SA$_{BET}$) over 1300 m^{2}g (*i.e.* at the desired level/ according to specification) resulting in a surface area production rate (SAPR) of 1.12 × 10^{12} m^2/m^3/day. This is two orders of magnitude more than the highest reported SAPR for HKUST-1 and shows that the materials produced using the MW-CF-OBR rig are of high quality.

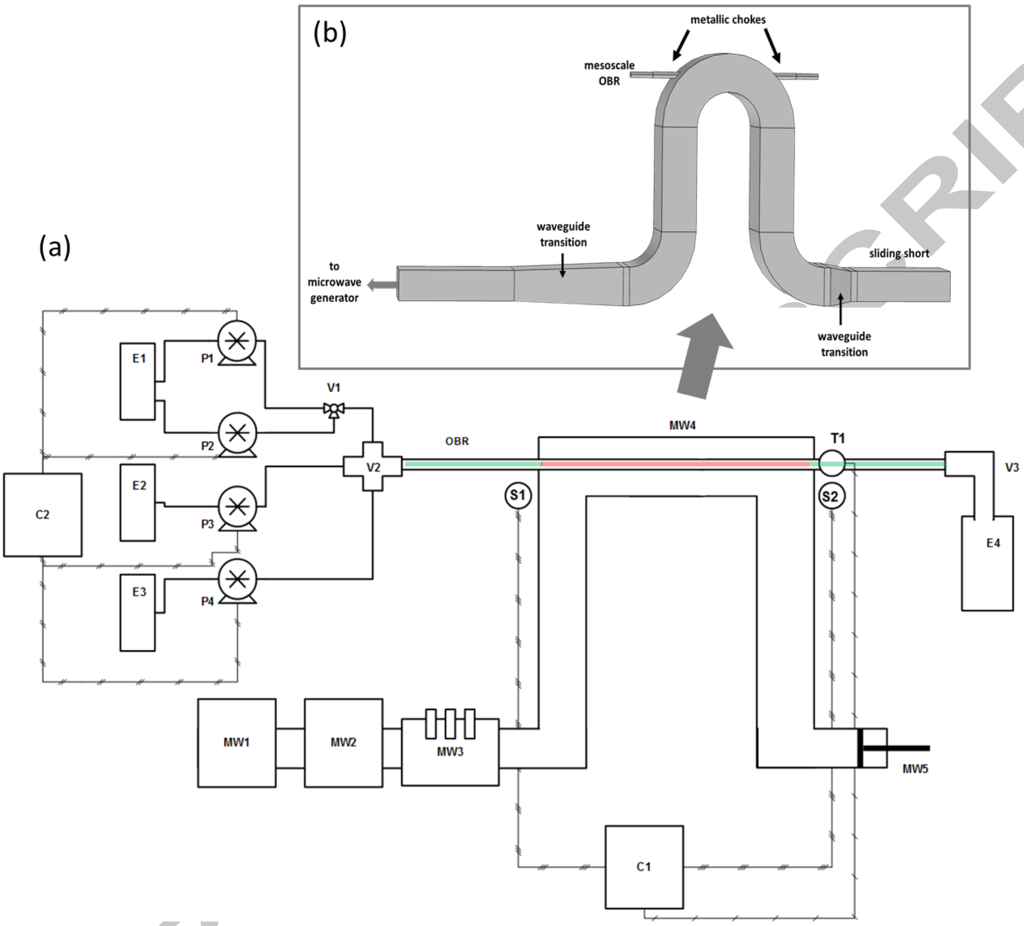


Figure 2: Schematic of MW-CF-OBR rig; (a) Whole rig; (b) 3D model of MW4 section. MW1: microwave generator; MW2: power meters; MW3: automatic 3-stub tuner; MW4: microwave cavity; MW5: sliding short; E1: vessel containing ethanol; E2 vessel containing metal salt dissolved in ethanol; E3: vessel containing linker dissolved in ethanol; E4: collection vessel; P1 to P4: syringe pumps; V1, V2, V3: Teflon connectors; T1: thermocouple; S1 and S2; microwave leakage meters; OBR: green corresponds to plastic baffle, red corresponds to interchangeable baffle section (metal or plastic); C1 and C2: PC controllers. Further information about the components is given in the Supporting Information (SI).

