Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Scalable Simultaneous Activation and Separation of Metal-Organic Frameworks

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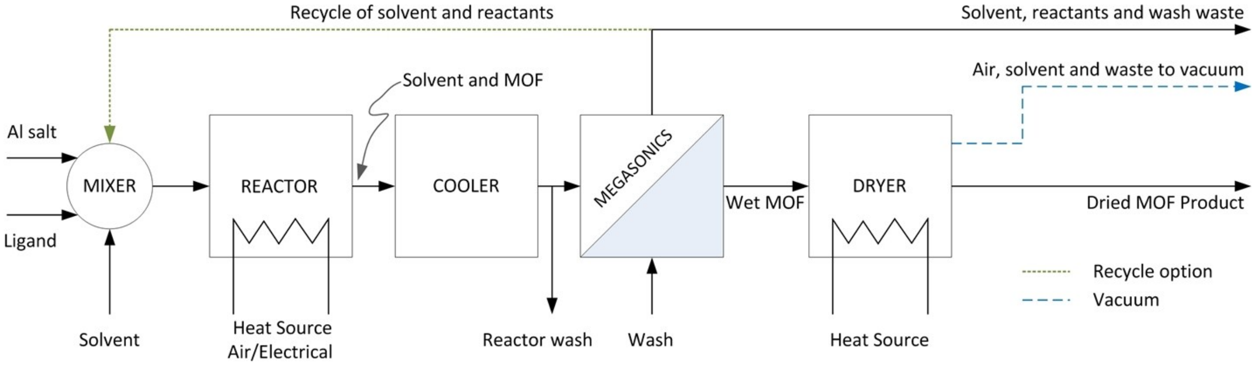
S1. General description of the continuous flow MOF process

S1.a. The different stages of the continuous flow process for MOFs production: synthesis, washing, separation and drying.



S1.b. Continuous flow MOF macroscale reactor

Continuous flow scale-up synthesis was performed in a Salamander Flow Reactor (Cambridge Reactor Design Ltd., Cottenham, UK) as previously detailed by Micic *et. al.*[1] . Briefly, it consists of a serpentine stainless steel tube (8 mm o.d., 6 mm i.d., 108 mL volume) and a thermostatically-controlled electrical heating system (ambient to 150 °C). An inline back-pressure regulator, situated at the outlet of the reactor, allows fine tuning of the reactor pressure (up to 20 bar). Static mixer units are placed within the linear sections of the reactor tubing to promote tubulent mixing and efficient heat transfer. Twin Gilson 305 dual piston pumps, (flow rates between 0.5 mL/min and 50 mL/min) provide the solvent and reagent feeds for the reactor system. Figure S1 shows a representative flow reactor configuration for MOF processing.

In a typical reaction, two separate solutions of the precursors are pumped through a T-type static mixer to promote diffusion mixing of the reagent input streams. The combined reagent streams are then directed into the heated reactor zone of the Salamander Flow Reactor for a predetermined residence time. On exiting the reactor, the stream is cooled in a external heat sink unit, based on a coiled tube in a water bath. Then the stream passes through a back-pressure regulator, and is collected for the next process steps.

