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Scalable continuous production of high quality HKUST-1 via conventional and microwave heating

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HIGHLIGHTS

- A scale-up methodology and a procedure for the production of high quality HKUST-1.
- The first continuous production of HKUST-1 in ethanol-only solvent using a CSTR.
- The first microwave assisted continuous production of HKUST-1 in ethanol.
- The highest production rates ever reported for HKUST-1.

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ABSTRACT

Metal Organic Frameworks (MOFs) are materials with large surface areas and internal volumes, which result in a number of useful properties for applications such as catalysis, separations and gas storage. However, MOFs are challenging to produce at a large scale creating a barrier to becoming truly viable alternatives to current technologies. As a first step towards industrial scale manufacture, we demonstrate here the first scalable, continuous synthesis of high-quality HKUST-1 using ethanol as the solvent, resulting in a greener and potentially much more economical process (as solvent does not decompose and thus can be recycled). We also show that microwave heating can be used to produce HKUST-1 continuously, in timescales several orders of magnitude faster than by conventional heating. We demonstrate a novel approach to microwave assisted synthesis of HKUST-1, based on a recycle loop with microwave irradiation, which is scalable under both batch and continuous conditions and allows an independent control of microwave irradiation regime and the overall reaction time. The use of microwave heating for continuous production of HKUST-1 enabled STY of 400,000 $kg\ m^{-3}\ d^{-1}$, which is higher than any production rates reported to date, even when using the preferred high yield solvent, DMF, and is 17 times more than the highest production rates reported to date for HKUST-1 in 'ethanol-only' systems.

1. Introduction

Metal Organic Frameworks (MOFs) are one of the emergent materials of the last decade, due to the unique properties granted by their nature, such as large internal volumes and reduced dead spaces, resulting in MOFs having larger surface areas (>1000 m^2/g) than is thought to be possible for other porous materials, such as activated carbons or zeolites [1,2]. This large internal volume and surface area allows MOFs to show significantly superior properties for uses in gas storage/separation [3] and catalysis [4].

MOFs are currently not used on an industrial scale due to the inability to economically produce desired high quality MOFs in sufficiently large quantities. MOFs are also potentially expensive compared to many materials with similar properties, such as zeolites due to the expensive solvents and ligands often required for MOF synthesis. A potential route to reduce the cost is to develop a scalable continuous synthesis process to replace current batch methods as continuous processing offers a number of benefits in terms of production rates, product quality and reliability. However, there are challenges pertaining to the design complexity of a continuous system, which need to be overcome [5]. The continuous synthesis of MOFs has been recently reviewed by Dunne, Lester and Walton [6], and it is clear that microfluidic reactors are commonly used at laboratory scale. Suspension of nanolitre scale

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droplets of reaction solution within oil allows for highly efficient heat and mass transfer due to the high surface area to volume ratio [7]; HKUST-1, MOF-5, MIL-53, IRMOF-3 and UiO-66 have all been successfully synthesized using this method [7].

Here we focus on HKUST-1 (also known as MOF-199) [8], which has the potential to be used in gas applications such as short chain hydrocarbon separation [9], hydrogen storage [10,11] or purification [12], and H_2S sequestration [13]. HKUST-1 possesses accessible un-coordinated metal sites with high bonding energy towards target species [14], allowing adsorbates to interact more strongly with the MOF. Combined with the fact that the copper dimers form dipoles, this can further increase the myriad potential applications of HKUST-1, and coupled with its stability [15–18], this makes HKUST-1 an ideal MOF to consider for scaled-up manufacture with increased efficiency. HKUST-1 has been synthesized continuously, where it was reported to form in short times by flowing reactants counter-currently at 300 °C and 250 bar, allowing the MOF to form in a 1 s residence time [19] with high surface area. Increasing the temperature and pressure of synthesis has been shown previously to provide thermodynamic conditions favourable for MOF formation [20], resulting in the formation of MOF at shorter times than for operation at ambient conditions. However, operating at elevated temperatures and pressures is likely to add significant cost to the overall process. It was subsequently shown that considerably less severe operating conditions can be used to form HKUST-1 in times of 5 min, however this still requires operation at 100 bar [21]. Rubio-Martinez et al. [22] showed the ability to operate relatively close to atmospheric pressure and produce high surface area HKUST-1. However, all syntheses described above use tubular micro-channels of low volumes (typically <20 mL).

Microwave assisted syntheses of MOFs – both in batch and continuous modes – have been reported, which are summarised in a recent review [6]. Of particular relevance, Ranocchiari and co-workers demonstrated continuous flow synthesis of MOFs using microwave heating [23]. They used a single pass microwave process using only DMF as a solvent to produce HKUST-1 with high STY values. Pressures of up to 6 bar were used to increase the solvent boiling point, although they reported that solvent boiling was nevertheless observed. Overheating of DMF and boiling even at pressures of up to 6 bars as reported by Ranocchiari seems to be especially problematic as decomposition pathways of DMF are not fully understood and it was previously suggested [24] that one of by-products is hydrogen gas. Hence a robust and sustainable method is required for safe implementation at industrial production scales.