Experimental

The schematic of the MW-CF-OBR rig is given in **Figure 2**. The rig consists of four continuous syringe pumps (labelled P1-P4 in **Figure 2**), three feedstocks (E1-E3, **Figure 2**), a mesoscale-oscillatory baffled reactor (consisting of two individual tubes connected together fitted with a helical plastic perfluoroalkoxyalkane, PFA, baffle; labelled OBR in **Figure 2**) fed through a choked microwave cavity (MW4, **Figure 2**) and a product collection vessel (E4, **Figure 2**). PFA was used for the baffles as it is compatible with the reaction mixtures and is microwave transparent. The microwave cavity was designed to ensure homogeneity of the treatment by considering the electromagnetic properties of the reaction mixture. This was achieved *via* electromagnetic simulations performed using COMSOL Multiphysics[32] (see SI, for further details and model). **Figure 3** shows the power density distribution inside the material (including baffles and reaction mixture). Power density variation was ± 6% across the treatment zone (**Figure 3**), indicative of uniform heating in the microwave applicator zone. Chokes were designed by considering the electromagnetic properties of the reaction mixture to prevent any microwave leakage and are compliant with health and safety legislation.[33] A thermocouple located directly after the microwave cavity (T1, **Figure 2**) was used to monitor the bulk temperature of the suspension following heating in order to ensure no disruption to the oscillatory flow in the microwave heated zone.

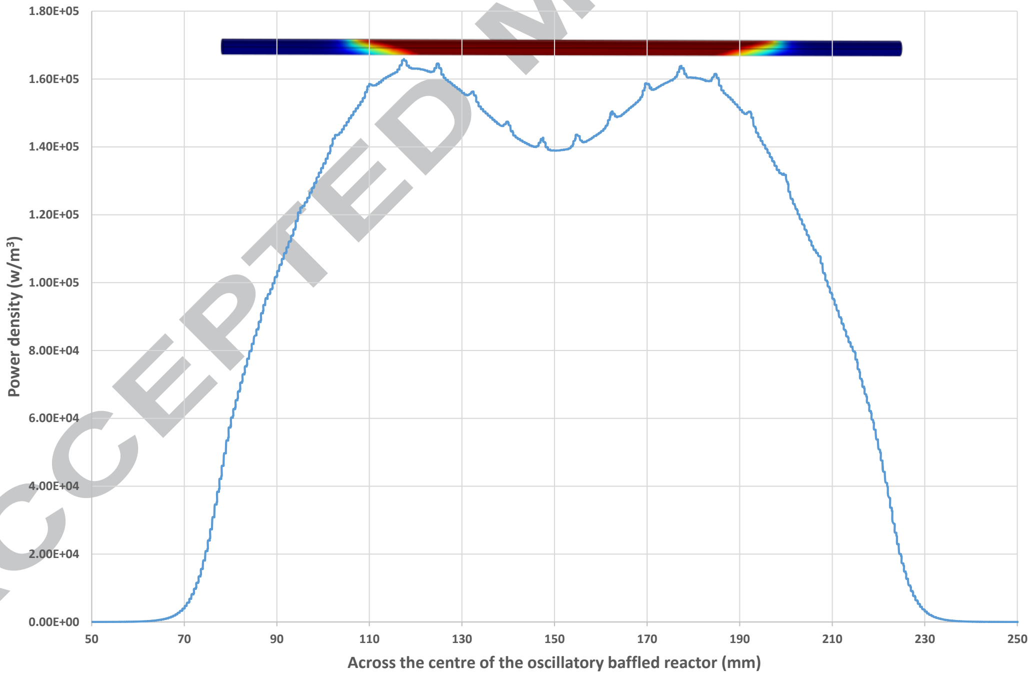


Figure 3: Power density distribution across the centre of the oscillatory baffle reactor simulated using the electromagnetic properties of the reaction mixture and COMSOL Multiphysics[32]. Further details are given in the supplementary information.

As mentioned in the introduction, HKUST-1 was selected as it has been produced *via* many different routes (*e.g.* electrochemical, mechanochemical/extrusion, spray drying, microwave heated reactions, conventional heated continuous flow synthesis and in batch systems such as CSTRs)[6]. This enables direct comparison of production rate, STY and quality (SAPR, porosity, particle size and morphology, crystallinity) for which some data already exist. For example, production of HKUST-1 in ethanol in a CSTR at 60 °C takes 5 hours with a yield of 32.3 %, STY of 41 kg/m^3/day, and an SAPR of 91 × 10^6 kg/m^3/day.[21]