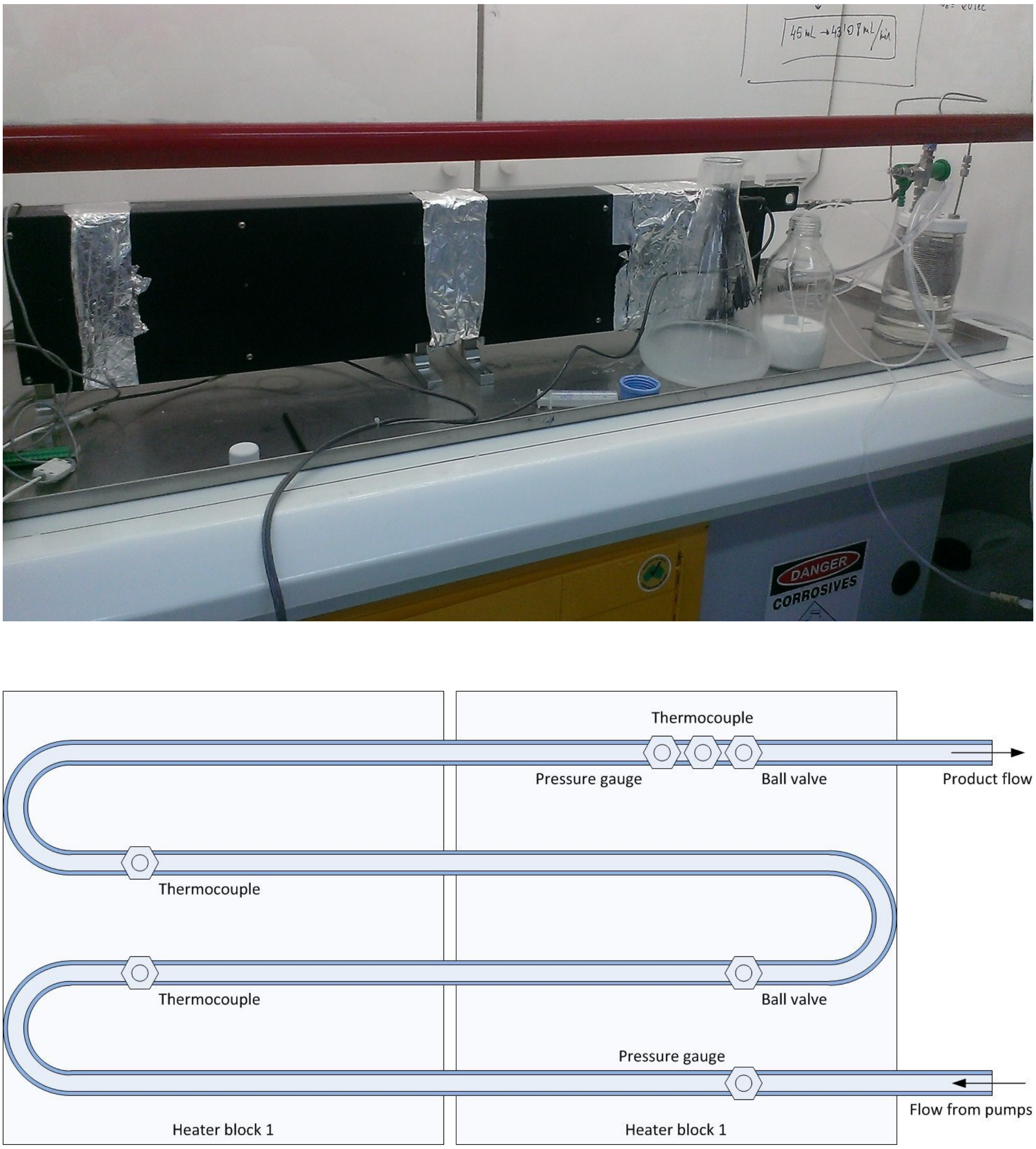


Figure S1. Photograph and schematic of the Salamander Flow Reactor (Cambridge Reactor Design) used for the large-scale production of the Al-Fumarate and MIL-53 MOFs. The system is comprised of two HPLC pumps (Gilson), a 108 mL stainless steel tubing reactor (0.6 mm i.d.), and custom static mixers throughout the length of tubing.

S2. Synthesis of Al-Fumarate and MIL-53 using Salamander flow reactor

S2.a. Synthesis of Al-Fumarate

The general procedure described in S1.b. was employed. An aqueous solution of 0.35M $Al_2(SO_4)_3$ $18H_2O$ and an aqueous solution of 0.7M of fumaric acid and 2M of NaOH solution were mixed under continuous flow conditions and heated in a tubular reactor. The synthesis was conducted at 65 ºC using a total flow rate of 90 mL•min-1, giving a total residence time of 1.2 min. The material was washed three times with fresh water and twice with ethanol and dried in vacuum (500 mbar) for 8 hours at 40 ºC. Yield: 100%.

S2.b. Synthesis of MIL-53 (Al)

The general procedure described in S1.b. was employed. An aqueous solution of 0.08M $Al(NO)_3$ and an aqueous solution of 0.08M of terephthalic acid and 0.24M of NaOH solution were mixed under continuous flow conditions and heated in a tubular reactor. The synthesis was conducted at 140 ºC using a total flow rate of 90 mL•min-1, giving a total residence time of 1.2 min. The material was washed three times with fresh water and twice with ethanol and dried in vacuum (500 mbar) for 8 hours at 40 ºC. Yield: 83%.

S2.c. Continuous flow MOF: separation and washing steps using megasonics

The separation of the MOF was carried out in a transparent Perspex acrylic chamber with a capacity of 6 L, in where the transducer is fixed in vertical position. All trials were conducted utilizing submersible stainless steel transducer plates (Sonosys Ultraschallsysteme GmbH, Neuenbuerg, Germany) operating at 2 MHz. The optimization of the system was performed in a stainless steel 1L container.

Each experiment consisted of filling the acoustic reactor with a diluted MOF solution (50% in water) and immediately sonicating for 10 min. A control system, where no ultrasound was applied, was simultaneously filled with a portion of the same MOFs solution to observe the differences. In all experiments the temperature increased up to 10℃, caused by acoustic energy dissipation, therefore an ice bath is used during the experiments.

Before and after the application of ultrasound, 10 mL samples were removed to measure the ζ-potential of the MOFs. Using megasonics the MOF product was washed three times with fresh water and twice with EtOH.

S3. Characterization

The scanning electron microscopy (SEM) images were collected on a Quanta 400 FEG ESEM (FEI) at acceleration voltage of 0.2-30 kV. Infrared (IR) spectra were recorded on a Tensor 27FTIR spectrophotometer (Bruker). The X-ray powder diffraction (XRPD) measurements were performed with an X'Pert Pro MPD diffractometer (Panalytical) over a 2θ range of 5º to 45º. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer STA-600 under a constant flow of N_2 at a temperature increase rate of 5 ºC/min. Zeta potential measurements were performed on a NanoZs Zetasizer from MALVERN whereas the Turbiscan measurements were performed with the MA 2000 (Formulaction, Toulouse, France). Gas adsorption isotherms for pressures in the range 0 – 120 kPa were measured by a volumetric approach using a Micrometrics ASAP 2420 instrument. All the samples were transferred to pre-dried and weighed analysis tubes and sealed with Transcal stoppers. Al-Fumarate and MIL-53 were evacuated and activated under dynamic vacuum at 10^{-6} Torr at 140 ºC for 8 hours. Ultra-high purity N_2, CH_4, H_2 and CO_2 gases were used for the experiments. N_2 and H_2 adsorption and desorption measurements were conducted at 77K. Surface area measurements were performed on N_2 isotherms at 77K using the Brunauer-Emmer-Teller (BET) model with adsorption values increasing range of 0.005 to 0.2 relative pressures while the CH_4 adsorption and CO_2 adsorption measurements were done at 273 and 298 K, respectively.

