

A Review on the Application of Metal-Organic Frameworks (MOFs) in Pressure Swing Adsorption (PSA) Nitrogen Gas Generation

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Abstract

Metal-organic frameworks (MOFs) can be advantageous over traditional materials in applications such as reaction catalysts, gas desulphurisation and carbon dioxide capture. Building on MOFs diverse range of applications they are suited to act as separation media within a pressure swing adsorption (PSA) Nitrogen generator. The properties of some MOFs; large surface area, high O₂/N₂ selectivity, large micropore volume and tuneable pore size make MOFs ideal for this separation technique. These criteria along with cost of synthesis and relative abundance in large quantities were used to identify three viable materials within the MOF family; MIL-101 (Cr), ZIF-8 and UiO-66 (Zr). The material properties of the three MOFs are given, with a comparison made to the most commonly used separation media - carbon molecular sieve (CMS). Proposals are then presented for the potential ways MOF media could be used in a PSA Nitrogen generator; either as a direct swap for CMS or utilising the properties of MOFs to rearrange the generation system. The merits and

limitations of MOFs when combined with binding material are analysed in forms such as; mixed-matrix membranes (MMMs), powder and monoliths. Non-separation-performance requirements of a viable PSA Nitrogen generation MOFs are discussed, focusing on lifetime, robustness and resistance to contaminants. The gaps in readiness before a MOF can be used within a manufactured PSA generator are identified with; production repeatability, lack of testing within a generator and uncertainty around the best MOF-based material structure forming the chief barriers to adoption.

Keywords: Metal-organic frameworks, Adsorption, Nitrogen, Generation, Micropore, Separation.

1. Introduction

1.1 Background

Nitrogen gas, N_2 is used in large quantities for industrial processes, from food production to fire blanketing, laser cutting to pharmaceutical manufacture. Currently, the most widely used commercial method of high-purity N_2 generation is Pressure Swing Adsorption (PSA), where air is split into constituent parts by using different diffusion rates of O_2 and N_2 into an adsorbent under pressure. For at least 20 years, the preferred adsorbent for PSA N_2 generation has been Carbon Molecular Sieve (CMS), a modified version of activated carbon in which the pore size has been tailored to function as a molecular sieve. This tailored pore size allows air to be split through a process of kinetic separation, where the O_2 molecules are preferentially adsorbed due to the similarity between O_2 molecule size and the adsorbent pore opening size.

Over the past two decades, a new field of materials has been researched with huge potential to be utilised for N_2 generation, Metal-Organic Frameworks (MOFs). MOFs appear to have

15 good potential to be used in N₂ generation due to both their extremely large surface area and
16 the ability to tune their material structure to adsorb a specific molecule. However, there has
17 currently been very little research into the potential of MOFs for use in N₂ generation, with
18 research generally focused on CO₂ capture, H₂ storage and reaction catalysts.

19 In this review, an assessment will be made of the current state of MOF technology and
20 technology readiness level of the technique, looking at the separation performance of MOF
21 media, particularly any applications which use a similar separation to that required for PSA
22 N₂ generation, O₂/N₂. The operation of current PSA N₂ generation system will be described,
23 including how MOF separation media could potentially be used within this system. The non-
24 separation-performance barriers to using MOF-based materials in a production N₂ generator
25 will be defined, including manufacturability and life. These will then be combined to produce
26 a list of requirements for a usable PSA N₂ generation MOF media, including material
27 properties, performance, manufacturability and lifetime. From this, potential MOF-based
28 materials which could be used within a PSA N₂ generator are proposed, with the gaps in
29 MOF research which must be closed before this potential can be realised also identified and
30 described.

31 2. Current N₂ Gas Generation System

32 2.1 Existing Methods of Nitrogen Gas Generation

33 For industrial processes requiring onsite N₂ gas generation, the processes used are either;
34 cryogenic distillation of liquefied air or air separation using either PSA or membrane
35 generation [1]. For very high-volume production, cryogenic distillation of liquid air is
36 preferable, whereas air separation is preferred for low to medium volume requirements, due
37 to lower energy and cost requirements [2].

38 For N₂ generation via air separation, PSA systems are preferable for N₂ outlet purities above
 39 95% and membranes more cost effective below 95% purity N₂ gas. This is due to the air to
 40 N₂ ratio (air in / N₂ produced) being much better for PSA generation than membrane
 41 generation at higher outlet purities [1].

42 Table 1 shows some example uses for low, medium and high purity N₂ gas.

43 **Table 1** Applications of different purity N₂ gases [3]

High Purity 10 ppm to 1000ppm (99.999% to 99.9%)	Mid Purity 0.1% to 1% (99.9% to 99%)	Low Purity 1% to 5% (99% to 95%)
Laser cutting - 50ppm to 500ppm Electronics soldering - 50ppm to 500ppm Pharmaceutical - 10ppm to 5000ppm	Food processing - 0.1% to 1% Beer dispense - 0.5% Brazing - 0.5% Injection moulding - 0.5% to 1% Wire annealing - 0.5%	Fire prevention - 5% Pressure testing - 5% Gas seal blanketing - 5% Autoclaves - 5% Laser sintering - 2% Dry boxes - 2%

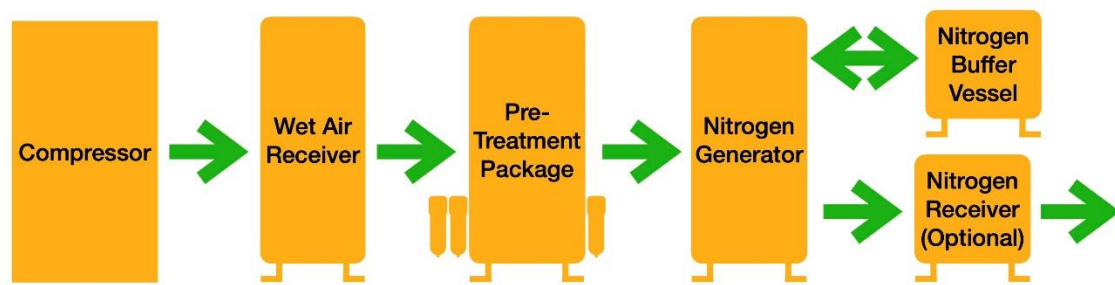
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45 2.2 Pressure Swing Adsorption (PSA) N₂ Generation

46 This review will focus on PSA N₂ generation, the preferred method of producing high-purity
 47 industrial N₂ gas. This process separates a mixture of gases into its component parts. The
 48 separation media used in PSA is a Carbon Molecular Sieve (CMS), which utilises differences
 49 in the kinetic diameters of N₂ and O₂ to preferentially adsorb O₂ [2].

50 PSA generators provide very stable N₂ purity, flow and pressure with good generator service
 51 life. N₂ gas produced by a PSA generator with pre-treatment system will have a dewpoint

52 around -55°C , equivalent to 3ppm of H_2O . However, a low dewpoint is also required for a
53 PSA generator to operate, as the CMS media within a PSA generator is very hydrophilic, so
54 would preferentially adsorb H_2O instead of O_2 . Due to this, pre-treatment is required before
55 air can enter an N_2 generator for separation [4]. As shown in Fig.1, air is first compressed,
56 then fed through a wet air receiver, which helps to remove bulk water from the air stream.
57 This is then fed through a pre-treatment package of a desiccant dryer, which removes water
58 vapour ensuring the air flow is dry enough for the N_2 generator to function, then filters which
59 remove particulate contaminants. This is an expensive and inefficient process [3]. A buffer
60 vessel is used in conjunction with the PSA N_2 generator to improve the purity of gas
61 produced, and to ensure that gas can be supplied at a constant flowrate and pressure.



62
63 **Fig. 1** N_2 PSA generation system layout

64 N_2 PSA generators work on a system of two beds, with one bed generating N_2 gas, whilst a
65 second bed regenerates with the adsorbed unwanted gas being purged and exhausted from the
66 column [5]. Table 2 shows a simplified twin column dryer cycle, with most of the generator
67 cycle spent in the producing / purging stages, in between which the pressure in the two
68 columns is equalised before the producing and purging columns swap over. By rapidly
69 depressurising the column to atmospheric pressure, O_2 is purged from the CMS media and
70 the cycle is ready to begin again.

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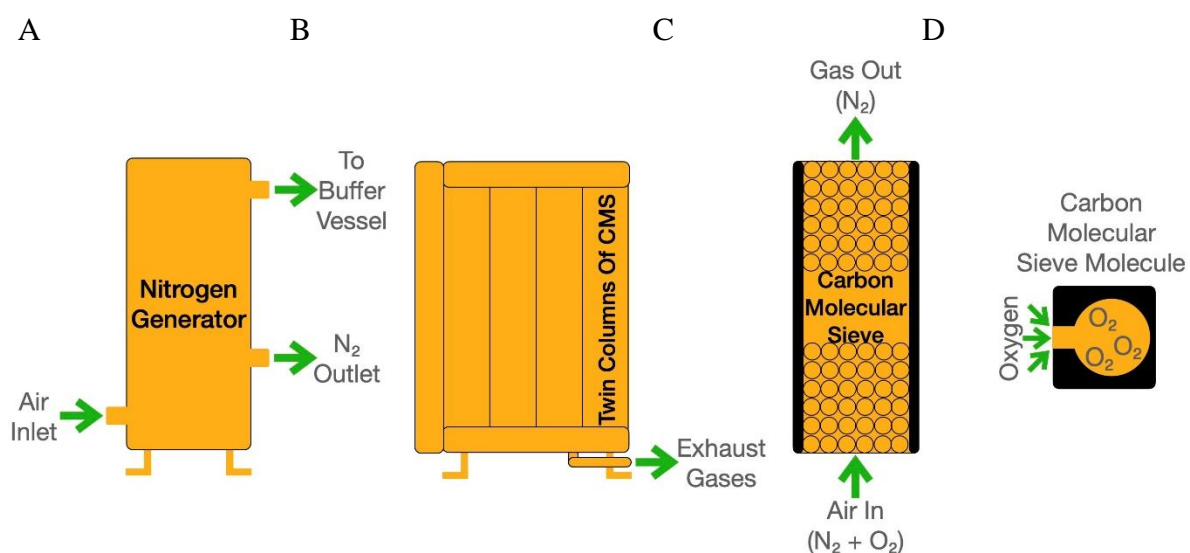
72 **Table 2** 6-Step twin column PSA N₂ generator cycle [2]

Half Cycle	Column Steps	
	Column 1	Column 2
1 st Half Cycle	Pressurising	Depressurising
	Producing	Purging / Regenerating
	Equalisation	Equalisation
2 nd Half Cycle	Depressurising	Pressurising
	Purging / Regenerating	Producing
	Equalisation	Equalisation

73

74 Once the air is in the CMS filled bed of the N₂ PSA generator, the diffusion rates of the gases
 75 into the adsorption media are dramatically different, allowing a much higher percentage of O₂
 76 to be accepted into the adsorbent [6]. In Fig. 2, View A shows the main gas transfers into /
 77 out of the N₂ generator, View B shows the cross-section of the column arrangement, View C
 78 shows the gas changes within a single column and View D shows the preferential adsorption
 79 of O₂ into each molecule of CMS.