Feedstocks were prepared according to previously reported stochiometries and concentrations for HKUST-1 synthesis.[21] Feedstock one (E1, **Figure 2**) consisted of an 8.94 mM solution of copper salt, made from copper nitrate hemipentahydrate (13.86 g) dissolved in ethanol (150 mL). Feedstock two (E2, **Figure 2**) comprised of a 4.75 mM solution of linker made from trimesic acid (6.66 g) dissolved in ethanol (150 mL). Both solutions were stirred prior to pumping to ensure complete dissolution of the solid into ethanol. Feedstock 3 (E3, **Figure 2**) was pure ethanol used by pumps P1 and P2 for oscillatory flow (Note: this liquid is used for oscillation only and not added to the net flow). Oscillation frequency was controlled by adjusting the speed of the piston movement and the amplitude was adjusted by setting the amount of volume dispensed. The parameters were monitored and controlled using the "SAPPHIRE" engineering software.

During treatment, feedstocks one and two were dispensed in equal proportion (in accordance with reported synthesis conditions)[34] at the desired flow rate (5, 10, 30, 50, 80 and 100 mL/min) and the oscillation was initiated. Further details about the oscillation conditions are provided in the SI. These flow rates correspond to residence times in the microwave heated zone of 2.2 to 44.4 seconds, covering a broad range of residence times and energy inputs. Next, the total volume of the OBR was completely filled with the reaction mixture at the respective flow rate and the mixture heated to 65 ± 5 °C (heating above this temperature resulted in 'boil off' owing to slightly hotter temperatures inside the microwave heated zone) by adjusting the microwave power at a frequency of 2.45 ± 0.0025 GHz (consistent with penetration depth measurements).

An automatic 3-stub tuner (S-TEAM)[35] was used for impedance matching to minimize reflected power and maximize energy absorption by the reaction mixture during microwave treatment. Once temperature had stabilized and the system had reached steady state (approximately 5 reactor volumes), samples were collected at the OBR outlet (after V3, **Figure 2**) at approximately 15 mL intervals during continuous HKUST-1 production. Power meters were used to measure the forward and reflected power from which the average absorbed power (forward minus reflected) and total absorbed energy were determined.

In order to assess the effect of localised electromagnetic heating of the baffles, both PFA and stainless steel baffles were used in the interchangeable baffle section (as indicated by the red zone in **Figure 2**). When metals are exposed to microwave energy, the majority of the microwave current flows in a thin layer (an eddy current) of the surface known as skin depth. The skin depth for stainless steel is 8.48 μm.[3] The remaining OBR length was fitted with PFA baffles (highlighted green in **Figure 2**) to ensure that the metal baffle did not protrude beyond the chokes of the microwave cavity thus preventing microwave leakage. Experiments conducted with stainless were performed at two flow rates, 10 and 50 mL/min.

After microwave treatment, the resulting blue suspensions were centrifuged for 10 minutes at 4200 revolutions per minute at 5 °C. The supernatant was then decanted and the blue powder washed with ethanol (*ca.* 10 mL) and re-centrifuged using the same conditions. The decant, wash and centrifugation step was repeated once more. After this, the supernatant was decanted and the powder was dried in an oven at 50 °C for 5 hours. A minimum of five samples from three separate reactions were obtained for analysis at each flow rate. The average yields of HKUST-1 at each flow rate were determined by thermogravimetric analysis of 2 samples from 3 separate experiments (*i.e.* the 'average yield' is determined from a total of 6 samples per flow rate). Data are given in **Table S2** in the SI.

Results and Discussion

Using our novel MW-CF-OBR rig (**Figure 2**), the effect of synthesis conditions, namely flow rate, applied power (and therefore energy), and baffle material, on the yield and properties (porosity, crystallinity and morphology) of HKUST-1 were investigated. Reactions were conducted in ethanol as this solvent does not decompose during HKUST-1 synthesis and can be recycled, thus reducing the cost, inherent safety issues, and environmental burden of the process.[36] The applied power was varied with flow rate to maintain a bulk reaction temperature of 65 ± 5 °C, as displayed in **Table 2**. Temperatures beyond 65 ± 5 °C were not investigated in order to prevent build-up of pressure from the boiling reaction mixture. Data in **Table 2** show that an increase in energy is required to maintain the target temperature with decreasing flow rate and in presence of a metal baffle; this is due to heat losses to the surrounding areas. Future experiments need to consider insulating the OBR if flow rates below 30 mL/min are required.