We have recently shown, with an example of MOF-5, that continuous stirred tank reactors (CSTR) provide several benefits when scaling-up MOF crystallisation [25,26]. In this context we aimed to investigate scale-up at significantly higher outputs and across different solvent choices using widely available CSTRs. In order to make the process industrially applicable, we aimed to identify sustainable solvent systems. For many MOFs, including HKUST-1, microwave heating has shown considerable benefits at small scale batch level, mainly reducing the reaction time for MOF synthesis, often moving from hours to minutes timescales [27], while maintaining the required properties of the MOF product, such as surface area. However, these systems adopt a single pass approach which implies that all microwave assisted heating has to happen within the residence time available and so the design space is limited due to overheating and pressure control limitations. Therefore we aimed to investigate using microwaves to provide increased efficiency for continuous solvothermal synthesis of HKUST-1. Further, in order to achieve a robust control of microwave heating, we proposed a novel approach based on a recycle loop with microwave radiation, which allows an independent control of microwave irradiation and the overall reaction time.

2. Experimental

2.1. Batch synthesis of HKUST-1

2.1.1. Synthesis using conventional heating

We reviewed the available literature to establish the most consistent and reliable synthetic procedures for the production of HKUST-1. Due to scalability issues and continuous processing difficulties with electrochemical and mechanochemical methods, we focused on solvothermal synthesis. We used a modified version of the synthesis route from Chowdhury et al. [28] as the basis for our experiments, modifying the procedure to produce material under conditions similar to Millange et al. [29] for comparison.

All batch tests were performed using 6 mL of total solvent volume and a metal:ligand (M:L) concentration ratio of 1.88:1, resulting in the metal being in excess (1.5:1 is the stoichiometric ratio). In all experiments, samples were stirred magnetically and heated using an oil bath and hot plate to reach the desired temperature, monitored by a thermocouple inserted into the reaction solution.

The solution was composed of equal parts in volume of *N,N*-dimethyl formamide (DMF) (Sigma Aldrich, 99.8%, anhydrous), deionised water and ethanol (Sigmas Aldrich, 99%). 0.231 g copper nitrate hemipentahydrate (Sigma Aldrich, 98%) and 0.111 g trimesic acid (Sigma Aldrich, 95%) were added to the solution (solids content of about 3% by mass). The sample vials were then capped and placed into an oil bath, which was preheated under constant stirring to the reaction temperature of 60 °C. Multiple samples were removed after various, preselected, time periods and analysed to determine how yield, purity, and porosity vary as a function of synthesis time. The experiment was then repeated using ethanol as the only solvent, keeping all other reaction parameters constant. The ethanol experiment was then repeated at a reaction temperature of 79 °C. This experiment was performed in a reflux condenser, and aliquots of identical volume were taken for analysis at preselected time intervals. To investigate the effect of process intensification on the ethanol only system, the experiment was repeated with reactant concentrations increased by up to a factor of 5, giving approximately 6%, 9% and 15% solids, based on theoretical yield.

2.1.2. Microwave assisted batch synthesis of HKUST-1

Using a domestic microwave oven, Logik L20MS10 (800 W), we investigated the main parameters affecting the production of HKUST-1 using microwave heating rather than conventional convective heating. It is important to note that, for safety reasons, we made no modifications to the casing of the microwave.

The solutions used were composed of 0.462 g copper nitrate hemipentahydrate and 0.222 g trimesic acid in 10 mL of ethanol (maintaining a M:L ratio of 1.88:1). As samples could not be agitated during the heating period, samples were stirred for 30 min by magnetic stirrer bar at room temperature before the stirrer bar was removed and the reaction vessel immediately placed in the centre of the microwave for reaction. A control sample was stirred at room temperature for 3 h without heating. As domestic microwaves do not produce a completely uniform field, hotspots within the chamber may vary [30]; we, therefore, placed the vials at the same location within the microwave to attempt to mitigate any variability due to this factor. In situ monitoring of temperature was not available, so final reaction temperature was determined using a thermocouple immediately upon reaction completion.

The samples were heated at 10% of the maximum power level of the microwave (∼80 W) for 180 s. To investigate the effect of increasing the reaction time, 300 s and 600 s reaction times were also investigated. In order to determine the effect of heating rate on system output, the initial experiment was repeated using 20% of the maximum power of the microwave. This experiment was again repeated using percentage solids of 9 and 15% (based on theoretical yield), in order to investigate the effect of higher power inputs on the formation of HKUST-1 under microwave heating. All experiments were carried out in triplicate.