80



81

82 **Fig. 2** N₂ PSA generator layout and CMS adsorption schematic

83 2.3 Current Nitrogen Generation Media and Performance

84 CMS exhibits excellent lifespan with a service life of at least 10 years and robust strength to
 85 prevent attrition and breakdown when the PSA columns are repeatedly pressurised and
 86 depressurised. The CMS media shows good O₂ / N₂ selectivity, which allows the PSA
 87 generators to have low air to N₂ ratios, reducing air and energy consumption and decreasing
 88 the required bed volume and therefore generators size [3]. The CMS currently used is formed
 89 into cylindrical pellets, with material properties as given in Table 3.

90 **Table 3** Physical properties of CMS pellets - Data from [7, 8]

Property	Carbon Molecular Sieve (CMS) GN-UC-H
Diameter (mm)	1.3 – 1.5
Specific Surface Area (m ² /g)	436.8 (BET method) / 640.9 (DR method)
Micropore Volume (cm ³ /g)	0.241
Mean Micropore Diameter (nm)	0.830
Packing Density (g/cm ³)	0.96
Skeletal Density (g/cm ³)	1.75

91 Gaffney (1996) looked at the uses of CMS within N₂ and O₂ generation, finding that the O₂ /
92 N₂ selectivity of CMS can be improved by from around 4 up to 20 by reducing the CMS pore
93 size [9]. However, doing this dramatically reduces adsorbent adsorption rates, so although the
94 air to N₂ ratio of a PSA generator could be improved by using a reduced pore size CMS, the
95 generator would have to be much larger to produce the same outlet flowrate. There is
96 therefore a trade-off to be found between the adsorption rates of an adsorbent and the O₂ / N₂
97 selectivity. This could be where MOFs display an advantage as they can have tight pore size
98 control and very large surface area, potentially enabling high selectivity and fast adsorption
99 rates.

100 Another existing material shown to be viable adsorbent in a PSA process are Zeolites, with
101 Reynolds *et al.* [10] finding that Zeolite media in a Pressure Vacuum Swing Adsorption
102 (PVSA) process gave an O₂/N₂ selectivity of 3.7. When used in a PVSA generator, this
103 produced 99.2% N₂ gas with an air to N₂ ratio of 4.3 and productivity of 71 h⁻¹ kg⁻¹. The
104 comparative data for CMS in a PSA generator at the same purity would be an air to N₂ ratio
105 of 2.7 and a productivity of 3461 h⁻¹ kg⁻¹. Rajasee and Moharir [11] demonstrated the ability
106 of a 5A zeolite to be used in PSA N₂ generation, simulating system operation to find O₂ and
107 N₂ diffusivities of; O₂: 2.0×10⁻⁴ cm² s⁻¹ N₂: 6.2×10⁻⁵ cm² s⁻¹, an O₂/N₂ selectivity of 3.

108 A further potential media for use in N₂ PSA generation found by Jayaraman and Yang [12]
109 were silver and cerium salt adsorbents. Their research found the best performing of these,
110 AgBr/SiO₂, showed an O₂/N₂ selectivity of 5 at 7 Barg.

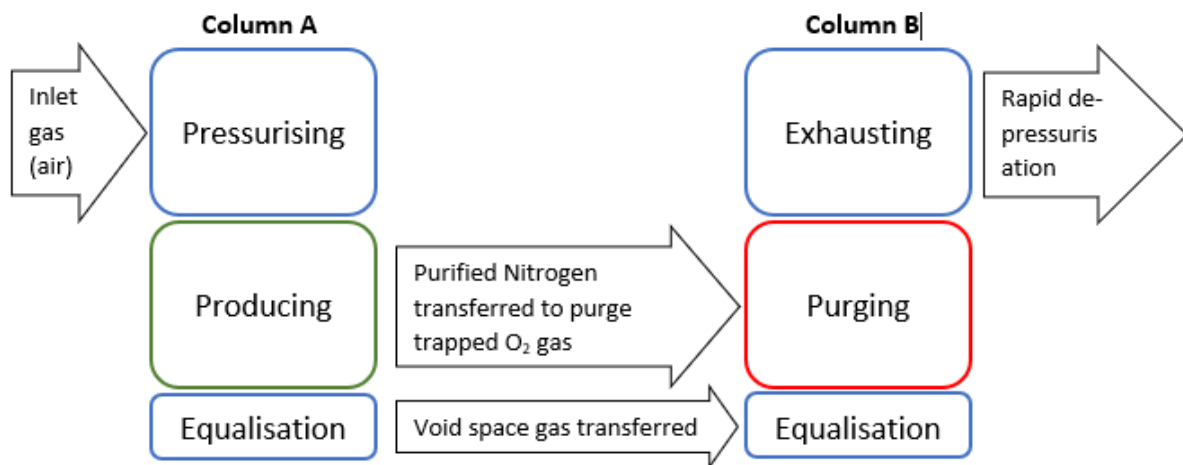
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112 2.4 Efficiency of current PSA system

113 A half-cycle of a current N₂ PSA generator, with the gas transfers and pressure losses, is
114 shown in Fig. 3. In this half cycle, the dry inlet air is being fed into column A which is

115 generating the purified N₂ gas whereas column B is being regenerated with purge gas
116 transferred from column A [5]. The efficiency of the cycle (independent of the adsorbent) is
117 driven by three main factors:

- 118 - The volume of purge gas, which is transferred then exhausted, varies depending on
119 generator purity and can be as high as 20% for high purity outlet N₂.
- 120 - The equalisation period at the end of each cycle, where around 4 bar of pressure is
121 transferred from column A to column B. Limiting the loss of pressure within the
122 generator, reduces cycle time and by minimises the volume of inlet air exhausted [13].
- 123 - The frequency of the half cycle operations and switches, where if the cycle time can
124 be extended without affecting gas purity, the efficiency of the system is greatly
125 improved.

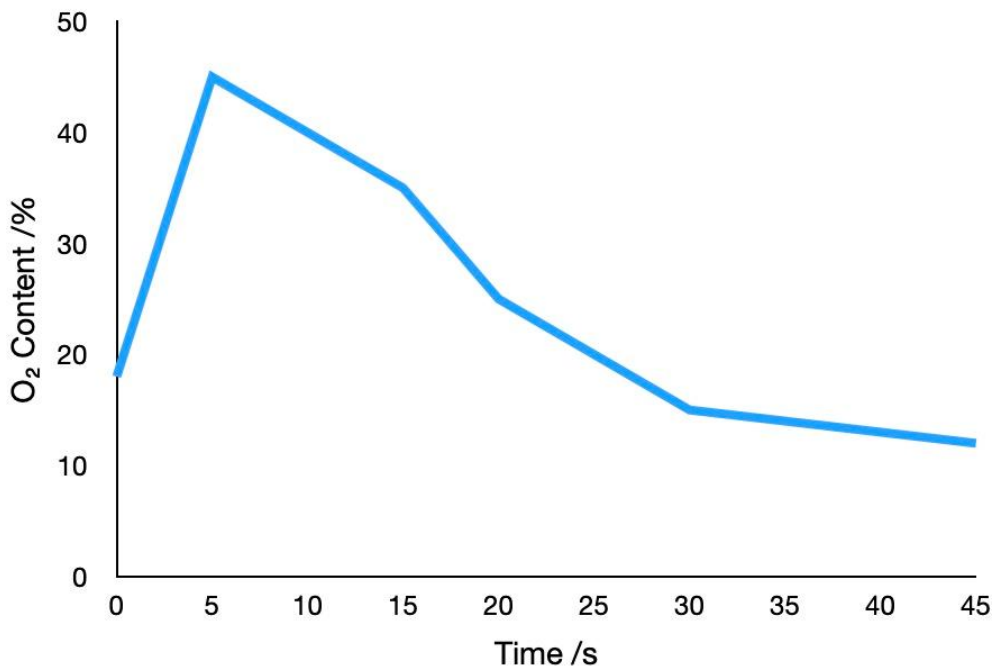


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127 **Fig. 3** PSA N₂ generator system half-cycle with gas transfers

128 As shown in Fig. 4, the gas exhausted by the N₂ generator peaks at 45% O₂, with the level
129 dropping below the O₂ concentration in air at the lowest point [14]. This is due to the
130 system's purge function, where purified N₂ gas is transferred from the online bed to the
131 regenerating bed to remove the trapped O₂ from the separation media. As an idealised system

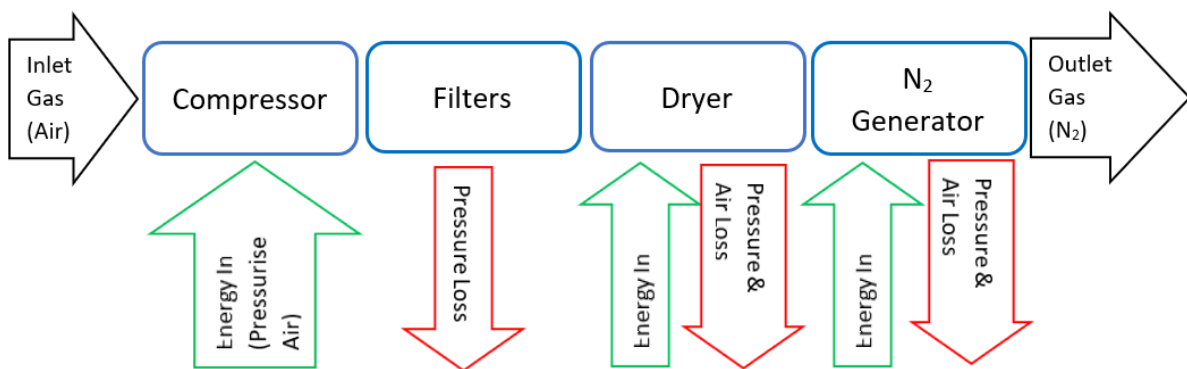
132 would exhaust 100% O₂, there are system efficiency improvements which can be made
133 within the generator.