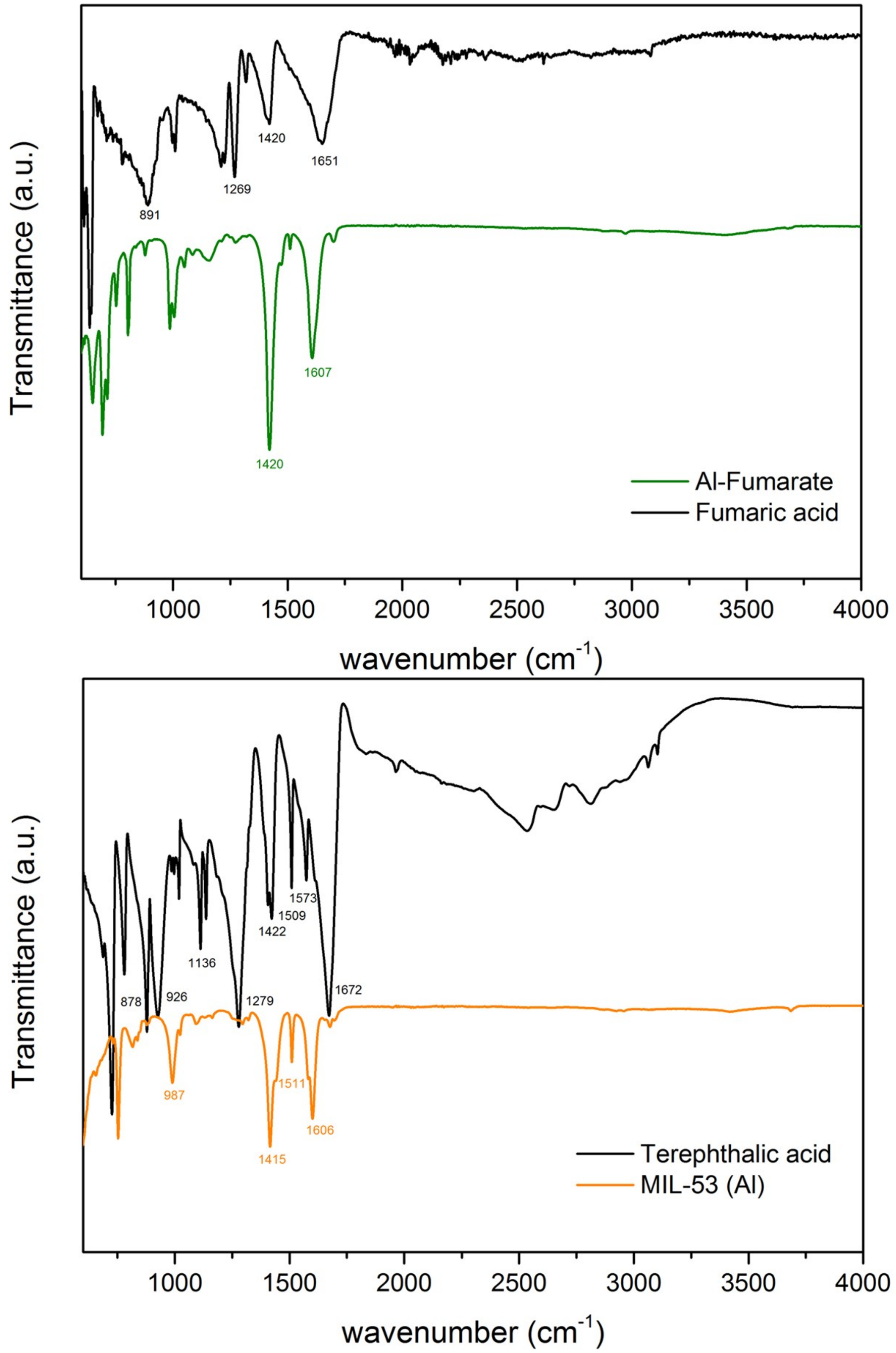


Figure S2. Infrared spectra of Al-Fumarate and Fumaric acid (top) and MIL-53 (Al) and Terephthalic acid (bottom).