2.2. Continuous synthesis of HKUST-1

2.2.1. Continuous synthesis with conventional heating

For the continuous flow system, the basic layout of the apparatus was as shown in Fig. 1a. The reactor vessel itself was equipped with a reflux condenser situated within an oil bath. A thermocouple was used to monitor the temperature of the solution within the reactor. The reactor was initially loaded with 100 mL ethanol solvent and heated to the desired reaction temperature. At the time when the feed pumps were turned on, 4.62 g copper nitrate hemipentahydrate and 2.22 g trimesic acid were added to the reactor vessel as solid powders. The time when the pumps were initiated was recorded as the zero time for the reaction, thereby allowing observation of any start-up phases before steady state was achieved. The copper salt feed consisted of 13.86 g copper nitrate hemipentahydrate dissolved in 150 mL ethanol. The trimesic acid feed consisted of 6.66 g trimesic acid dissolved in 150 mL ethanol. Initially, the flow rates of the Watson Marlow 101-U calibrated pumps were set to deliver 33 mL h^{-1} of each of the feeds while the collection pump was set to remove 66 mL h^{-1}, giving an overall average residence time within the reactor of 1.5 h. Samples were collected over separate 15 min time intervals before filtration and washing with ethanol. The solid outputs were subsequently analysed as described in Section 2.3. This experiment was repeated with the volumes of feed increased by a factor of two, with all concentrations and flowrates kept constant, and was run for 9 h total, giving 6 full residence times for this reaction, in order to determine if the steady state yield had been reached.

In order to further probe the potential scalability of this system, we ran the reaction at 500 mL scale using a Radleys Reactor-Ready system, operating at a temperature of 65 °C. The reaction temperature was maintained by passing heated fluid through the jacket of the vessel. The concentrations of all reactants were kept at the same values as described above for the smaller scale continuous syntheses. As with the smaller scale experiments, at the same time as the pumps were switched on, the reactor vessel starting conditions required the addition of 23.1 g copper nitrate hemipentahydrate and 11.1 g trimesic acid to the 500 mL of ethanol at 65 °C. The copper salt feed consisted of 92.4 g copper nitrate hemipentahydrate dissolved in 1 L ethanol. The trimesic acid feed consisted of 44.4 g trimesic acid dissolved in 1 L ethanol. Reactor feed and extraction rates were maintained via calibrated pumps operating to give an average residence time of 1.5 h. The experimental set up of the large scale system is shown in Supporting Information (Fig. S1).

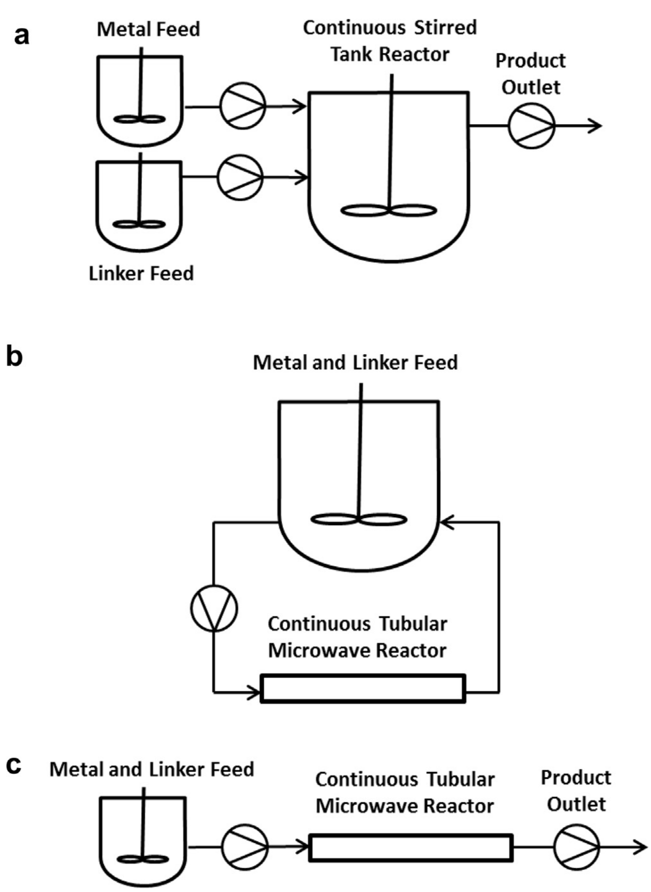

Fig. 1. Layouts of the continuous HKUST-1 synthesis systems used in this study. a: A CSTR used with conventional heating. b: A multi-pass continuous microwave assisted synthesis. c: A single-pass continuous microwave assisted synthesis.