Yield of HKUST-1

Products synthesised using the MW-CF-OBR rig exhibit powder X-ray diffraction (PXRD) peaks corresponding to pure HKUST-1, showing that no other MOF phases or impurities were produced (see **Figure S4**, SI). As mentioned in the introduction, it is important to calculate yield in terms of the production rate and STY as these parameters are typically used to evaluate process efficiency and to compare between different production routes. **Figure 4** shows an increase in production rate with increasing flow rate. The highest production rate of 97.42 g/h is observed at the maximum flow rate, 100 mL/min, with a residence time of 2.2 seconds in the microwave heated zone of the MW-CF-OBR rig. This is shortest reported synthesis time for any MOF produced *via* any method to-date. The corresponding STY is 6.32×10^5 kg/m^3/day which is the highest reported for HKUST-1, 1.58 times higher than the previous maximum reported STY, of 4.00×10^5 kg/m^3/day. An average yield of 27.03 % based on the theoretical conversion was achieved. This percentage yield is consistent with the recent work of McKinstry *et al.* in which a maximum yield of 32.3 % was reported using the same conditions as that used in our study, *i.e.* 1.5:1 of BTC:$Cu(NO_3)_2$ in ethanol.[21] It may be possible to improve the conversion by altering the concentration of reactants,[21] the metal:linker ratio,[37] or by increasing the reaction temperature[21] but our current experimental set-up is limited by the reduced penetration depths observed for more concentrated metal salt solutions and by the pressure generated at elevated temperatures. Further work is ongoing to investigate these factors.

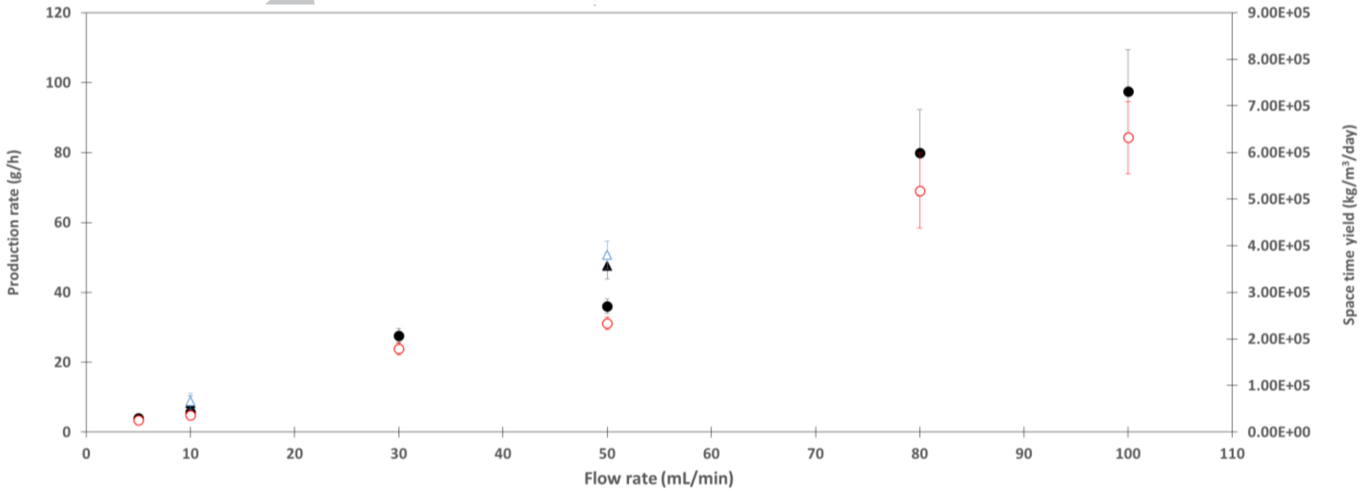
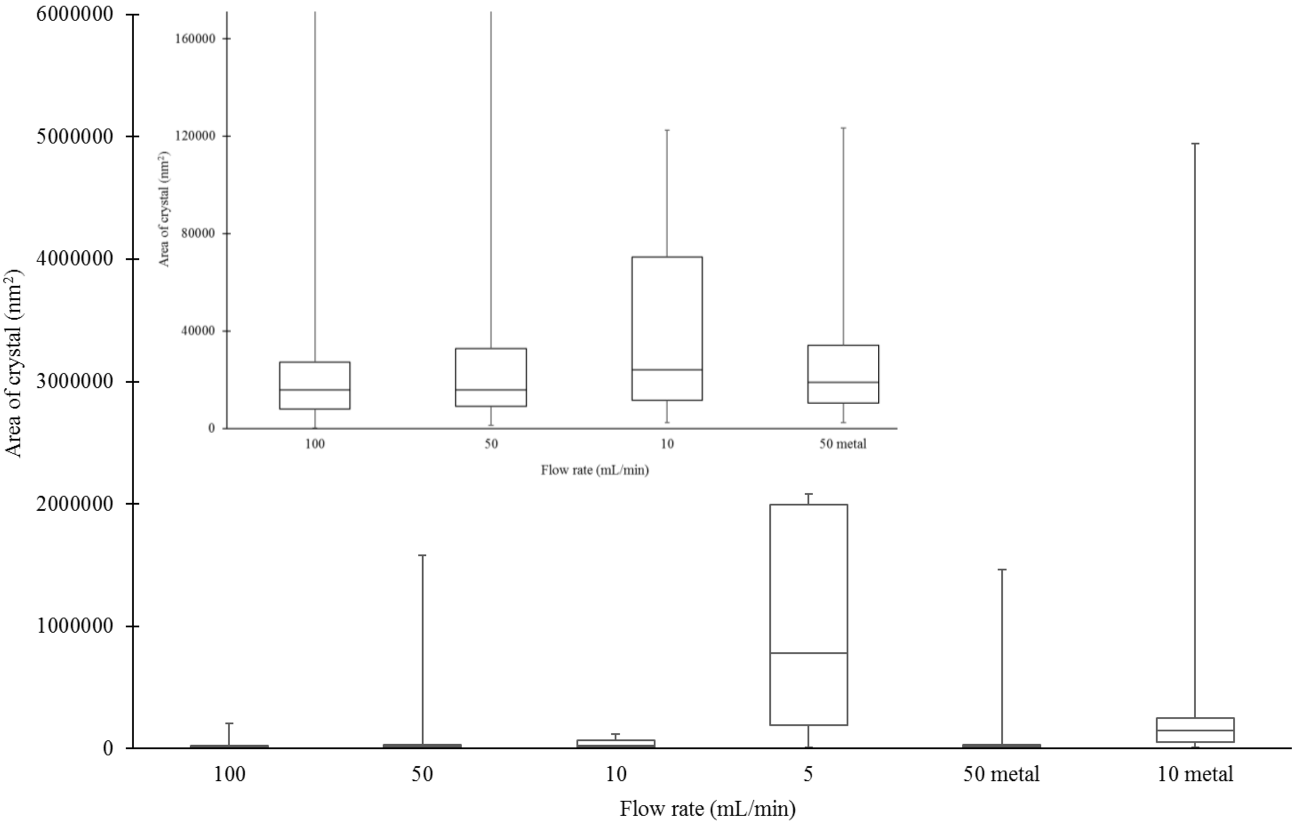