134

135 **Fig. 4** O₂ content of gas exhausted from N₂ generator [14]

136 As well as improving the efficiency of the generator, the overall system efficiency could be
137 improved. Fig. 5 shows the whole N₂ generation system, with the energy inputs and gas
138 losses at each stage of the system. Reducing the energy input or gas losses from any of these
139 stages would improve system efficiency and even reconfiguring the order of items may
140 improve efficiency.



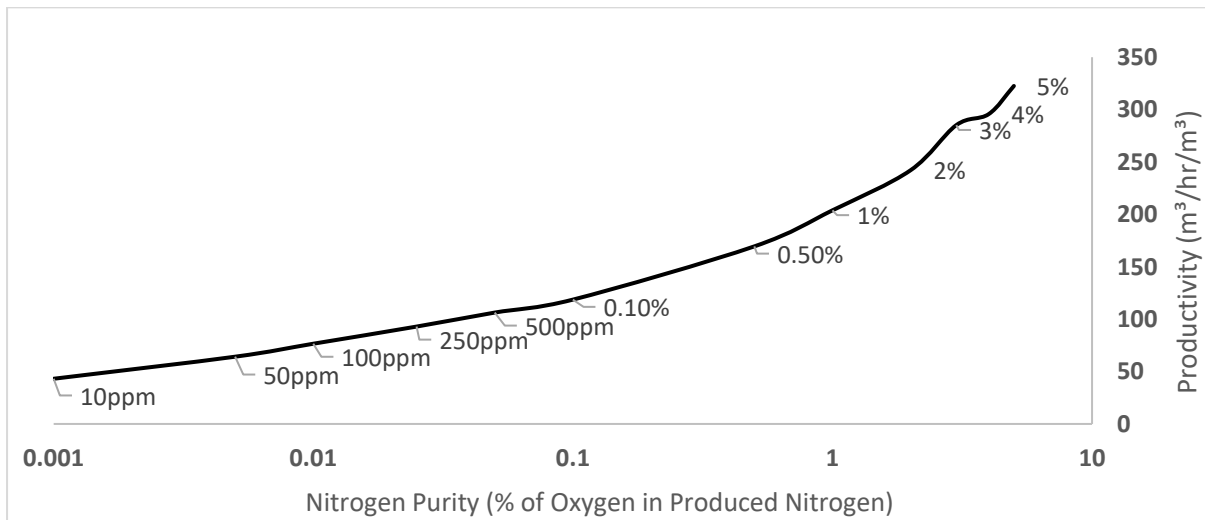
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142 **Fig. 5** Current N₂ generation system, with energy inputs and air losses

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144 2.5 Performance of PSA Generator

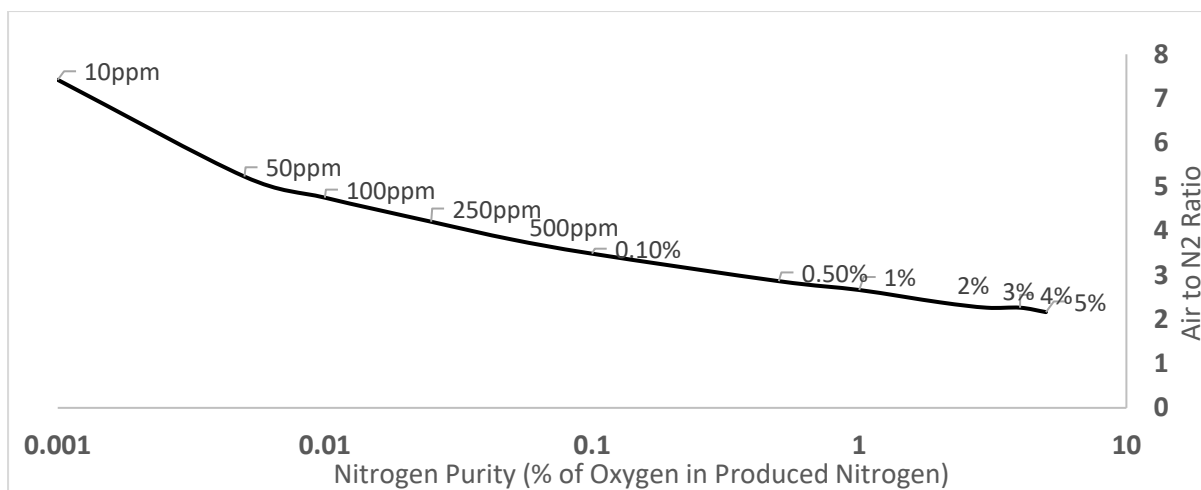
145 The performance of a N₂ generator is calculated using two metrics: productivity and
146 efficiency. The productivity is a measure of the volume of gas a generator can produce per
147 hour. The efficiency is a measure of the ratio between the volume of compressed inlet air
148 which needs to be fed into a generator to generate a set volume of N₂ gas. As shown in Fig. 6,
149 7 and table 4, both the productivity and efficiency of a generator are highly dependent on the
150 desired outlet gas purity. The higher outlet gas purities can only be reached by increasing the
151 contact time between the compressed air and separation media, which reduces productivity.
152 Once the air is inside the generator, the air must be cycled between the columns more
153 frequently and purified N₂ also drawn back from the outlet buffer vessel, increasing the
154 volume of air exhausted, reducing efficiency.



155
156

157 **Fig. 6** Productivity of CMS in Parker ‘NitroSource’ N₂ generator at varying outlet N₂ purity

158



159
160

161 **Fig. 7** Efficiency of CMS in Parker 'NitroSource' N₂ generator at varying outlet N₂ purity

162

163 **Table 4** Inlet air volumes to provide different outlet N₂ gas purities in PSA N₂ generator

Inlet Air Volume (Nm ³ /hr) at Varying Outlet N ₂ Gas Purity												
Outlet N ₂ Purity	95%	96%	97%	98%	99%	99.50%	99.9%	99.95%	99.975%	99.99%	99.995%	99.999%
Inlet Air Volume	699	670	646	578	544	486	414	405	391	364	336	320

164

165

166 3. Properties and Challenges of Metal Organic Frameworks

167 (MOFs)

168 3.1 Overview of Metal Organic Frameworks (MOFs)

169 Metal-organic frameworks (MOFs) are coordination compounds created by metal ions and

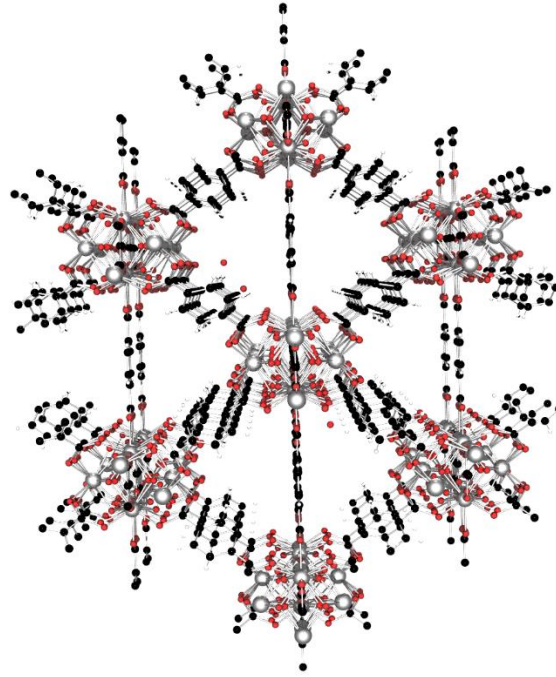
170 organic linkers extending into 1D, 2D or 3D frameworks, (fig 8). There is a vast library of

171 MOFs currently available, with theoretically infinite combinations of metal ions and organic

172 linkers. MOFs are well known and produced for their tuneable pore size, resulting in large
173 surface areas and high efficacy for adsorption. This tuneable pore sizes allows the targeting
174 and excluding for molecules of interest leading to applications as gas storage devices, carbon
175 capture, drug delivery, reaction catalysts, light emitting devices and sensors [15, 16]. It is
176 only relatively recently that advances in process engineering have emerged and enabled
177 MOFs to be synthesised on a commercial scale, with a continuous synthetic technique [17].
178 Before this, MOFs would be produced in a solvothermal batch process, with long reaction
179 times, lack of versatility and creation of minor variations between batches, that for industry
180 would be problematic and unreproducible [18]. Solvothermal synthesis may be rapidly
181 accelerated using microwave or ultrasonic thermal methods, however this is limited to the
182 size of the reaction vessel. Other methods such as spray-drying and mechanochemical
183 synthesis could be explored. However, most economically viable for time and cost, would be
184 to remove the cyclic process of batch production with decreased preparation, heating and
185 cooling costs, reduced labour costs, decreased reactor volume and decreased down time not
186 experienced by continuous production. The production of MOFs from a reagent perspective
187 would in the first instance remain comparable, however with the rise of green solvents and
188 the potential to implement solvent recycling techniques there is potential to reduce costs
189 further. Practically MOF production is relatively expensive, but the benefits of MOFs is by
190 far undervalued for their dual functionality and tunability.

191 Currently, for the topic of gas separation, there has been limited commercial use of MOFs,
192 but theoretically MOF materials are ideal for gas separators displaying large surface areas,
193 tuneable pore size and selective chemisorption [19].

194



195

196 **Fig. 8** UiO-66, zirconium centres (metallic) with terephthalic linker groups consisting of
197 carbon (black) and O₂ (red) (Generated from CIF 4512072).

198

199 3.2 MOFs Performance for Gas Separation

200 Gas separation is the ability to exclude undesired molecules or compounds and for MOFs this
201 relies on two processes molecular sieving and/or chemisorption. Gas separation is achieved
202 by controlling: surface area, micro and macro pore volumes, tuneable pore size and
203 chemisorption from functionalisation of the MOF.