2.2.2. Continuous microwave assisted synthesis of HKUST-1

For the microwave assisted HKUST-1 reaction system, a domestic microwave (Logik L20MS10 (800 W)) was used, where small bore PTFE tubing (d_i = 1 mm) was fed through the side vents, in order to avoid any alterations to the cavity casing, out of safety considerations. Due to potential issues with hotspots forming in bulk solution under batch conditions, a tubular flow-through system was used for continuous operation, with the solution cycled through the microwave cavity multiple times, before removal of aliquots for analysis (see Fig. 1b).

The feed vessel consisted of 13.86 g copper nitrate hemipentahydrate and 6.66 g trimesic acid dissolved in 300 mL of ethanol. This solution was kept at ambient temperature and stirred for 30 min to ensure complete dissolution of all reactants before the reaction was initiated by turning on the microwave. The resulting solution was pumped through the tubing within the microwave cavity at a rate of 300 mL h^{-1}, giving a residence time of 5 min. The solution was then fed back into the original feed vessel which was stirred constantly. Samples were removed periodically, at preselected time intervals.

In order to investigate a single pass yield and find the highest space-time yield of materials, we used a single pass reactor system as shown in Fig. 1c. The feed vessel consisted of 13.86 g copper nitrate hemipentahydrate and 6.66 g trimesic acid dissolved in 300 mL of ethanol. This solution was kept at ambient temperature and stirred for 30 min to ensure complete dissolution of all reactants. The resulting solution was pumped via peristaltic pump, set to deliver a flowrate of 300 mL h^{-1} through a PTFE tube (d_i = 6 mm) within the reactor system, with 25 mL total volume, giving a residence time of 5 min. The microwave was operated on the lowest power setting (∼80 W), with the output temperature maintained at approximately 45 ± 5 °C. The output temperature was monitored by a thermocouple within the solution leaving the microwave cavity. This setup was repeated using a smaller reaction tube (d_i = 1 mm), with 2 mL total volume and a flow rate of 550 mL h^{-1} in order to probe the minimum time required to produce HKUST-1 using continuous microwave assisted processing.

2.3. Characterisation

The collected samples were dried by vacuum filtration before washing with a solution of equal volumes of ethanol and deionised water. Dry masses were determined by heating samples to 170 °C under vacuum. Samples were then characterised by Powder X-ray Diffraction (PXRD), Fourier-Transform Infra-Red (FT-IR) spectroscopy and nitrogen sorption studies. PXRD results were collected using Cu K α (λ = 1.54 Å) radiation on aluminium plates. Nitrogen adsorption-desorption measurements were performed using a Micromeritics ASAP 2420 at −196 °C; prior to analysis samples were degassed by heating at 170 °C for 12 h, under vacuum. FT-IR was carried out using an ABB MB-3000 with Attenuated Total Reflectance (ATR), and a resolution of 4 wavenumbers for 64 scans, before baseline correction and smoothing using GRAMS AI.

3. Results and discussion

3.1. Selection of process conditions for scale-up

Initially, we investigated various solvent systems and solid loadings for batch systems to understand their effects on HKUST-1 synthesis. The synthesis, and the solids obtained, were analysed by determining dry yield, space time yields (STY, kg product/m^3 reactor volume/day), Langmuir specific surface area (SSA, m^2/g) and crystallinity. The specific surface area was used as one of the key measures of product quality while STYs provided information on production rates. As it is known that increasing production rates often compromise product quality, in order to provide clear comparisons between experiments, we used *surface area production rates* (SAPRs), i.e. the amount of surface area of MOF produced per unit volume of the reactor per time (m^2/m^3/day).

Fig. 2a shows that, at 60 °C, over the 5 h observation window, the DMF/ethanol/water system produced the highest overall yield, and also shows HKUST-1 forms faster in the mixed solvent system than in the ethanol only solutions (Table 1). Although using ethanol as the only solvent at 60 °C appears to be very slow and produces poor yields, at a higher temperature (79 °C), we see that the HKUST-1 yield reached a little over 40% by 5 h.

PXRD, FTIR and Langmuir SSA were measured and used to assess the quality of HKUST-1 produced. PXRD patterns (Fig. 2b) show that both solvent systems produced HKUST-1, with locations of expected Bragg peaks matching the powder pattern generated from single crystal data. There were no significant differences observed with respect to the crystallinity of the products from both systems. FT-IR spectra for the HKUST-1 produced (Fig. S2) showed peaks at 1645, 1616, 1554 and 1455 cm^{-1} indicating C=O and aromatic C=C, and 1375 cm^{-1} indicating C—O from the BTC ligand, in good agreement with published sources [11,32]. Gas adsorption confirmed the formation of a microporous material with pore diameters of <1 nm, and Type I isotherms [33] (Fig. S3). The DMF/ethanol/water system produced crystals with a Langmuir SSA of 1200 ± 50 $m^2\ g^{-1}$ at 4 h synthesis time (Table 1), while both ethanol systems (60 and 79 °C) showed higher Langmuir SSAs (>2000 ± 200 $m^2\ g^{-1}$).