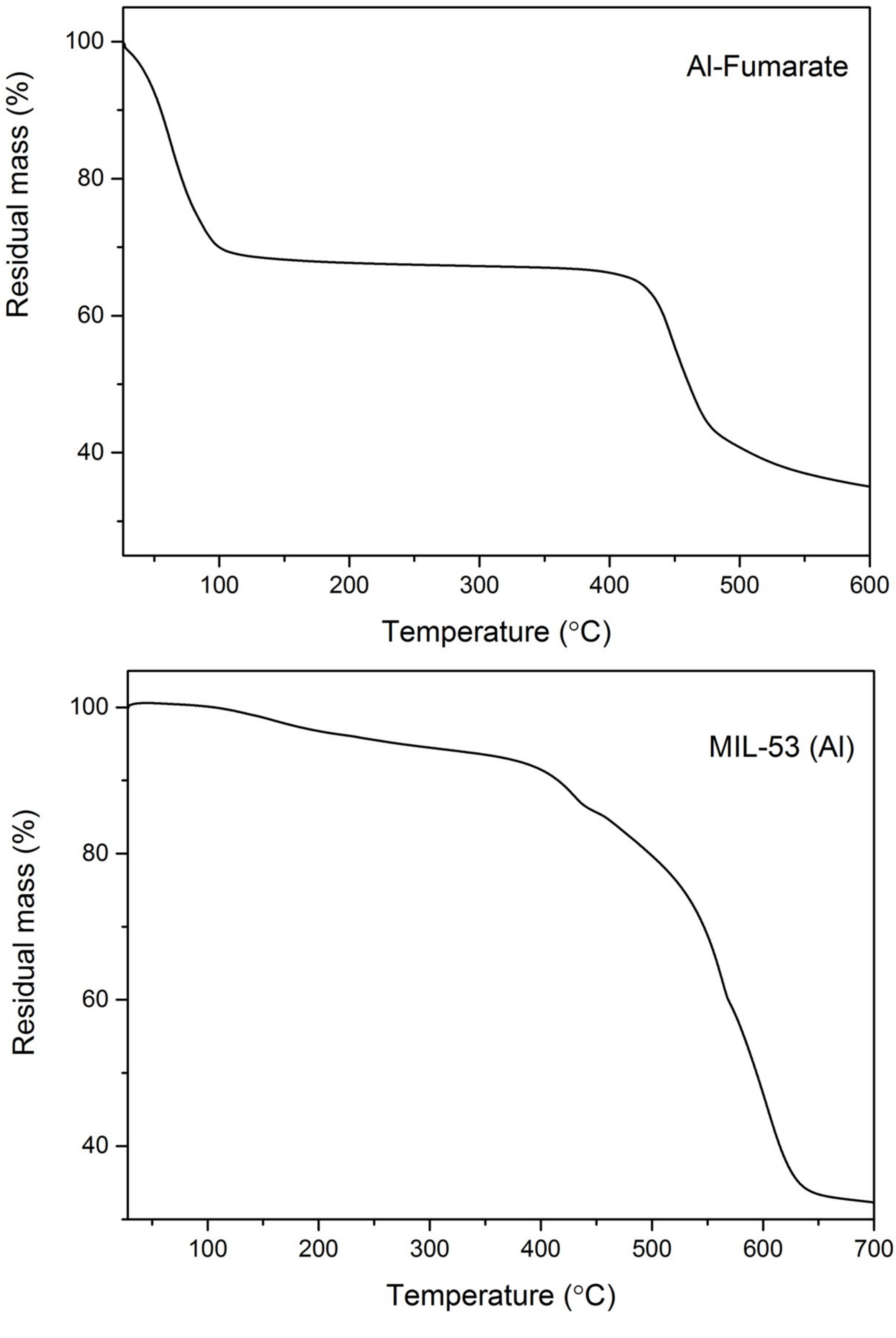
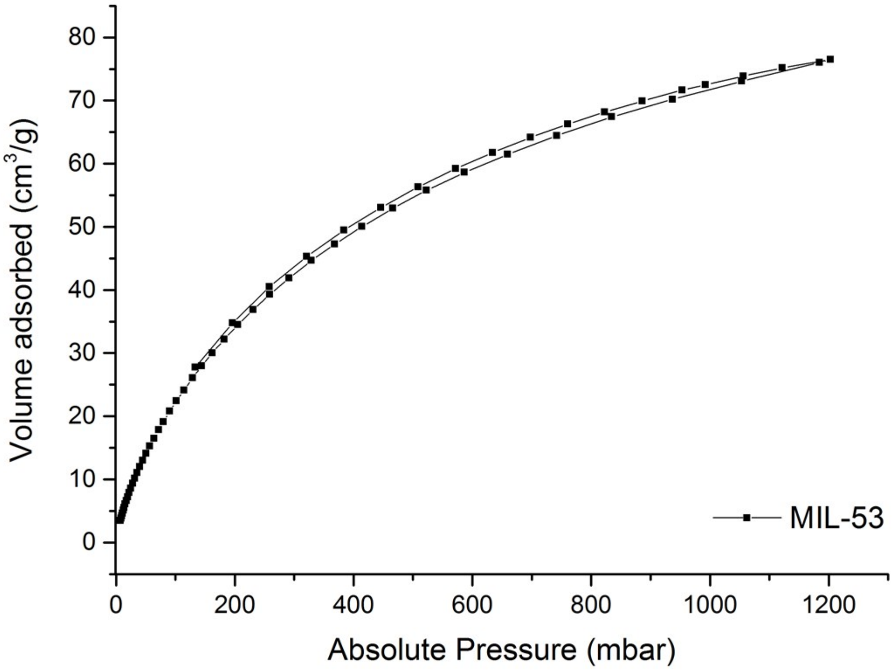


Figure S3. Thermogravimetric analysis of Al-Fumarate and MIL-53 (Al) (heating rate: 5 ºC/min).



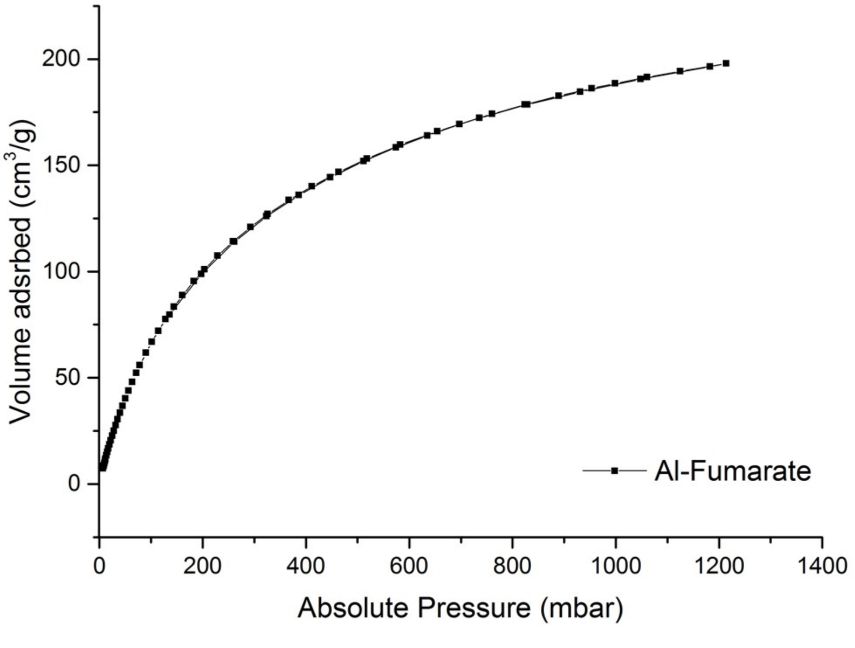


Figure S4. Experimental H_2 isotherms of Al-Fumarate and MIL-53 acquired at 77K.