204 The large surface area of a MOF enables for greater adsorption capability, which leads to an
205 increased in generator productivity. Furukawa *et al.* [20] demonstrated the large available
206 surface area of MOFs, with a maximum surface area of 10,000m²/g seen, far exceeding the
207 surface area traditional zeolite and CMS materials. Within a MOF's highly porous
208 marcoporous architecture resides a high micropore volume. Allowing for intricate networks
209 that not only increase surface area volumes but allow sites for molecular storage or catalysis

210 to occur, potentially increasing generator productivity. Gr nker *et al.* [21] found a Zn₄O-
211 based MOF which exhibited a micropore volume over 10x higher than CMS, 3.16cm³/g. This
212 material porosity can theoretically be expanded even further, by using longer organic linkers,
213 but in practice this causes difficulties with an increased likelihood of intertwined frameworks,
214 increased reagent cost and lower yields.

215 The tuneable pore size of MOFs allows a much higher proportion of a chosen contaminant to
216 be adsorbed via kinetic separation. Adil *et al.* [22] look to characterise and define the
217 relationship between the structure of a MOF and the associated gas separation performance,
218 with ultra-microporous MOFs identified with pore sizes as small as 4.0   x 4.0   used for
219 CO₂ capture and CO₂/N₂ selectivity as high as 140 recorded for a SIFSIX-2-Cu-I material.
220 However, as Li and Huo [23] identify, there is a trade-off to be found between the selectivity
221 and adsorption rates in MOF structure, with materials exhibiting very high separation ratios
222 often proving too impermeable to be useable.

223 The mechanism for molecular sieving relies on the surface area and pore volumes and works
224 by size exclusion, separating out molecules that cannot fit through the MOF pore. Using the
225 example of UiO-66 (Fig 8), the pore size is typically 6   and it would allow the passing of
226 nitrogen 3.16   and oxygen 2.96   it would not allow butanol, 6  . More complex MOFs
227 exist, such as NU-1000, with a large surface area that have 1,2 or 3D pores of meso and
228 micropores, that can work to size exclude larger organic molecules or synthetic compounds
229 [24]. However, molecular sieving is more common in membrane techniques, MOFs can also
230 be utilised for their chemisorption ability. MOF surfaces can be tuned, and with greatest ease
231 by the creation of amino-based MOFs and then post synthetic functionalisation to create
232 carbonyl, nitril functional groups with greater affinity to adsorb desired compounds [25].

233 A large consideration in gas separation technologies is the effect of humid conditions on the
234 device, this is especially so with MOF materials that may be hydrophilic in nature or have
235 poor selectivity between gaseous contaminants such as H₂O. However, Aguado *et al.* [26]
236 devised a reproducible process to create thin MOF membrane structures, which were then
237 able to perform CO₂/N₂ separations on dry and humid gas mixtures, with a separation factor
238 of 4.5 observed with humid air input to the membrane. Furthermore, Furukawa *et al.* [27]
239 researched into MOFs as an adsorbent media for the capture of water, comparing the porosity
240 performance of MOFs against zeolites, finding two suitable, water-stable MOF compounds;
241 MOF-801-P and MOF-841. Not all MOFs would be appropriate for the use in gas separation
242 and criteria would have to consider stability to water, surface area, pore volume, ability to be
243 functionalised and chemisorption mechanism.

244

245 3.3 Comparison of using MOFs Over Traditional Materials

246 CMS and PSA were developed closely together for the separation of gases as in the 1960s
247 certain carbon-based materials exhibited the molecular sieving effect. Such basic research,
248 was noted with anthracite and bituminous coal, both known to be porous [28]. It wasn't until
249 the 1970's that larger scale production and uniform producibility saw the commercial rise of
250 CMS for use in PSA plants. CMS differ from activated carbon, mainly in the pore size
251 distribution. CMS pore size is much narrower around 3-5 Å, while activated carbons have a
252 much wider range but average 20 Å. The main source of CMS comes from coal or coconut
253 shell, with the process requiring pyrolysis or steam activation [29]. Before the comparison of
254 CMS and MOFs, it is worth noting and defining the porous material family they both sit
255 under. Both have structure giving rise to porosity, surface area, pore shape and functionality
256 and the possibility to synthesise on-demand tailored properties. The difference occurs from
257 the constitutions. A CMS is in the family of zeolites, inorganic and naturally derived

258 materials whereas a MOF, is a hybrid inorganic-organic and are synthetically created [30]. A
 259 MOF, due to the presence of long chain organic linker groups can expand pore diameters,
 260 volume and surface areas to vast figures, whilst providing functionality for catalysis,
 261 supercapacitors and gas separations [31]. Table 5 demonstrates a comparison of MOFs with
 262 CMS and is demonstrated here to show the vast difference in the tunability of MOF pore
 263 diameter, volume and surface area, with the added benefit of crystallinity.

264 Table 5 Comparison of CMS, MOF (in general) and UiO-66.

Property	CMS	MOF	MOF – UiO-66
Average pore diameter (Å)	3-12	3 – 47	6
Pore Volume (cm ³ /g)	0.15 -0.5	0.28 - 5	0.70
Surface Area (m ² /g)	250 - 1500	1000 – 10,000	1180 – 1240
Morphology	Amorphous	Crystalline	Crystalline
Reference	[32]	[33, 34]	[35]

265

266 To illustrate the potential and realised applications of MOF material, researchers have
 267 compared the performance of MOFs to the performance of traditional materials. Lin *et al.*

268 [36] and Adams *et al.* [37] highlight one of the key benefits of MOFs against traditional
269 media, such as zeolites or carbon-based media. That being the ability to customise the
270 structure of MOFs to enable a material to be tuned and refined for an application, with
271 preferential adsorption of just one compound.

272 An application where MOFs are preferable to traditional materials was highlighted by
273 Dhakshinamoorthy and Garcia [38], showing the benefits of MOFs as a reaction catalyst,
274 with improved performance driven by their large surface areas and high porous volume. Lee
275 *et al.* [39] also demonstrates the application of MOFs as catalysts, with 24 different
276 experimental applications proven. MOF performance is now exceeding that of traditional
277 materials in the ease of post-reaction separation, improved catalyst recyclability and highly
278 enhanced catalyst stability. However, Dhaksinamoorthy and Garcia [38] also draw attention
279 to issues with the stability and lifetime of many MOFs, with a tendency for the structures to
280 collapse under harsh working conditions, particularly in the presence of H₂O.

281 The benefits of MOFs for O₂ generation were demonstrated by Wang *et al.* [40], outlining the
282 energy and material efficiency benefits of MOFs versus zeolites and alumina bead, with their
283 findings showing an efficiency improvement by a factor of four. A further gas separation
284 application was shown by Peng and Cao [41] investigating the relative performance of
285 MOFs, zeolites and CMS for the desulphurisation of natural gas, finding MOFs to be
286 preferential for two reasons. Firstly, MOF material can be more easily regenerated, removing
287 the adsorbed gas, and secondly the MOF can adsorb a desired gas in the prescience of other
288 contaminants.

289 MOF material has also been shown to perform strongly in CO₂/CH₄ separations, both in
290 selectivity and porosity. Bao *et al.* [42] investigated a specific copper-based MOF for use in
291 kinetic separation of CO₂ & CH₄ using a PSA process, with a kinetic selectivity of 26 (26x

292 more CO₂ adsorbed) far exceeding current media performance. Noro *et al.* (cited in [43])
293 found that a CuSiF MOF was able to absorb more methane by framework weight than the
294 current optimum zeolite media.

295

296 3.4 MOF Challenges and Technology Readiness

297 One of the key historical barriers to full adoption of MOF materials in industrial processes
298 was a large gap between the materials which have been proven to work in laboratory
299 conditions and commercially ready, manufacturable materials. Seoane *et al.* [44] showed that
300 theoretically, MOF technology was sufficiently mature for use in the field of CO₂ capture, but
301 the ability to manufacture large quantities of media with a consistent and repeatable structure
302 was missing. Ren *et al.* [45] analysed research to highlight the gap between the known MOFs
303 proven to work in the lab and the much more limited number of cost-effective MOFs
304 available commercially. However, a number of companies have now begun to offer
305 commercially available MOFs, for applications as shown in Table 6.

306 **Table 6** Commercially available MOFs: producers and applications

Company	Application
Immaterial	Fuel Filtration, Natural Gas Adsorption
novoMOF	Batteries, Gas Storage
Water Harvesting Inc	Water Extraction from Air
MOF Technologies	CO ₂ Capture
Prof MOF	Methane Adsorption

307

308 A further challenge when developing new MOFs was set out by James [43], showing the
309 difficulty of predicting the structure geometry which will be formed when the metal ions and

310 organic bonds interact. This causes issues in new research as it is not easily predictable what
311 will happen when a new interaction is attempted. However, Haldoupis *et al.* [46] were able to
312 use computational analysis to assess to ability of MOFs to separate gases through kinetic
313 separation, suggesting that potential MOFs could initially be shortlisted by calculation.

314 During manufacture, the formation of the MOF structure causes different issues, as the
315 makeup of the desired MOF compound is known, but repeatability of MOF manufacture is
316 difficult [47]. Crawford *et al.* [48] look at one potential solution to this issue, for MOFs to be
317 manufactured via extrusion without the use of solvents, finding that material should be able
318 to be produced in hundred kg/hr quantities with consistent pore size and structure.

319 A further issue, with specific relevance to N₂ gas generation and air separation, is the
320 susceptibility to water vapour. Hong-Cai and Kitagawa [16] allude to widespread issues with
321 individual MOFs being highly water sensitive. MOFs can be particularly susceptible to the
322 presence of water vapour, as this water vapour condenses in the MOF micropores after being
323 adsorbed, then causing a capillary action which can collapse the structure of the MOF.

324 However, Qadir *et al.* [49] identify methods to improve the hydrostability of MOFs to enable
325 adsorption in aqueous media without combining with a secondary material.

326 The limiting factor in the amount of separation media which can be used within a PSA N₂
327 generator is the volume to media occupies. This means that any separation media must have a
328 good packing density to allow a lot of separation media to be packed into the columns of the
329 generator. This can cause an issue for MOFs as their crystalline natures means they are not
330 naturally good at being packed, although Nandasiri *et al.* 50 and Yuan *et al.* [51] have
331 proposed potential methods for MOF densification.

332

333 3.5 MOF Material Types

334 Conventionally, MOFs are manufactured via a solvothermal reaction process which produces
335 a powdered crystalline material [52]. However, to improve the performance, usability and
336 manufacturability of MOFs, a lot of research has been undertaken to combine MOFs with
337 other compounds, creating material structures ranging from Mixed-Matrix Membranes
338 (MMMs) to MOF Monoliths and MOF Nanosheets. From computational analysis, Haldoupis
339 *et al.* [46] hypothesised that MOFs may be most useful for kinetic separations if structured as
340 membranes.