Figure 4: Plot of flow rate *vs.* production rate (left axis; filled in symbols) and space time yield (right axis; red and blue hollow symbols) for HKUST-1 produced using the MW-CF-OBR rig. Circles and triangles represent experiments conducted with a plastic and metal baffle, respectively. Error bars represent the largest absolute experimental deviation from the mean/average values.

Quality of HKUST-1: crystallinity, morphology and porosity

The effect of treatment conditions on the quality of HKUST-1 was also investigated by analysing the crystallinity, morphology and porosity of HKUST-1 produced using the MW-CF-OBR rig. As mentioned in the introduction, MOFs that exhibit high surface areas are particularly desirable for gas storage and capture[6, 22] whereas MOFs consisting of highly crystalline particles of uniform size and morphology are appropriate for separations[23-25] and controlled drug release[26].

Crystallinity and morphology: SEM analyses show that HKUST-1 materials recovered from the MW-CF-OBR rig mainly consist of nano-sized crystals below 15 μm^2. This is consistent with previous reports in which microwave heating produces smaller crystals than conventional heating owing to nucleation at hotspots that form due to local superheating of the solvent[8] and solvated metal ions.[7, 30] In this work, five dominant morphologies namely, plates, circular, irregular, triangular based prisms and octahedral crystals are observed (see Section 4, SI). Irregular,[38] circular[38] and octahedral shaped crystals have been reported previously for HKUST-1 with octahedral crystals >5μm being the most common.[38-42] The shape of the crystals is unlikely to be critical for industrial applications of MOFs, however, the production of crystals with uniform size and shape is desirable. Using an aforementioned particle size distribution analysis method,[7, 43] our present work shows that HKUST-1



Fi al denotes the use of metal baffles during MOF production. Data based on SEM analyses (see SI for further details). Inset: zoom of data for flow rates of 100 and 10 mL/min using plastic baffles and 50 mL/min using plastic and metal baffles. Error bars represent the largest and smallest crystal sizes. Boxes represent the interquartile range (outer line) and median (central line) crystal sizes.

particle size and morphology is dependent on the flow rate and, therefore, mixing effects and microwave treatment (power and time, consistent with previous reports[7, 44]). However, there is no obvious correlation between the yield of HKUST-1 and particle size (see **Table S2** in SI).