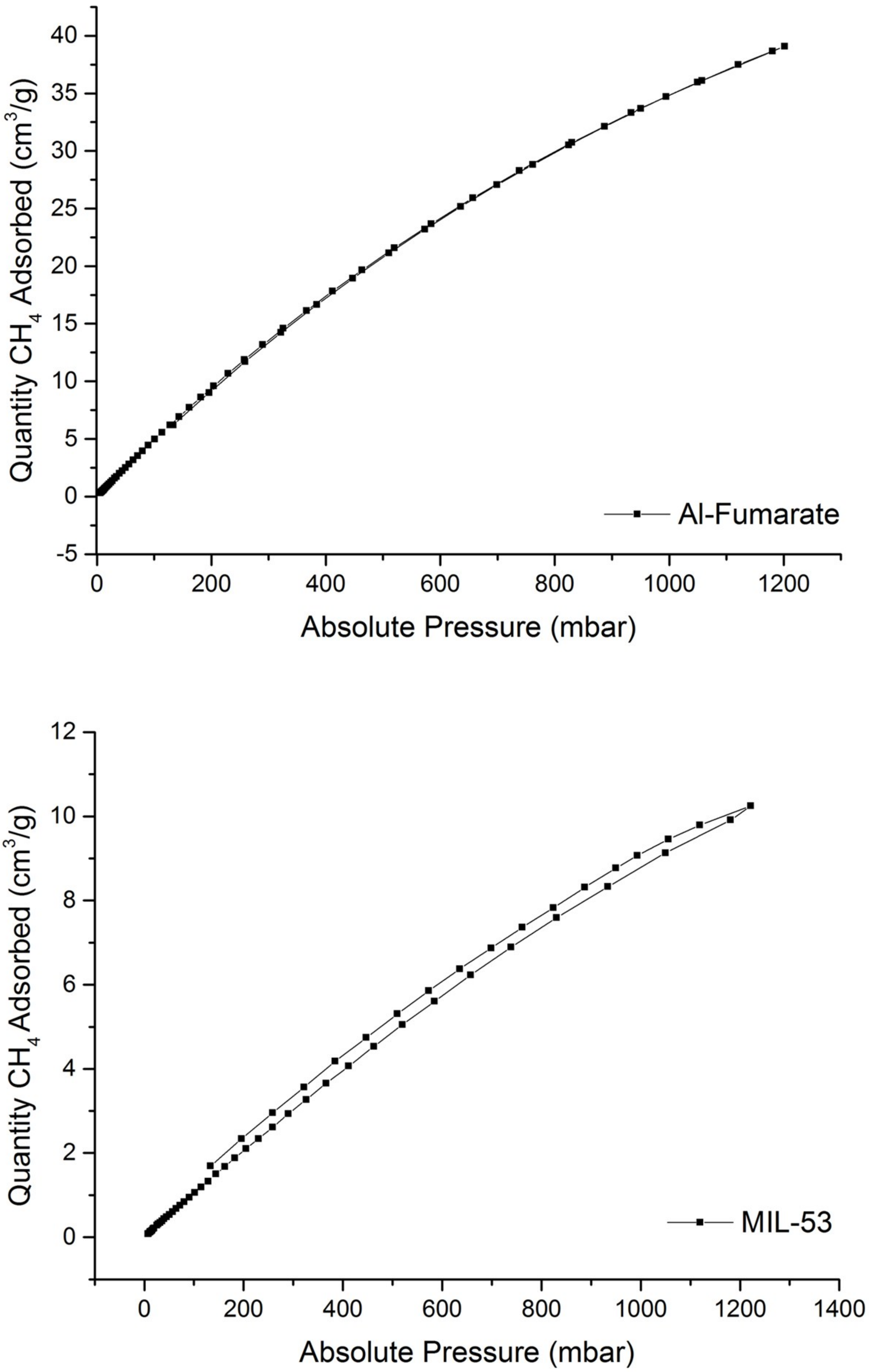


Figure S5. Experimental CH$_4$ isotherms of Al-Fumarate and MIL-53 acquired at 273 K.