341 MMMs are materials comprised of an adsorbent media suspended within polymeric hollow
342 fibres and have been investigated as a method to overcome the issue of scalable and
343 inexpensive MOF manufacture [53]. Yilmaz and Keskin [54] investigated MMMs filled with
344 both MOFs and Zeolites for CO₂/N₂ separations, with both have promising potential, but the
345 tunability of pore size in the MOF media making this MMM preferable. Seoane *et al.* [44]
346 highlight the potential for MOF MMMs to be used in the capture of CO₂, improving the
347 efficiency of a power station. Qiu *et al.* [55] also identify methods of incorporating MOFs
348 into a membrane structure, demonstrating two MOF membranes with suitability for CO₂/N₂
349 separation: ZIF-69 attached to α -Al₂O₃ discs, producing a separation factor of 6.3 and
350 permeance of 1×10^{-7} mol m⁻²s⁻¹Pa⁻¹ at room temperature and SIM-1 attached to α -Al₂O₃ tube,
351 producing a separation factor of 4.5 and permeance of 8×10^{-8} mol m⁻²s⁻¹Pa⁻¹. Tanh Jeazet *et*
352 *al.* [56] identify a suitable MMM for O₂/N₂ separations, MIL-101-PSF. After testing this
353 MMM with differing percentage loadings of MOF material, the 19% MOF MIL-101-PSF
354 found to have the best separation performance, with a O₂/N₂ selectivity of 5-6 at room
355 temperature and 3 Barg.

356 Hong, Perera and Burrows [52] took the same MOF, MIL-101, but instead processed the raw
357 powdered material to form MOF monolith structures. These structures were found to be

358 compressively strong, a key property for the usability of existing CMS desiccant material,
359 showed excellent porosity for O₂ adsorption and could be regenerated thermally. Monolith
360 structures also have a benefit over membrane structures of much higher loading of the MOF
361 material compared to binding material. In a typical membrane structure, it will be comprised
362 of at most 20% MOF material, with the rest being supportive polymer, but Hong's monoliths
363 are 60% comprised of MOF material, with 40% binder. In traditional N₂ PSA gas generators,
364 forming separation media into monolith structures has also been found to lower the pressure
365 drop of the system when compared to pellet media, improving overall energy efficiency [5].

366 A further proposed structure where MOF is combined with a polymer are MOF nanosheets, a
367 two-dimensional structure with a thickness of around 1nm [57]. Wei *et al.* [58] combined
368 MOF nanosheets with a polyamide matrix to produce a material which could separate
369 hydrocarbons from an aqueous solution. This is of great interest as it presents a more extreme
370 form an application this review is aiming to find; the separation of a gas from an air stream
371 with water present. Peng *et al.* [57] synthesised MOF nanosheets displaying excellent
372 porosity and CO₂/H₂ selectivity, but also reported challenges retaining structural integrity
373 within the 1nm thick nanosheets. This shows there is still a long way to go before MOF
374 nanosheets are a viable material, as one of the main benefits of combining MOF material with
375 a polymer should be greater structural integrity.

376 For use within a PSA generator, a MOF needs to be formed into a pellet, bead, or monolith
377 structure, with a monolith providing the least pressure drop [59]. Although the reported O₂/N₂
378 selectivity for the MMMs (membranes) is good, this uses a different diffusion mechanism
379 than that which would be seen in a PSA generator. These MMMs use a mechanism of an O₂ /
380 N₂ mix being fed through tubes surrounded by MOF MMM, with proportionally more O₂
381 being allowed through the walls of the membrane. In a PSA generator, the air is fed into a
382 column filled with media, where the O₂ must be diffused into the pores of the separation

383 media and held there until the columns are switched over and the O₂ is purged by a rapid
384 depressurisation.

385

386 4. Potential application of MOFs in PSA N₂ Generation

387 Realised Applications of MOFs in Gas Filtration, Separation and Generation MOFs have been
388 developed and proven for a number of other filtration, separation and generation processes as
389 summarised in table 7.

390 **Table 7** Realised Applications of MOFs in Gas Filtration, Separation and Generation

Application	MOF
Carbon Capture	MOF-508b, Mg ₂ (dobdc) nanocrystal MOF, MOF-200, NU-901
O ₂ generation	RPM3-Zn, Co-MOF-74
Hydrogen and methane storage	NU-100, PCN-14, Cu ₃ (btc) ₂ , MIL-53-NH ₂ (Al), MAMS-1, Mn(HCOO) ₂ , Cu(etz), HKUST-1
Alkane Separation	MOF-508

391

392 A highly intensive area of MOF research is in the use of MOFs for carbon capture, where the
393 adsorption media is required to separate CO₂ and N₂. This ability was first demonstrated
394 under lab conditions by Bastin *et al.* [60] who found MOF-508b was highly kinetically
395 selective for CO₂ at 4.5 Bar. Bae and Long [61] demonstrated the same separation ability, but
396 utilising a different material structure, fabricating Mg₂(dobdc) nanocrystal MOFs with
397 different MOF and host materials. The Mg₂(dobdc) nanocrystals were found to have a
398 CO₂/N₂ selectivity of 184, although the surface area and adsorption capacity of the crystal
399 material was reduced when compared to powdered MOF material. Lyndon *et al.* [62]
400 demonstrated that a MOF used for carbon capture could be tuned to adsorb or release CO₂
401 based on a photodynamic trigger, allowing for 26 wt% CO₂ desorption capacity. Lyndon *et*

402 *al.* [62] also show that the MOF pores can be exposed on demand when subjected to visible
403 light, only adsorbing CO₂ when triggered. These properties could only be exhibited by a
404 MOF, an obvious enhancement over traditional media.

405 Another researched separation application of MOFs is O₂ generation, where a reversed
406 process to N₂ generation is used, with N₂ adsorbed and O₂ as the process gas. Wang *et al.*
407 [40] look at RPM3-Zn, which can be used to generate O₂ via a PSA process, showing that at
408 very low temperatures (77K to 87K) almost no N₂ is adsorbed, with selectivity >1,000. Melag
409 *et al.* [64] experiment using Co-MOF-74 Magnetic Framework Composite to adsorb O₂ from
410 air, then use a catalyst and Magnetic Induction Swing Adsorption (MISA) to desorb O₂ from
411 the MOF and produce a gas flow. To instead utilise this process for N₂ generation, the O₂
412 selective part of this process would be used to remove O₂ from the gas stream, then the
413 magnetic desorption process could be used to regenerate the adsorbent media.

414 A MOF application highlighted by Furukawa *et al.* [20] and Li *et al.* [65] is the usage of
415 MOFs in hydrogen and methane storage and carbon dioxide capture. For CO₂ capture, MOFs
416 have been shown in lab conditions to uptake large CO₂ volumes for the comparative media
417 volume and require much less energy to be regenerated than current aqueous media [65]. The
418 best performing MOFs for the three gas storage applications are;

- 419 - H₂: NU-100 has 9 wt% uptake (77K, 56Bar)
- 420 - CH₄: PCN-14 has an uptake of 212mg/g
- 421 - CO₂: MOF-200 has an uptake of 2347mg/g

422 To apply these MOF material properties to a N₂ gas generation application, similar properties
423 would be desired, but with pore size tuned to remove O₂ as the adsorbed gas.

424 One of the difficulties in separating O₂/N₂ via kinetic separation is the similarity of the
425 molecule sizes, with kinetic diameters of 3.46 Å for O₂ and 3.64 Å for N₂ [66]. Wang and Li

426 [67] find an application where MOFs can separate noble gases with very similar molecular
 427 sizes, given the tuneability of structure and pore size to allow a kinetic separation not possible
 428 with traditional materials. Similarly, Nijem *et al.* [68] demonstrate the potential for MOFs to
 429 be used to kinetically separate gases where not previously possible, in this case demonstrating
 430 large energy savings by selectively separating hydrocarbons from gas streams. Bao *et al.* [69]
 431 show that MOFs can also be used to separate mixtures of different hydrocarbons, with
 432 preferential adsorption of methane over other hydrocarbons. Li *et al.* [70] expand on this
 433 potential to experimentally demonstrate the ability one new MOF, NbU-1, to kinetically
 434 separate hydrocarbons, with this MOF having the additional benefit of low-cost material
 435 construction.

436

437 The MOFs which have been shown to exhibit O₂ / N₂ separation, with the structure formation
 438 and operating protocol tested are summarised in Table 8. There is very limited research into
 439 the separation required for N₂ gas generation via PSA, preferential adsorption of O₂ from air
 440 at room temperature and between 3 & 14 Barg. The assumption is being made that a MOF
 441 which has demonstrated good membrane separation performance may also show good PSA
 442 performance. Further research would be required into the adsorption capacity of the
 443 compounds and the ease of O₂ desorption.

444 **Table 8** MOFs exhibiting O₂/N₂ separation under experimental conditions

MOF	Material Structure	Operating Protocol Used
Mg ₃ (ndc) ₃	Powder	Size exclusion
PCN-13	Powder	Size exclusion
PCN-17	Powder	Size exclusion
MIL-101(Cr)	mixed-matrix membrane (MMM)	Membrane Separation

UiO-66(Zr)	MMM	Membrane Separation
ZIF-8	MMM	Membrane Separation

445

446 Kuppler *et al.* [71] draw attention to studies demonstrating MOF O₂/N₂ separation, with
447 Mg₃(ndc)₃ showing no adsorption of N₂ at low temperature (77K) and PCN-17 able to
448 selectively adsorb greater than ten times as much O₂ as N₂. A further benefit is given by Ma
449 *et al.*, [66] who experimentally showed that at 77K, PCN-13 will absorb 7x more O₂ than N₂
450 and the separation occurs in a hydrophobic channel, potentially negating the issue of H₂O
451 susceptibility. MIL-101 is an attractive material for air separation as it shows good separation
452 performance under atmospheric conditions and is stable even in the presence of water [72].
453 Rodrigues *et al.* [73] identify two MOFs which could be used to generate N₂ gas from air
454 under PSA conditions; MIL-101(Cr) and UiO-66(Zr). Both MOFs were shown to have good
455 O₂/N₂ selectivity at 4 bar and room temperature. Hu *et al.*, [74] identified another MOF
456 material with high O₂/N₂ selectivity at lower pressures, ZIF-8.