Materials recovered from the MW-CF-OBR rig show a reduction in median particle size with increasing flow rate. For example, at a flow rate of 5 mL/min (plastic baffles) HKUST-1 particles consist of triangular based prisms and octahedral crystals with a median crystal size of 0.78 μm^2 as observed by scanning-electron microscopy (SEM, see **Figure 5** and SI). However at a flow rate of 100 mL/min (plastic baffles) HKUST-1 particles consist of much smaller irregular and circular shaped crystals with a median size of 0.016 μm^2 (see **Figure 5**). The same trend is observed for HKUST-1 produced using metal baffles; the median particle size decreases from 0.15 (octahedral and triangular prisms) to 0.019 μm^2 (irregular and circular crystals) between flow rates of 10 and 50 mL/min, respectively (see **Figure 5**). The smaller and irregular shaped crystals recovered at high flow rates are likely the result of decreased reaction time, *i.e.* crystals are earlier in the crystallisation process, or crystal breakage due to rapid and harsh mixing. Further work is ongoing to investigate these effects.

The relative crystallinity of HKUST-1 materials were determined using the method of Vivani *et al.*[45] by comparing the reciprocals of the full width half maximum (1/FWHM) for a selected peak in the PXRD patterns. FWHM were calculated using a split pseudo-Voigt peak fitting function (**Figure S5**, SI). Data in **Table 1** show no obvious correlation between treatment conditions and relative crystallinity. HKUST-1 produced at 100 mL/min shows the lowest 1/FWHM (see **Table 1**) and therefore is the least crystalline material produced using the MW-CF-OBR rig. This is consistent with SEM analyses in which irregular shaped crystals were produced at 100 mL/min and is an acceptable level of crystallinity compared to other commercially available materials[46, 47].

Table 1: Summary of relative crystallinity of HKUST-1 produced using the MW-CF-OBR rig. High values of 1/full width half maximum indicate highly crystalline materials.

Flow rate (mL/min)	Relative crystallinity (1/FWHM) of 220 peak
5	4.6
10	4.9
10#	4.1
50	4.2
50#	5.2
100	3.5

#Metal baffle used during microwave treatments.

Porosity: A summary of N_2 gas sorption data for HKUST-1 produced in the MW-CF-OBR rig is given in **Table 2**. HKUST-1 prepared at flow rates of 5 and 10 mL/min exhibit Type I isotherms with little hysteresis,[48] characteristic of microporous materials and typically exhibited by HKUST-1[49, 50]. HKUST-1 prepared at flow rates of 50, 80 and 100 mL/min exhibit Type I isotherms with some Type IV character and H4 hysteresis indicative of inter-particulate mesoporosity,[48, 51] also reported previously for HKUST-1[52]. All materials exhibit Langmuir (SA_{Lang}) and Brunauer–Emmett–Teller surface areas (SA_{BET}) over 1300 m^2/g with no obvious correlation between treatment conditions and surface area (see **Table 2**).

In our present work, the highest (SA_{BET}) of 2004 ± 0.4 m^2/g was exhibited by HKUST-1 prepared at a flow rate of 30 mL/min which is higher than that reported for HKUST-1 prepared by mechanochemical (1600 m^2/g), electrochemical (1820 m^2/g), solvothermal (1550 m^2/g) and continuous flow (1950 m^2/g) synthesis.[6] A relationship between flow rate and relative microporosity of HKUST-1 was determined by calculating the ratio of the pore volume at low pressure to the pore volume at high relative pressure ($V_{0.1}/V_{Tot}$).[7, 53] Data in **Table 2** (and **Figure S6**, SI) show that as the flow rate increases the value of $V_{0.1}/V_{Tot}$ tends away from one, indicating that highly microporous HKUST-1 is produced at flow rates below 50 mL/min and above this intergranular mesoporosity arises. This is consistent with SEM analyses (see SI) and another report where high V_{Tot} and H4 hysteresis were exhibited by expanded aggregated particles of HKUST-1.[54]

Table 2: Summary of gas sorption data collected at 77 K using N_2 as the sorbate for HKUST-1 produced in the MW-CF-OBR rig and oscillation conditions.