In order to optimise yield by maximising the SAPRs, we increased the solids content from 3% to 6, 9, and 15%. The trade-off here is the potential reduction in MOF surface areas. While both solvent choices show a decrease in surface area with increasing % solid loading (Fig. 2c), the ethanol system produced higher surface area MOFs when compared to those produced using DMF. When the SAPRs were calculated from the data in Fig. 2c, and compared, the DMF system underperformed consistently by ∼20% for all solid contents investigated.

As a determining factor in the decision of which system to use as the basis for a CSTR based synthesis; yield, cost, safety and availability of solvents, and the surface areas of the products obtained, were considered (see Table 1). Each synthesis process resulted in similar costs, based on initial estimates [31]. When scaling-up this process, it is important to consider that ethanol does not break

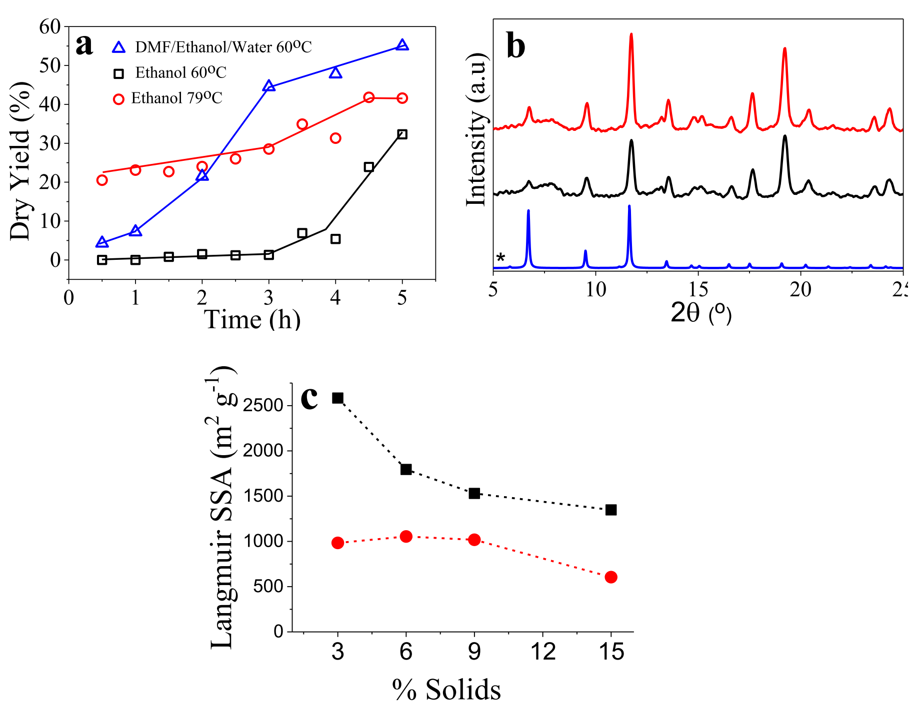

Fig. 2. (a) Comparison of yields of batch systems as a function of time. (b) PXRD showing HKUST-1, as synthesized in 4 h at 60 °C, from DMF/ethanol/water (top line), ethanol only (middle line), *indicates simulated PXRD date from single crystal data [8] (bottom line). (c) Comparison of Langmuir Specific Surface Area (SSA, filled symbols) as a function of % solids; circles: DMF/water/ethanol system (60 °C), squares: ethanol only (60 °C).

Table 1
Comparison of various batch synthesis routes for HKUST-1 synthesis*

Solvent(s)		DMF/Water/Ethanol	Ethanol	Ethanol
Reaction Temperature (°C)		60	60	79
Dry Yield (%)	3 h	45	1.3	28.5
	4 h	47	5.4	31.3
	5 h	55	32.3	41.6
Average Langmuir SSA $m^2\ g^{-1}$		1200	2200	2100
Solvent Cost (£/g HKUST-1)		3.60	8.95	6.81
Highest STY ($kg\ m^{-3}\ d^{-1}$)		70	41	53
Surface Area Production Rate ($m^2\ m^{-3}\ d^{-1}$)		84×10^6	91×10^6	112×10^6
Rough Cost**	(£/m^2)	0.003273	0.0040	0.003243
	Relative Cost	0.804	1	0.797

* For solids content of 3%.
** Cost estimations obtained from [31].