457 MOFs are an interesting potential material for use in PSA N₂ generation, due to high specific
458 surface area, tuneable pore size and stability in the presence of contaminants. There are also a
459 limited number of MOFs currently proven to work for O₂/N₂ separations. Of the MOFs
460 proven to show selectivity for O₂ over N₂, the separation required for PSA N₂ generation, the
461 most selective and potentially promising are; PCN-13, PCN-17, MIL-101(Cr), UiO-66(Zr)
462 and ZIF-8. A potential weakness of MOFs identified earlier is the effect of humidity on the
463 MOFs ability to perform, while techniques may be in place to combat high levels of
464 humidity, the potential for water to interact with the MOF and bind or block pores is a threat
465 and would reduce MOFs ability to function. However, work has been undertaken towards
466 functionalised MOFs with the ability to maintain performance at high levels of humidity [75].

467

468 4.1 How the MOF media could be utilised in a N₂ PSA generator

469 There are two ways in which MOF media could be utilised for PSA N₂ generation; It could
470 either be used as a direct swap for the existing CMS material, with no modifications made to
471 the generator and surrounding system infrastructure, or the novel material properties of a
472 MOF media could be used to improve and redesign the surrounding generator and generation
473 system.

474 When considering the first case, using MOF material to drive improvements in the N₂
475 generation system, improvements should be seen both in the system efficiency and the media
476 efficiency. The system efficiency improvements could be made by using the ability of MOFs
477 to adsorb one compound with multiple contaminants present, reducing the amount of pre-
478 treatment the compressed air needs before it enters the PSA generator.

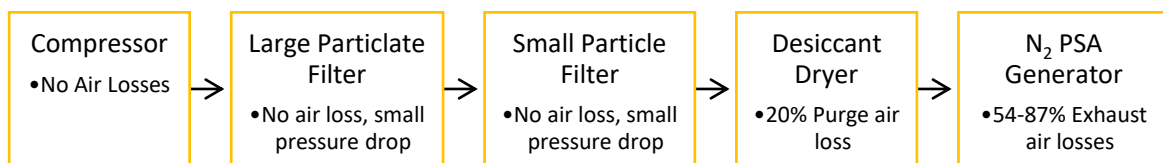
479 For the second case, using MOF material as a direct replacement for CMS, minimal changes
480 will be made to the PSA generator and surrounding components. The pre-treatment of the
481 compressed air and the order of the processes within the N₂ generation system will be
482 unchanged, with only optimisations made to the sizing and timing cycles of the PSA
483 generator.

484 For either of these two methods, the MOF material will be working the same way within the
485 generator. The MOF media, like the CMS media currently used, will be looking to separate
486 O₂ and N₂ in air using a process of kinetic separation. This separation is based on the close
487 matching micropore sizes in the separation media and the size of the desired molecule to be
488 adsorbed, producing a selectivity for one molecule over another. For PSA generation, it is not
489 true adsorption of a molecule into a media which is required, more of a difference in the
490 relative diffusivity of O₂ and N₂ into the media. In this case, the MOF material needs to show

491 preferential diffusivity for O₂, which can be held within the media whilst the purified N₂ gas
492 flows through the column. Then, when the columns switch over and the online column goes
493 offline, the O₂ must be able to be easily desorbed from the MOF media, regenerating the
494 material, emptying the micropores of adsorbed gas, readying the column to come back online
495 and generate more purified N₂ gas [13].

496 4.2 Potential system benefits of using MOF media for N₂ generation

497 The individual steps and air losses of the PSA N₂ gas generation process are described in Fig.
498 9. As shown, before the pressurised air has even reached the PSA N₂ generator, 20% of the
499 air has been purged and exhausted from the gas stream by the desiccant dryer as bulk water
500 and water vapour must be removed from the gas stream for CMS to perform [4].



501

502 **Fig. 9** Flowchart of current N₂ gas generation via PSA process

503

504 This is where MOF media could provide a benefit over CMS media, due to the tuneability of
505 pore sizes and material characteristics, it has been shown to be possible for MOFs to
506 preferentially adsorb O₂ over N₂ even when water is present in the gas stream [72]. This
507 could allow the system surrounding the generator to be rearranged, with the N₂ PSA
508 generator moved upstream of the desiccant dryer. As pressurised air is exhausted during the
509 N₂ generation process, a much smaller desiccant dryer could be used. This could reduce the
510 capital expenditure needed when installing a new N₂ generation system.

511 There could also be benefits in improved efficiency and reduced running costs during the
 512 operational life of the N₂ generator. Currently, 54-87% of the gas entering the PSA N₂
 513 generator is exhausted and this exhausted gas has already undergone energy intensive
 514 processes of compression and drying. By rearranging the process could the value of this
 515 exhausted air be reduced and the overall system efficiency improved? Whether these
 516 efficiency savings are realised would be based on a calculation between the comparative
 517 costs of compressing, separating and drying air. The calculated process could then be
 518 rearranged to swap the positions of the dryer and generator to see if the system efficiency is
 519 improved.

520 As well as rearranging the system, a MOF able to perform separations without removing the
 521 water from a gas stream could also allow the drying phase to be removed from the gas
 522 generation system completely. As shown in Table 9, this would not be suitable for all
 523 applications, as having contaminant water in the N₂ gas stream would be hugely problematic
 524 in markets such as; food packaging, pharmaceutical manufacture and beverage sealing.
 525 However, wet N₂ could potentially be used in either blanketing, where N₂ gas is used to
 526 prevent reactions, or in controlled atmospheres, for example the prevention of fruit decay
 527 during transport on a cargo vessel.

528 **Table 9** Potential applications for wet N₂ gas

	Wet N ₂ Definitely Unsuitable	Wet N ₂ Potentially Useable
Applications	Food & Beverage	Blanketing
	Pharmaceutical	Controlled Atmospheres
	Conversion to Liquid N ₂	

529

530 If this proposal to offer wet N₂ gas by eliminating the dryer from the generation system is
531 realised, further tweaks to the generator will be needed. It is likely that although a
532 hydrophobic MOF would not adsorb water, gaseous water would still be condensed by
533 passing through the adsorbent bed, therefore the exhaust of the generator must be able to
534 handle liquid water. Any equipment downstream of the generator, whether these are buffer
535 vessels or coalescing filters, must also be able to function effectively with contaminant water
536 in the gas flow. Due to the limited applications and required system changes, finding a MOF
537 which is hydrophobic and can generate N₂ from air in the presence of contaminant water
538 should not be a priority. Research would be more worthwhile looking for a MOF media
539 which can be used as a direct swap for CMS within a PSA N₂ generator.

540

541 4.3 Defining performance criteria to compare CMS and MOF performance

542 The two performance criteria which needed to compare MOF and CMS media are:

- 543 - Air to N₂ ratio, which is used to calculate the system efficiency and therefore running
544 costs
- 545 - Productivity, which is used to calculate the volume of media required to produce a
546 volume of N₂ gas, defining the initial capital expense costs.

547 The air to N₂ ratio is a unitless number and differs over the range of outlet N₂ purities from
548 95% N₂ to 99.999% N₂. The lower the air to N₂ ratio the better, as this means that less air will
549 need to be compressed, and less energy expended compressing it, for the same volume of
550 outlet N₂ gas. As the inlet air is comprised of 78.09% N₂, the idealised air to N₂ ratio is
551 $1/0.7809 = 1.28$, where only O₂ gas would be exhausted from the system. The main energy
552 cost in running a PSA N₂ system is air compression, so the less air compressed, the more
553 efficient the system. The air to N₂ ratio is higher for purer N₂ gas, as the contact time between

554 the compressed air and the separation media needs to increase to improve the outlet purity, so
555 the air to N₂ ratio increases as outlet N₂ purity increases.

556 The productivity of the separation media is expressed as factor of m³ of N₂ produced, per
557 hour, per m³ of media, where the m³ of media figure used is the packed density. The higher
558 the productivity of the media, the less separation media and smaller the generator, the lower
559 the purchase cost.

560 There could be a trade-off between the efficiency of MOF media and the productivity of the
561 media, where a material with high productivity but also high air to N₂ ratio offers a reduced
562 initial capital outlay cost but has higher long-term running costs. To realise the benefits of
563 either improved efficiency or productivity, there are number of material properties MOFs
564 need to have. Table 10 outlines the key comparison metrics for a suitable MOFs.

565 Table 10 Adsorption media comparison metrics with associated units of measure

Property	Units
MOF packing density	g/cm ³
O ₂ /N ₂ selectivity	-
Micropore volume	cm ³ /g
Specific surface area	m ² /g
Ease of O ₂ desorption from media	-
Compressive Strength	N

566

567 One of the key factors which needs to be accounted for is packing density of the MOF
568 material and therefore the void space within the column of the N₂ generator. During the
569 equalisation phase of the PSA cycle, the void gas which fills the space between the separation

570 media must be transferred from the offline to online column. The higher the volume of air
571 which needs to be transferred, the more energy needed, so if the media cannot be tightly
572 packed then a lot of energy will be consumed moving the void space gas between the online
573 & offline columns.

574 The O₂/N₂ selectivity is a key metric for defining both the potential efficiency and
575 productivity of a PSA generator. This gives the ratio of gases diffused into the micropores of
576 the separation media. It is assumed that all the gas which is diffused into the media will
577 eventually be purged and exhausted, so the less N₂ adsorbed, the better the air to N₂ ratio. The
578 O₂/N₂ selectivity also contributes to the productivity, as a more selective media will use a
579 higher percentage of the available micropore volume to store O₂. This would allow a smaller
580 volume of media to adsorb the same volume of O₂.

581 As well as having a good O₂/N₂ ratio in the adsorbed gases, to have high productivity, a MOF
582 also needs to be able to adsorb a high volume of gas. The best property to estimate the
583 volume of gas a MOF can hold, without PSA testing, is the micropore volume. The
584 assumption being that MOF media with higher micropore volume would be able to adsorb
585 more gas and therefore be more productive.

586 Another factor which could improve the productivity of a generator would be to quicken the
587 rate of diffusion of the gases into the separation media. It is assumed that this could be
588 quickened by increasing the specific surface area of the MOF, with the compressed gas more
589 likely to collide with a separation media within a column if that media is occupying a larger
590 surface area. A change in the rate of adsorption would not alter the volume of gas adsorbed
591 each time a column is filled with air but would reduce the required cycle time to separate
592 unwanted gases from a set volume of air in a column.