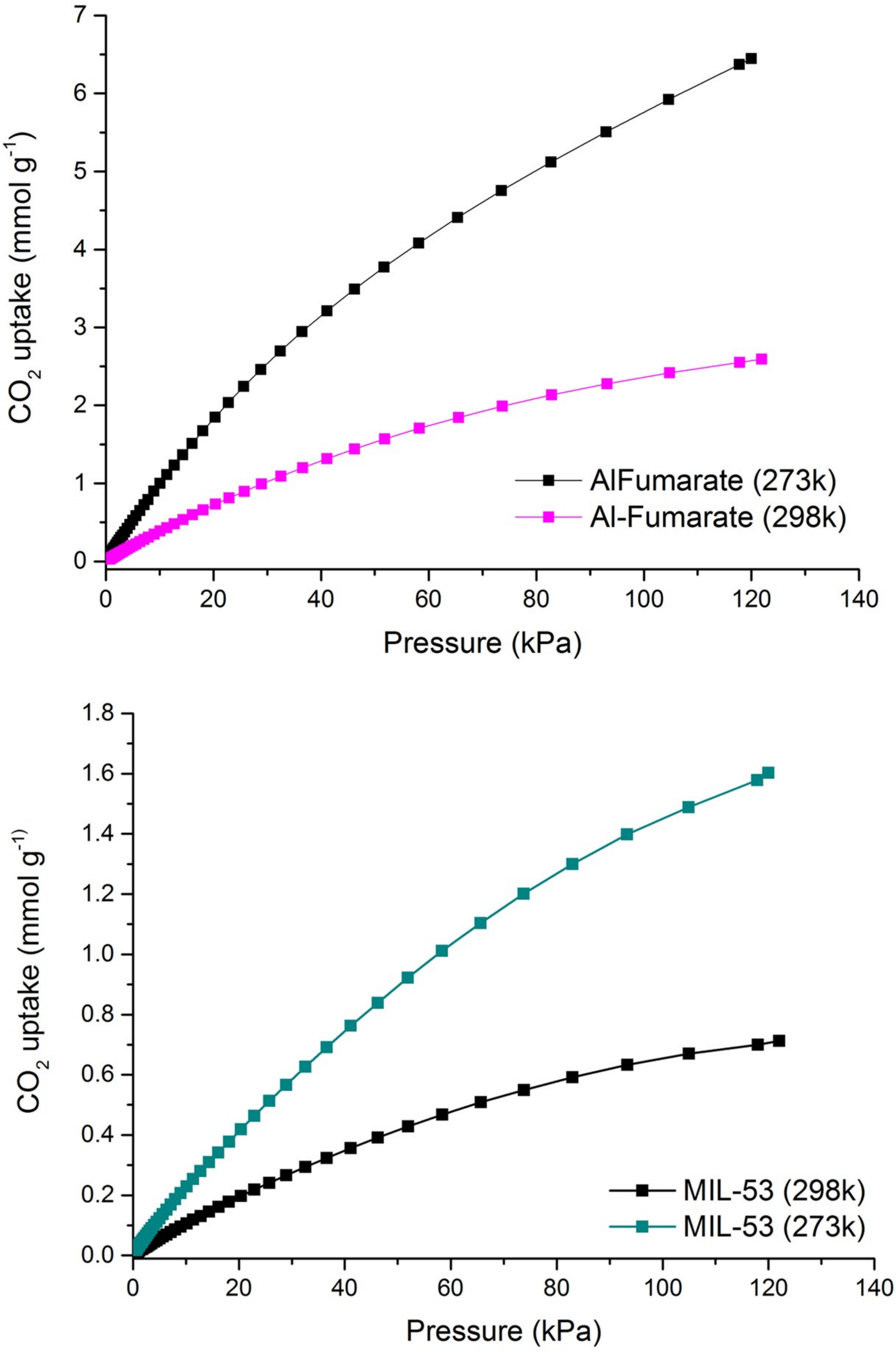


Figure S6. Experimental CO_2 isotherms of Al-Fumarate and MIL-53 acquired at 273 and 298 K.