down in the process, hence, it can be recycled. On the other hand, DMF is subject to breakdown when exposed to water and heat, therefore, it cannot be recycled and the amines produced from DMF decomposition present environmental risks. When economic analysis of this method was performed, it was reported that using ethanol and recycling the solvent can result in a profitable manufacturing process [31]. Our focus was developing greener continuous processes for production of HKUST-1, by using ethanol instead of DMF and lower process temperatures. Unlike DMF, ethanol does not undergo decomposition and, thus, it can be recycled, resulting in a significant improvement of process economics [34]. We investigated temperatures below the boiling point of ethanol in order to avoid high pressure operation and/or boiling of solvent which cause additional safety issues as well as an increase in process costs. Thus, on the basis of production quality, cost, sustainability and safety, we selected to focus further syntheses on pure ethanolic systems.

Using the experimental findings from batch syntheses, we investigated continuous synthesis and scale-up. Fig. 3 shows the results from the continuous synthesis systems at 100 mL and 500 mL scales. It is clear, from Fig. 3a, that HKUST-1 can be produced continuously in ethanol using a CSTR. We note that this is the first report of the use of CSTR for continuous production of HKUST-1, and also the first study at 500 mL scale; all previous studies used tubular (micro)reactors [6]. PXRD confirmed the solid products were HKUST-1 (Fig. S4). Although the system produces HKUST-1, product crystallinity does appear to vary over time, as evidenced by the relative intensities and widths of various Bragg peaks (Fig. S4).

We observed that, at both scales, the yields from the continuous systems compare favourably to the equivalent batch syntheses. This is likely an effect of the system self-seeding, and being in a favourable state for the production of HKUST-1, highlighting one of the key benefits of using CSTR synthesis over tubular plug flow reactors. The dry yield of HKUST-1 collected varies almost linearly with time (Fig. 3a) and the SAPRs increased to $377 \times 10^6\ m^2/m^3/d$ (Fig. 3c and Table 2), which is an increase when compared with equivalent batch syntheses (see Table 1).

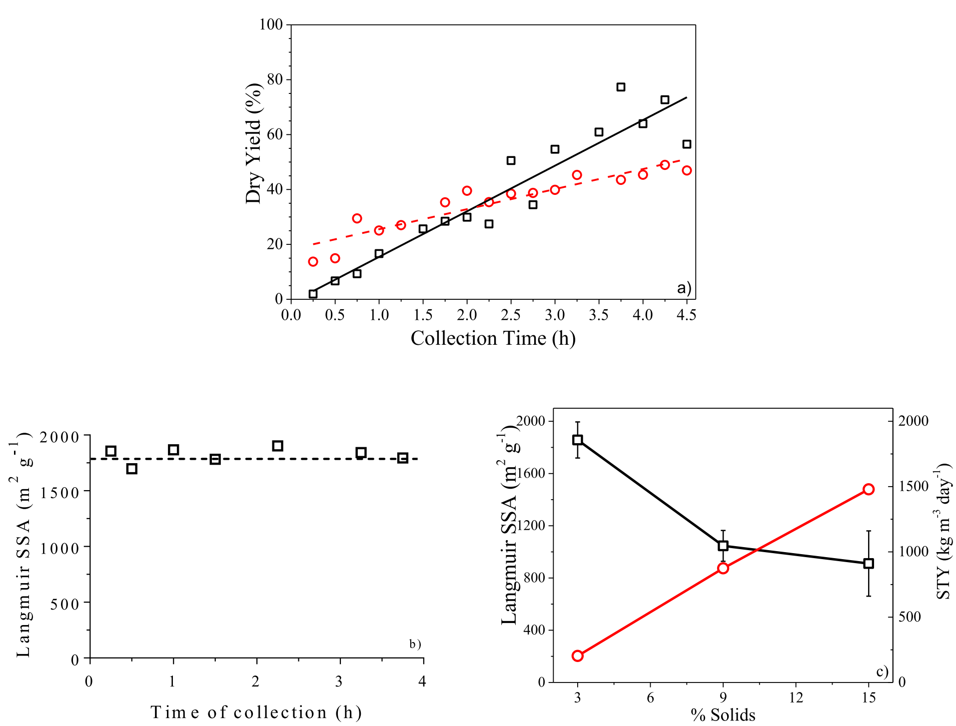

Fig. 3. (a) Collected dry yield of HKUST-1; circles: 100 mL scale at 79 °C, dashed line indicating approximate trend, squares: 500 mL scale at 65 °C, solid line indicating approximate trend. Results show a lower yield at t < 2 h, while showing scale-up gives significantly better production at t > 3 h. (b) Langmuir Specific Surface Area (SSA) results from 4 repeats at various collection times. (c) squares: average Langmuir SSA ($m^2\ g^{-1}$), circles: calculated space time yield (STY, $kg\ m^{-3}\ d^{-1}$).