593 The property limiting the volume of media within a generator is not the weight of media, but
594 the volume it occupies. Therefore, all properties listed by mass, such as specific surface area
595 (m^2/g) and micropore volume (cm^3/g), must be converted into a per volume figure to ensure
596 accurate comparison to CMS. It also needs to be considered that MOFs generally must be
597 combined with a binder material to form a usable structure. When forming this composite
598 material, the lower the %wt of MOF, the worse the separation performance will be, with
599 reductions in micropore volume and surface area. When forming a MOF composite, there is
600 potential for the binder material to block all porosity within the MOFs, however processes are
601 being developed to overcome blocked Pores. The resulting solid composite structure has high
602 porosity [31].

603 In addition to high productivity and efficiency, there are other non-separation-performance
604 requirements for a MOF media to be useable in a PSA N_2 generator. Firstly, to be used within
605 existing equipment, it must be possible to regenerate MOF media using a blow-down rapid
606 depressurisation. To fulfil this criterion, the MOF media should have a desorption profile
607 which desorbs the O_2 gas when the pressure in the column is quickly reduced from 7 Barg to
608 1 Barg. It is not acceptable to have a MOF media which can only be regenerated by say, a
609 temperature change or magnetic induction.

610 Due to this process of regeneration through rapid depressurisation, it is also important that the
611 MOF media is physically robust enough to withstand repeated cycles of this pressure drop
612 over a long period of time. Table 11 shows the calculated crush strength of CMS GN-UC-H
613 pellets, giving a guide to how robust MOF material beads or pellets must be. If the MOF
614 pellets are less robust, there is potential for them to be crushed which would; introduce dust
615 into the outlet gas stream, reduce separation performance and increase pressure loss. The
616 requirements for robustness and separation performance are likely to create a trade-off in

617 MOF composites, as a higher percentage concentration of binder will increase robustness but
 618 reduce separation performance.

619 **Table 11** Crush strength of CMS Kuraray GN-UC-H pellets – average 1.5mm diameter

Sample No	1	2	3	4	5	6	7	8	9	10
Load At Max. Compressive Load /N	31.01	32.24	33.68	24.61	22.01	43.85	20.93	43.01	14.89	45.51
Maximum:	45.51	Minimum:		14.89	Range:		30.62	Average:		31.17

620

621 MOF media must also be able to compete commercially with CMS, both in the initial cost of
 622 media, and maintaining the media over the life of a generator. Currently, the life of CMS
 623 within a generator is exceptional, with a changeout of once every 10 years a common PSA
 624 manufacturer offering. As MOF material is newer and the manufacturing process is less
 625 repeatable, it is unlikely that a MOF media could be introduced to the market with the same
 626 long-life guarantee. An analysis could be made between the reduction in system energy costs
 627 and increase in media replacement frequency.

628

629 4.4 Gaps in MOF readiness

630 There are numerous barriers to the adoption of MOFs in production PSA units, the first of
 631 which is the immaturity of the technology required to repeatedly manufacture MOFs. Whilst
 632 laboratory-manufactured small batches of MOF material have been shown to exhibit good
 633 properties for O₂/N₂ separation, this hasn't yet been tested with MOFs produced by a scalable
 634 manufacturing process. A key challenge is in devising a manufacturing process which will be
 635 repeatable and reliable, producing the same MOF compound and structure each time. Until

636 this process can be finalised, there will be uncertainty in the commercial viability of the
637 MOFs as a replacement for CMS. It is unknown both how expensive N₂ PSA MOFs will be
638 to manufacture and what the lifetime of the manufactured material will be, although DeSantis
639 *et al.*[76] identified opportunities for MOF production costs to become under \$10/kg. Until
640 these questions have been answered and the performance of MOF material within a PSA
641 generator is assessed, an analysis to work out the cost benefits of a MOF cannot be
642 conducted.

643 Another challenge in producing a manufactured separation MOF is in creating a compound
644 where the MOF is combined with a binder to form a robust material structure. This material
645 structure, likely a pellet or monolith, needs to maintain the separation properties of the pure,
646 powdered MOF. For example, MIL-101 (Cr) and UiO-66 (Zr) both exhibit excellent surface
647 area, but this surface area is linked to the way in which the material is formed. The data
648 shows that the large surface area is calculated on powdered material, which is not useable
649 within a PSA generator. To form a useable MOF, this powder needs to be converted to a
650 pellet or monolith which will increase the amount of binding material and therefore reduce
651 the surface area available [77]. This can be difficult due to the crystalline nature of MOFs
652 which inhibits good packing density. Hastürk *et al.* [78] state that in a composite, only 30-
653 70% of the MOF pore volume is retained and Hong *et al.* [52] reported that for monolith
654 MOF structures, intrusion volume was 61%-68% lower than powdered material and the
655 surface area was reduced by 10%-35%.

656 Valekar *et al.* [79] produced a MOF composite pellets from two of the investigated O₂/N₂
657 separation MOFs – MIL-101(Cr) and UiO66(Zr) – where the MOF was combined with a
658 much lower percentage of binder (5% binder, 95% MOF). As shown in Table 12, this
659 produced a composite material with much less loss of surface area and, in the case of MIL-
660 101(Cr), negligible reduction in the overall pore volume. The drawback of a MOF compound

661 with a very low percentage weight of binder is shown in the crush strength of the material,
662 where the crush strength is respectively 7.5x and 12x lower than the average value for CMS.
663 This would cause concern that MOF compounds with low binder content would have a
664 shorter lifetime in a PSA generator and be much more prone to degradation and desiccant
665 dusting.

666 **Table 12** Material properties of MOFs containing 5% MRA binder (data taken from [79])

MOF	% Reduction in Surface Area (Pellet vs Powder)	% Reduction in Pore Volume (Pellet vs Powder)	Average Crush Strength (N)
MIL-101(Cr)	4.6%	0%	4.1
UiO-66(Zr)	8.7%	37%	2.5

667 5. Conclusions and Future Directions

668 5.1 Best Potential MOF Media for N₂ Generation

669 As identified in section 4.2, there are five potentially viable MOFs which could be used as
670 PSA N₂ generation media:

- 671 - PCN-13 (O₂/N₂ selectivity of 7)
- 672 - PCN-17 (O₂/N₂ selectivity of 10)
- 673 - MIL-101(Cr) (O₂/N₂ selectivity of 5-6 @ 3 Barg)
- 674 - ZIF-8 (O₂/N₂ selectivity of 8.3)
- 675 - UiO-66(Zr) (O₂/N₂ selectivity of 6.1)

676 However, the PCN compounds, PCN-13 and PCN-17, have only been shown to separate O₂
677 and N₂ at temperatures between 77 – 273K (up to 0°C) [71]. This is not acceptable for PSA
678 N₂ generation, which occurs without cooling over a nominal room temperature range.

679 Therefore, these PCN compounds have been discounted from the evaluation. The viable
680 MOFs under consideration are now; MIL-101(Cr), ZIF-8 & UiO-66(Zr) and these will be
681 compared to the CMS media (GN-UC-H). They will be compared using the known physical
682 and performance characteristics, which are:

- 683 - Specific surface area (m²/g) – The surface area of an adsorbent material per given
684 mass
- 685 - Micropore volume (cm³/g) – The volume of pores tuned to adsorb a desired gas per
686 mass
- 687 - % MOF in MMM – Of a quoted, useable MMM what % of the MMM is comprised of
688 MOF
- 689 - Bulk density (g/cm³) – Density of the adsorbent material

690 - O₂/N₂ Selectivity – Ratio between the volume of O₂ adsorbed and the volume of N₂
691 adsorbed

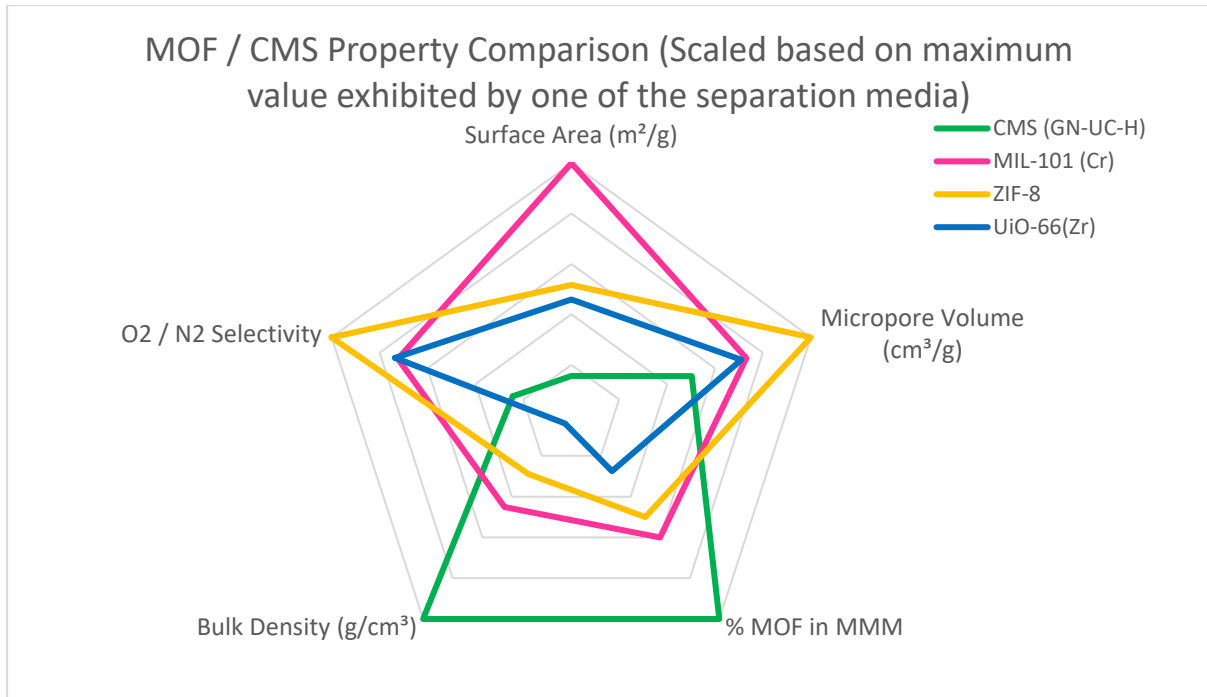
692 Table 13 shows the material properties taken from prior literature and Fig. 10 shows a radar
693 graph visually displaying the strengths of each separation media in five criteria; specific
694 surface area, micropore volume, bulk density, O₂/N₂ selectivity and % MOF in MMM. All
695 three of the MOFs compare favourably to CMS in the performance indicating properties of;
696 specific surface area, micropore volume and O₂/N₂ selectivity. This would indicate that all
697 three of the MOFs would be preferential to the CMS media, however there are a couple of
698 factors limiting the amount of MOF which can be used. The bulk density of the CMS is much
699 higher, so whilst the MOFs may perform better per mass, less mass of MOF can be placed in
700 a generator column. Additionally, whilst the CMS is comprised solely of CMS material, the
701 MOF compounds have been combined with a polymer to form an MMM. Although a
702 polymer MMM would not be useable within a PSA generator, due to the adsorption
703 mechanism, this material structure has been used for the comparison as it is the only structure
704 of each of these MOFs which has been tested for O₂/N₂ separation. Kiyono *et al.* [80] and
705 Campo *et al.* [81] proved that CMS can be combined with a polymer membrane structure to
706 allow CMS to be used in membrane N₂ generation. It would therefore be theorised that the
707 opposite could be achieved with MOF compounds and a PSA-suitable pellet structure could
708 be manufactured.