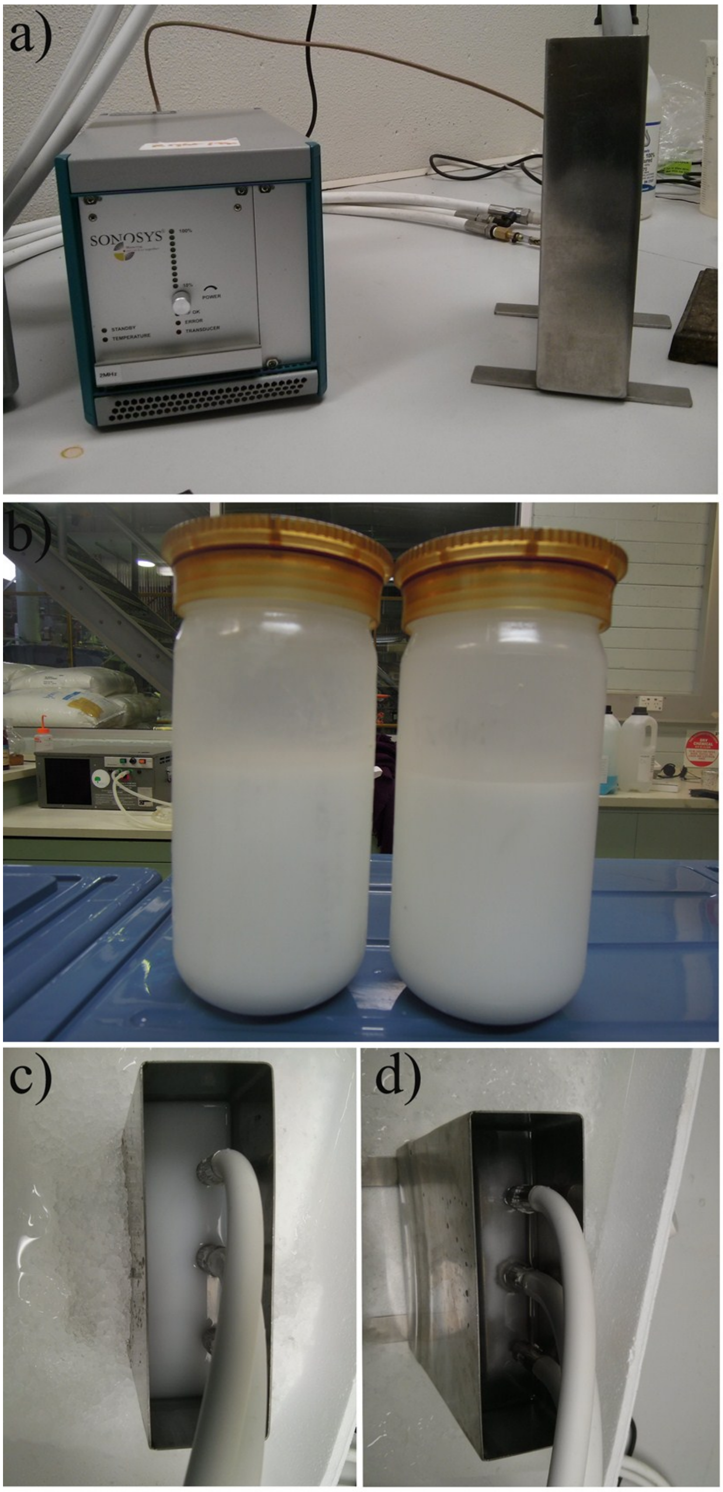


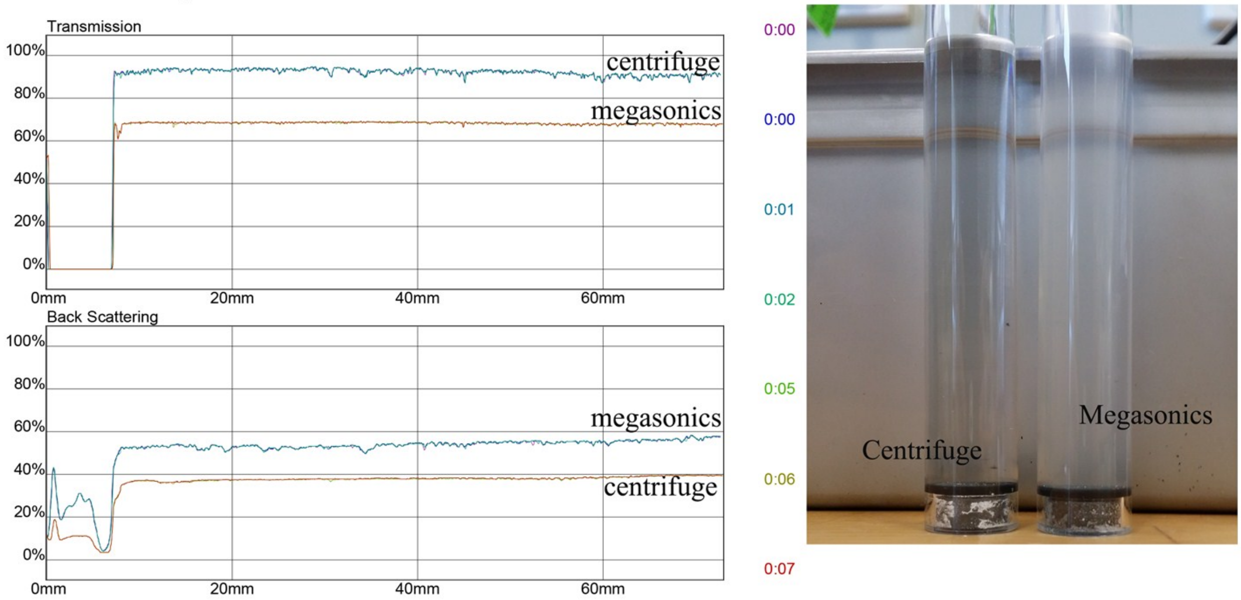
Figure S7. (a) Photograph of the megasonics unit using a 1L container for the separation and washing steps. (b) Image showing the Al-Fumarate solutions produced with the flow reactor (Salamander) that are employed for testing the megasonics technique. (c) Image of the initial MOF solution into the 1L stainless steel vessel before applying the high frequency. (d) Image after applying a 2 MHz frequency after 10 minutes.

Figure S8. (a) Photograph of the megasonics unit using a 1L container for the separation and washing steps. (b) Image showing the MIL-53 solutions produced with the flow reactor (Salamander) that are employed for testing the megasonics technique. (c) Image of the initial MOF solution into the 1L stainless steel vessel before applying the high frequency. (d) Image after applying a 2 MHz frequency after 10 minutes**.**

MOF washing process (Megasonics)	**ζ- potential (mV)**
Al-Fumarate flow reactor	+8.3 ± 0.4
Al-Fumarate wash 1 in H_2O	+8.8 ± 0.0
Al-Fumarate wash 2 in H_2O	+8.8 ± 0.1
Al-Fumarate wash 3 in H_2O	+8.9 ± 0.2
Al-Fumarate wash 4 in EtOH	+10.6 ± 0.2
Al-Fumarate wash 5 in EtOH	+11.3 ± 0.8
MIL-53 flow reactor	+13.3 ± 0.4
MIL-53 wash 1 in H_2O	+15.1 ± 0.5
MIL-53 wash 2 in H_2O	+14.7 ± 0.3
MIL-53 wash 3 in H_2O	+12.6 ± 0.5
MIL-53 wash 4 in EtOH	+12.7 ± 0.2
MIL-53 wash 5 in EtOH	+14.6 ± 0.1

Table 1. ζ- Potential of the Al-Fumarate and MIL-53 MOF material after each wash step using Megasonics using water as a dispersant.