Flow rate (mL/min)	**Velocity ratio (Ψ)= Re_o/Re_n**$^{\#*1}$	**Average absorbed power (W)**^{*1}	**Average absorbed energy (kJ)**^{*2}	**Average absorbed energy per volume of reaction mixture (kJ/mL)**^{*2}	**Langmuir surface area (m^2g^{-1})**^{*a}	**BET surface area (m^2g^{-1})**^{*b}	**$V_{0.1}/V_{Tot}$**^{*c}
5	27.76	53 ± 1	6.56 ± 0.13	0.52 ± 0.01	1893	***1850***	0.91
10	13.88	51 ± 5	3.49 ± 1.25	0.28 ± 0.13	1661	***1621***	0.90
10^{*d}	13.88	95 ± 5	5.84 ± 0.31	0.58 ± 0.03	1964	***1916***	0.90
30	4.63	86 ± 4	1.85 ± 0.07	0.18 ± 0.00	2054	***2004***	0.86
50	2.78	104 ± 1	2.22 ± 0.02	0.13 ± 0.00	1386	1345	0.81
50^{*d}	2.78	158± 2	3.39 ± 0.30	0.20 ± 0.02	1734	***1686***	0.76
80	1.73	128 ± 0	1.70 ± 0.01	0.12 ± 0.00	1728	***1680***	0.65
100	1.39	156± 2	1.75 ± 0.02	0.10 ± 0.00	1772	***1751***	0.68

[*1] Values written to nearest integer. [a] P/P_0 range 0.001 to 0.01. [b] The Rouquerol plot was used in the P/P_0 range 0.001 to 0.01 to give positive C values for the BET surface area. [*c] Pore volume at $P/P_0 = 0.1$ divided by the total pore volume at $P/P_0 = 0.99$; values are written to two decimal places. [*d] Metal baffle used during microwave treatments. BET surface areas in italics and bold are within the reported range of commercially available HKUST-1.[55] [*2] Values written to two decimal places. [#] Calculation and explanation of velocity ratio given in the SI.

In order to compare the surface area of HKUST-1 produced using our MW-CF-OBR rig with that obtained *via* other processes, we have determined the SAPR. The SAPR of HKUST-1 produced using our MW-CF-OBR rig increases with increasing flow rate owing to high SA_{BET} (>1300 m^2/g) as shown in **Figure 6** and **Table 2**, respectively. While this result is expected, a related microwave-heated continuous flow study by McKinstry *et al.*,[21] reported a decrease in the SA_{Lang} of HKUST-1 from 1930 to 1550 m^2/g with an increase in flow rate from 300 to 550 mL/h.[21] The reduction in surface area observed by McKinstry *et al*. may be a consequence of using a non-optimised system, *i.e.* the energy absorbed per unit mass was not controlled, thus resulting in a difference in temperature between the different flow rates and a reduction in quality of the MOF produced.[7]

In this work SAPRs between 3.36×10^7 and 1.12×10^{12} m^2/m^3/day (where a day corresponds to 24 hours) were achieved, with the highest SAPR reached at a flow rate of 100 mL/min (see **Figure 6**). Our highest SAPR is two orders of magnitude higher than the current top SAPR of 2.40×10^9 m^2/m^3/day owing to the superior porosity exhibited by HKUST-1 produced using our rig (Langmuir surface area of 1772 compared to 600 m^2/g).[21]