Table 2
Comparison of reactor output at differing concentrations between 3 and 15% solids for continuous synthesis at 100 mL reactor volume and 79 °C (STY = Space-Time Yield; Langmuir SSA = Langmuir Specific Surface Area; SAPR = Surface Area Production Rate).

% Solids	STY (kg m^{-3} d^{-1})	Langmuir SSA (m^2 g^{-1})	SAPR (m^2 m^{-3} d^{-1})
3	203	1857 ± 138	377×10^6
9	874	1046 ± 118	914×10^6
15	1479	911 ± 250	1347×10^6

Fig. 3b shows the consistency of the high surface areas produced from this system, highlighting that we were able to reliably produce crystals with reasonably high surface areas. As increasing solid content showed benefits in batch operation, with respect to STY for MOF production, we decided to use the 100 mL scale system described above, operating at 79 °C, to study the effects of solids content (3% to 15% solids) in a continuous system. One of the most significant changes observed, when increasing reactant concentration, was the increase in yield, from ~40% at 3% solids to ~60% yield at 9 and 15% solids. The average surface areas of MOFs produced show a decrease with increasing solids content (Fig. 3c), however, the total SAPR reached over 1300×10^6 m^2 per m^3 of reactor volume per day for 15% solids content (Table 2). STY values for continuous systems were based on the outlet product flow rate (obtained from the overall flow rate, overall solid content and yield) divided by the reaction volume. As we have specified reaction volumes for each experiment, calculation of production rates in g/h from STY is also possible.

3.2. Microwave assisted synthesis and scale-up

Due to the potential benefits in heating efficiency and rate of formation of MOFs, we investigated the use of microwave heating. To identify operating conditions that can be used for continuous synthesis, we initially performed batch experiments; microwave power, residence time, and solids content were investigated. Under low microwave power (10% ≈ 80 W), increasing the residence time increased the product specific surface area, and the yield (Fig. S5 and Table 3). Further, by increasing the microwave power, it was found that the surface area increased. Reaction time was not investigated at higher power levels due to the solution being close to the boiling point of the reaction mixture; therefore, operating at short times was required to prevent build-up of pressure within the vials. When the solids content were increased from 3% to 9%, the HKUST-1 produced exhibited moderate surface area but low yield.

PXRD data (Fig. S5) shows phase pure HKUST-1 formed in all cases, however, the relative crystallinity varied between samples. Crystallinity appears to increase with reaction time (i, ii and iii) which is expected. Fig. S5 (iv) shows the highest crystallinity of the 5 conditions analysed and also produced the highest average surface area, suggesting the increase in temperature, at the increased power level, is likely to produce higher quality crystals, even at relatively short time scales. The SAPRs for microwave assisted batch syntheses range between 1300 to 5900×10^6 m^2 m^{-3} d^{-1} (Table 3), which are significantly higher when compared to conventional heating (see Table 1).

Using the information obtained from batch synthesis, we performed continuous synthesis experiments in a single pass microwave system. Initially the residence time was set at 6 min, resulting in a reaction solution to be heated to a temperature of 60 ± 10 °C, as measured at the outlet from the microwave cavity. The HKUST-1 produced had an average surface area of 1930 m^2 g^{-1} (Table 3), with STY of 2700 kg m^{-3} d^{-1} and SAPR of 5.2×10^9 m^2 m^{-3} d^{-1}, which is an order of magnitude increase from the 203 kg m^{-3} d^{-1} ($0.377 \times 2 \times 10^9$ m^2 m^{-3} d^{-1}) obtained for the conventionally heated continuous system. We note that this is the first report of the use of microwave heating for continuous production of HKUST-1 using only ethanol as the solvent. Previously reported microwave syntheses of HKUST-1 use DMF (with or without ethanol) [6]. The issues of overheating and boiling in the DMF systems even at pressures of up to 6 bars were reported by Ranocchiari and co-workers [23]; our approach addresses these problems by achieving a robust control of microwave heating to avoid solvent overheating and undesirable side reactions. Given the economical and environmental benefits of avoiding the use of DMF, our results show significant improvements in HKUST-1 production.

When increasing the flowrate to 550 mL h^{-1}, from 300 mL h^{-1}, and decreasing the reactor volume to 2 mL from the original 25 mL, the residence time was reduced from 5 min to 13 s. The output temperature was found to average 45 ± 5 °C for this system. HKUST-1 was still found to form (Fig. 4) with yields similar to the system operating with a residence time of 5 min (around 30%). This significant reduction in reaction duration results in an approximate STY of 80,000 kg m^{-3} d^{-1}.