Al-Fumarate supernatant



MIL-53 (Al) supernatant

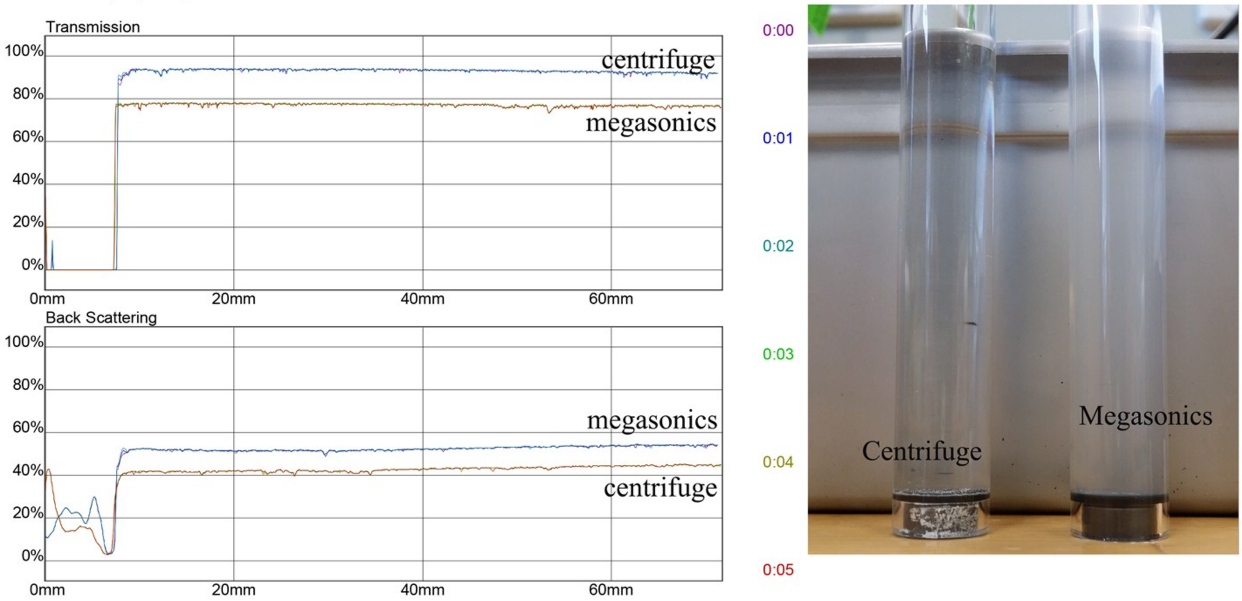
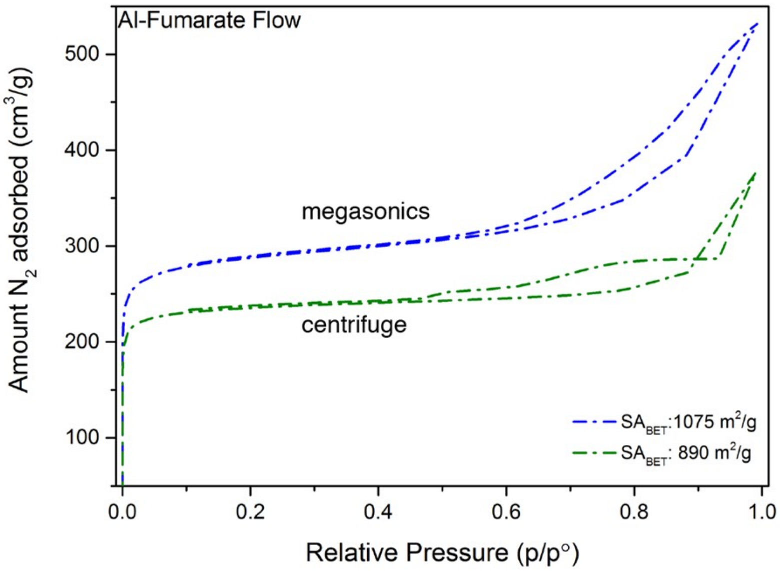


Figure S9. Comparison of the backscattering and transmission data of the supernatant collected from the first separation of the MOF solution using centrifuge and megasonics.

	Reaction time	**g h^{-1}**	**Yield (%)**	**STY (kg·m^{-3}·d^{-1})**	**SA$_{BET}$ (m^2 g^{-1})**
From reactor					
Al-fum	1.2 min	338.04	109.0	25,040	--
MIL-53	1.2 min	50.68	112.8	3,754	--
Centrifuge x 5					
Al-fum	1.2 min	281.88	90.9	20,880	890
MIL-53	1.2 min	42.14	93.8	3,121	806
Megasonics x 5					
Al-fum	1.2 min	225.07	72.6	16,672	1075
MIL-53	1.2 min	35.10	78.1	2,600	1183
Commercial[a] Al-fum	10.2 min	174	86	5339	1140
Commercial[b] MIL-53	4 hours	125	86	1300	919

Table 2: Comparisons of the reaction time between MOFs synthesized by conventional batch (using water as a reaction solvent) and by flow chemistry. BET surface areas, grams of MOF produced per 1 hour using flow chemistry and STY. [2]Data from ref. [3]Data from ref.



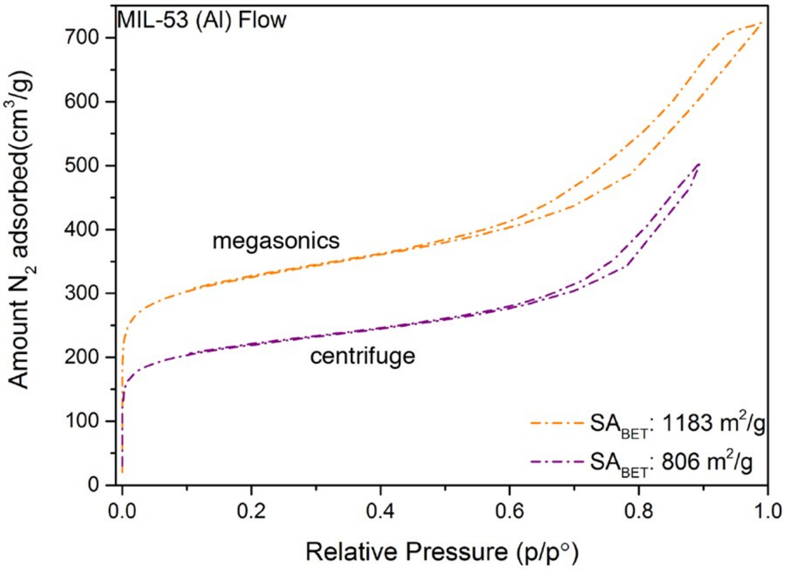


Figure S10. Representation of BET surface area, SA_{BET} showing the difference between the product isolated with megasonic and centrifuge for Al-fum and MIL-53, respectively.

References

1. Micic, N.; Young, A.; Rosselgong, J.; Hornung, C.H. Scale-up of the Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization Using Continuous Flow Processing. *Processes* **2014**, *2*, 58-70.
2. http://mofapps.com/Order.html
3. http://www.sigmaaldrich.com/catalog/product/aldrich/688738?lang=en&region=AU