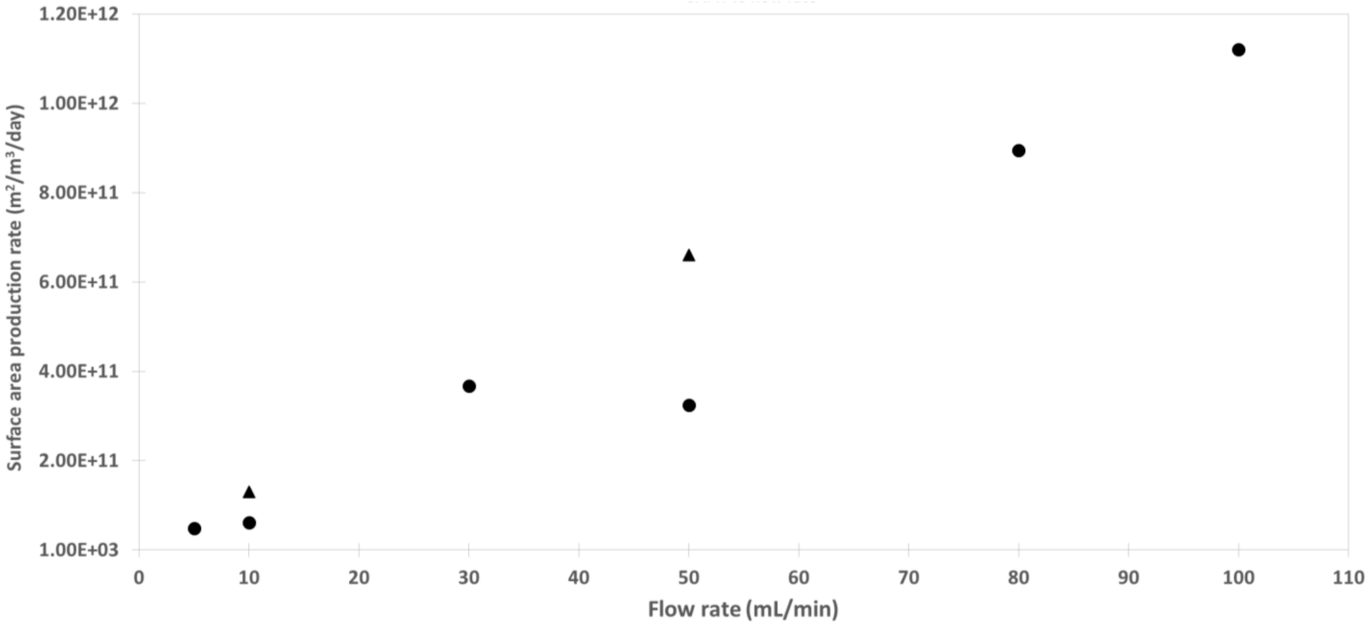


Figure 6: Plot of flow rate *vs.* surface area production rate for representative samples of HKUST-1 produced using the MW-CF-OBR rig. Circles and triangles represent experiments conducted with a plastic and metal baffle, respectively.

Conclusions

We have developed a microwave heated oscillatory baffled reactor (MW-CF-OBR) rig for synthesising HKUST-1 in ethanol under mild conditions (ambient pressure and temperatures below 70 °C). Oscillatory baffled reactors were employed to generate uniform mixing of reactants and suspension of solids, and to facilitate rapid heat transfer to the bulk mixture. Microwave heating enabled a significant reduction in synthesis time with production rates of 97.42 g/h and a space time yield (STY) of 6.32×10^5 kg/m^3/day achieved. This is the highest reported STY and fastest synthesis rate (2.2 seconds) for any MOF produced to-date using any production method. Process intensification is enabled by both technologies through efficient mixing (uniform suspension of solids and high level of plug flow, OBR technology) and rapid delivery of energy requirements (microwave heating). The rapidity of energy delivery is further enhanced by selective microwave heating of the metal ions in solution.[7, 56]

The quality of HKUST-1 materials produced using the MW-CF-OBR rig were assessed by analysing the crystallinity, morphology and porosity. HKUST-1 particle size and morphology were found to be dependent on the flow rate. For example, syntheses conducted at 5 mL/min gave relatively large octahedral and triangular prism shaped crystals (median particle size 0.78 μm^2) whereas flow rates above 50 mL/min gave much smaller irregular shaped crystals (median particle size ≤0.019 μm^2). A slight reduction in relative crystallinity (although still in line with commercial sources)[46, 47] is exhibited by HKUST-1 produced at flow rates of 100 mL/min compared to lower flow rates, which is probably due shorter reaction times (less time for crystallisation), or crystal breakage due to rapid and harsh mixing. All the HKUST-1 materials produced were highly porous and exhibited Brunauer–Emmett–Teller surface areas (SA_{BET}) over 1300 m^{2}g resulting in a surface area production rate (SAPR) of 1.12×10^{12} m^2/m^3/day. This is two orders of magnitude more than the highest reported for HKUST-1 and confirms that the materials produced using the MW-CF-OBR rig are of high quality.

Supporting Information

Supporting Information associated with this can be found online at (to be insterted).

Acknowledgements

AL acknowledges the University of Nottingham for the award of a Nottingham Research Fellowship. We thank the Nanoscale and Microscale Research Centre (nMRC, University of Nottingham) for access to SEM facilities which are supported by the Engineering and Physical Sciences Research Council (EPSRC) under grant EP/L022494/1. Finally, we thank Christopher G. Morris for training and helpful discussions regarding the PXRD peak fitting.

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Highlights for “Combining continuous flow oscillatory baffled reactors and microwave heating: process intensification and accelerated synthesis of metal-organic frameworks”

- 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