The product has an average Langmuir SSA of 1550 m^2 g^{-1}, suggesting that the rapid formation of crystals within the microwave system may cause unreacted metal/ligand to be retained within the pores, thereby reducing the available surface area. We recognise that there may be multiple reasons for an observed reduction of the available surface area in the microwave system, including network interpenetration [35], occlusion of unreacted material [35] or partial network collapse upon characterisation [36], when synthesis conditions are changed. However, distinguishing between these effects is not trivial and sometimes not possible. In our experience, the use of TGA or FTIR is unable to accurately detect the presence of trapped (unbound) ligand. Thus, in order to avoid significant amount of ligand trapping in, we had thoroughly washed the solids. When increasing the concentration of the feed to 15% solids, HKUST-1 was still formed, although the

Table 3
Comparison of microwave assisted batch and continuous synthesis routes for HKUST-1 (Langmuir SSA = Langmuir Specific Surface Area; SAPR = Surface Area Production Rate).

Reaction Time (s)	Power Level (%)	%Solids	STY (kg m^{-3} d^{-1})	Langmuir SSA (m^2 g^{-1})	SAPR ($\times 10^6$ m^2 m^{-3} d^{-1})
Batch synthesis					
180	10	3	1970	1116 ± 680	2200
300	10	3	1560	1411 ± 393	2200
600	10	3	770	1685 ± 299	1300
180	20	3	1910	1880 ± 271	3600
300	10	9	3550	1664 ± 595	5900
Continuous synthesis					
300	10	3	2700	1930 ± 90	5211
13	10	3	80000	1530 ± 120	122400
13	10	15	400000	600 ± 100	240000

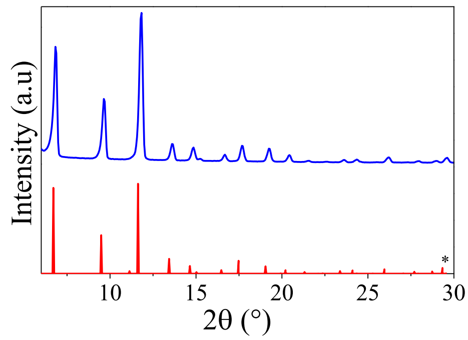

Fig. 4. Powder X-ray diffraction data for HKUST-1 formed with 13 s residence time using continuous microwave assisted processing. Black lines show Bragg peak locations as generated by the crystallographic information for HKUST-1. *indicates simulated PXRD data from single crystal data [8].

Langmuir SSA was reduced to 600 $m^2\,g^{-1}$, with STYs of 400,000 $kg\,m^{-3}\,d^{-1}$. This STY is the highest ever STY reported for HKUST-1. The highest STY reported previously with any solvent was 64,800 $kg\,m^{-3}\,d^{-1}$ with DMF [23], while the highest STY reported with ethanol (without DMF) was 4533 $kg\,m^{-3}\,d^{-1}$ [22]. The resulting SAPR from our study is $240 \times 10^9\,m^2\,m^{-3}\,d^{-1}$, which is also the highest reported to date and it is 2.4 times higher than any other reported so far [23].

4. Conclusions

In our work, we demonstrated the first scalable continuous synthesis of HKUST-1 using ethanol only as the solvent, resulting in a greener and potentially much more economical process (as solvent does not decompose and thus can be recycled). We showed that either CSTR, single pass plug flow microwave assisted or a combined approach can be used effectively to produce high quality products at scale. We have shown that a conventionally heated continuous reaction system can be used to produce HKUST-1 in a relatively short time period, while maintaining high surface areas, increasing the potential output from a batch system (Table 4). Further, we demonstrated a novel approach to microwave assisted synthesis of HKUST-1, based on a recycle loop with microwave irradiation, which can be scalable under both batch and continuous conditions and allows an independent control of irradiation regime and the overall reaction time. We also showed that microwave heating can be used to significantly improve the STY of both batch and continuous systems while maintaining a surface area similar to conventionally heated processes. This represents the production of $2.4 \times 10^{11}\,m^2$ of Langmuir SSA for one m^3 reactor volume per day. This is higher than any production rates reported to date, even when using DMF as the reaction solvent, and it is orders of magnitude more than the highest production rates reported for HKUST-1 in 'ethanol-only' systems.

Table 4
Summary of results discussed within main body of this work.

System	% Solids	Langmuir SSA ($m^2\,g^{-1}$)	Surface Area Production Rate $\times 10^6$ ($m^2\,m^{-3}\,d^{-1}$)
Continuous CSTR, (EtOH, 100 mL, 79 °C)	15	910 ± 250	1347
Continuous microwave system (EtOH, 13 s)	15	600 ± 100	240000
Commercially Available Product*	–	1680	378

* Basolite C300, produced by BASF, reported STY = 225 $kg/m^3/d$ and Langmuir SSA of 1680 m^2/g.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.05.169.

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