709 **Table 13** Separation media properties taken from prior research. Data taken from [7,40, 52,
710 73-74, 78, 82-88]

MOF Media:	CMS (GN-UC-H)	MIL-101 (Cr)	ZIF-8	UiO-66(Zr)
Specific Surface Area (m ² /g)	436.8	2806.1	1450	1288

Micropore Volume (cm ³ /g)	0.241	0.35	0.479	0.34
% MOF in MMM	100.0% (N/A)	60.0%	50.0%	27.5%
Bulk Density (g/cm ³)	1.75	0.79	1.12	0.25
O ₂ / N ₂ Selectivity	2.02	6	8.3	6.1

711



712

713 **Fig. 10** Radar graph comparing properties of viable separation MOF media and current CMS
714 media

715

716 A number of these properties given in Table 13 and Fig. 10 are given as a volume per unit
717 mass however, when used in a generator, the volume of media is dictated by set volume, not a
718 set mass. Table 14 shows the properties converted to a per volume number, using the bulk
719 density to convert from a per unit mass to a per unit volume figure. Ideally, the packed
720 density of a MOF pellet would be better to use for this conversion, but this data is not
721 currently available for these MOFs. When compared to CMS based on the volume of MOF

722 material which could be stored inside a generator column, some of the MOFs start to look
723 less preferable.

724 ZIF-8 still compares favourably to CMS in micropore volume, micropore volume filled by O₂
725 [Micropore volume*(1-(1/O₂N₂Selectivity))] and specific surface area. MIL-101(Cr) exhibits
726 preferential specific surface area, but the micropore volume and micropore volume filled by
727 O₂ are both lower than seen for CMS, whilst UiO-66(Zr) performs worse in all three criteria.
728 UiO-66(Zr) is severely disadvantaged by both a very low density and a low %wt of MOF in
729 the MMM, resulting it there being too little MOF material inside a generator column to
730 maintain good separation properties. MIL-101(Cr) and ZIF-8 have higher density and %wt of
731 MOF in their MMM, but the MMM is still just 60% and 50% MOF respectively and the
732 density is around half that of CMS. If improved MOF structures could be found, increasing
733 the %wt of MOF in a composite and packing the material more tightly, all three MOFs could
734 have much better potential separation performance than CMS.

735

736 **Table 14** Calculated separation media properties

MOF Media:	CMS (GN-UC-H)	MIL-101(Cr)	ZIF-8	UiO-66(Zr)
Micropore Volume / Media Volume (cm ³ /cm ³)	0.422	0.277	0.536	0.085
Micropore volume filled by O ₂ (not N ₂) / Media Volume (cm ³ /cm ³)	0.28	0.24	0.48	0.07
Specific Surface Area / Media Volume (m ² /cm ³)	764.4	2216.8	1624.0	322.0

737

738 The list of all the desired material properties for a viable PSA N₂ generation MOF is given in
739 Table 15, with the assumed benefit of each of the material properties described. As more
740 research is conducted into using MOFs as PSA separation media and a calculation can be
741 made between the properties and generator performance, a numerical value could be put
742 against all these criteria.

743 **Table 15** Required material properties for a viable PSA N₂ separation MOF

Material Property	Benefit of Material Property
High O ₂ /N ₂ Selectivity (Preferential Diffusion)	Good O ₂ /N ₂ ratio of the gases trapped within the micropores, improves productivity & efficiency
Large Micropore Volume	Media could be able to adsorb more gas, improving generator efficiency
Quick Rate of Gas Diffusion into the Micropores	Adsorption time is reduced, allowing the cycle time to be reduced and productivity increased
High Packing Density	Less void space gas in the columns, reducing gas transfer volume at cycle end, improving efficiency
Large Specific Surface Area	Increases the likelihood of gas / media interaction - faster adsorption rate and increased productivity
Rapid Depressurisation Desorption Profile	Allows the O ₂ to be desorbed and media regenerated using the existing PSA cycle
O ₂ /N ₂ Selectivity seen at Room	Media can function in an existing PSA

Temperature (25°C)	generator without energy inputs to change the temperature
High %wt of MOF in a Composite Material	Maintains the separation performance of raw 100% MOF material
Good MOF Bead Crush Strength (>20N)	Media should have good resistance to repeated pressure cycles, increasing life
Long MOF Lifetime	Allows the media and generator to be serviced less frequently, improving cost effectiveness

744

745 5.2 Gaps in Prior Research

746 There are numerous barriers to adoption and gaps in research knowledge when looking at
747 MOFs for PSA N₂ generation, either as a direct replacement for CMS and when trying to
748 rearrange the system for MOF media. A principle barrier to directly swapping MOF media
749 for CMS is in the limited data available regarding how a MOF media would be regenerated
750 within a PSA generator. It is being assumed that a MOF media could be regenerated in the
751 same way as CMS, using a rapid pressure drop to release the trapped O₂ from the media. This
752 has not yet been experimentally proven with a MOF material, but this desorption profile
753 needs to be retained.

754 The main issue with using MOFs in a rearranged system, where the N₂ generator sits
755 upstream of the dryer, is how the presence of contaminants affects the MOF. As Hong-Cai
756 and Kitagawa [16] found, a main problem contaminant for MOFs is water, which can
757 collapse the structure of the MOF through capillary action once adsorbed. This issue could be
758 mitigated by either; developing a hydrophobic MOF or by shortening the regeneration cycle
759 time so no water is adsorbed into the MOF. To achieve this through a shorter cycle time
760 would need cycle duration to reduce dramatically, to a couple of seconds, which would have

761 a very negative effect on generator efficiency. Therefore, the only viable option is to develop
762 a hydrophobic MOF such as that proposed by Ma *et al.* [64].

763 Due to this being a novel application of MOF material, there is no test data for MOF media in
764 a PSA system and very limited material properties of a bead, pellet or monolith composite
765 MOF structure. As the packing density of a MOF bead or pellet material is unknown, when
766 the weight to volume conversion was made in Table 14, the bulk densities had to be used.
767 There is also a challenge in the previously reported O₂/N₂ selectivity figures, as all the
768 previously reported selectivity figures have been derived from a membrane-style selectivity
769 test, where an air mix is fed down a tube surrounded by MOF membrane material, with the
770 gas concentrations escaping the tube measured. This method of calculating O₂/N₂ selectivity
771 is ideal for other applications, such as gas capture or membrane N₂ generation, but it is not an
772 accurate test of the adsorption mechanism used in a PSA generator. Therefore, the MOFs
773 which are shown to be highly selective in a membrane test should be trialled as a pellet
774 material in a PSA generator, to validate whether MOFs which perform well in membrane
775 separation will also perform well in PSA separation.

776 The assumed benefits of the material properties listed in Table 15 also need to be tested, to
777 check the accuracy of the relationships made between the properties of MOF media; surface
778 area, micropore volume and O₂/N₂ selectivity and the desired generator performance
779 properties; air to N₂ ratio and productivity. The first assumption is that a media with a higher
780 specific micropore volume (per volume of media) will be able to adsorb proportionally more
781 gas. The second is that the rate of adsorption will be proportional to the surface area of the
782 media, the higher the surface area, the more likely gas molecules are to collide with the media
783 and therefore the faster the adsorption rate. The third assumption is that the ratio of quoted
784 O₂/N₂ selectivity figures between the different media remains consistent as the desired outlet

785 N₂ gas purity is changed. This doesn't account for a media which could efficiently produce
786 low-purity N₂ gas, but not high purity N₂ gas.

787

788 5.3 Future work and research

789 This review focuses on consolidating the reported material properties for MOFs to be used
790 within a PSA N₂ generator. As MOFs manufacture is not perfectly repeatable, the
791 consolidation of reported properties carries the potential for error. Further work should focus
792 on a report calculating the material properties for each MOF: MIL-101(Cr), ZIF-8 & UiO-
793 66(Zr) from the same manufacturing sample to increase the accuracy of and confidence in the
794 results. The potential for MOF materials to be used within a PSA N₂ generator has been
795 shown. An experimental study to evaluate MOF media within a PSA environment is needed.
796 This work would give much more confidence that MOFs are a viable separation media for N₂
797 gas generation and could reveal any unidentified issues which need to be resolved before a
798 useable material is available. Evaluation could also highlight unexpected benefits of MOFs
799 when compared to CMS, which would then inform the design modifications for the next
800 generation of PSA N₂ generators. Test data could be calculated for the three MOFs listed in
801 this review, plus any future MOFs with suitable O₂/N₂ selectivity as defined in this paper.

802 There are a couple of other applications within the N₂ generation system which would be
803 interesting to investigate the suitability of MOFs for. Firstly, whether MOFs could also prove
804 to be a viable replacement separation media for the desiccant dryers within N₂ generation
805 system. MOFs could also prove preferential over traditional material in this application.
806 Secondly, if MOF MMMs become much more efficient, with excellent separation ratios,
807 could membrane generation be used for higher purity (>95%) N₂ applications, where
808 membrane generation has previously been uncompetitive compared to PSA.

809

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813 6. References

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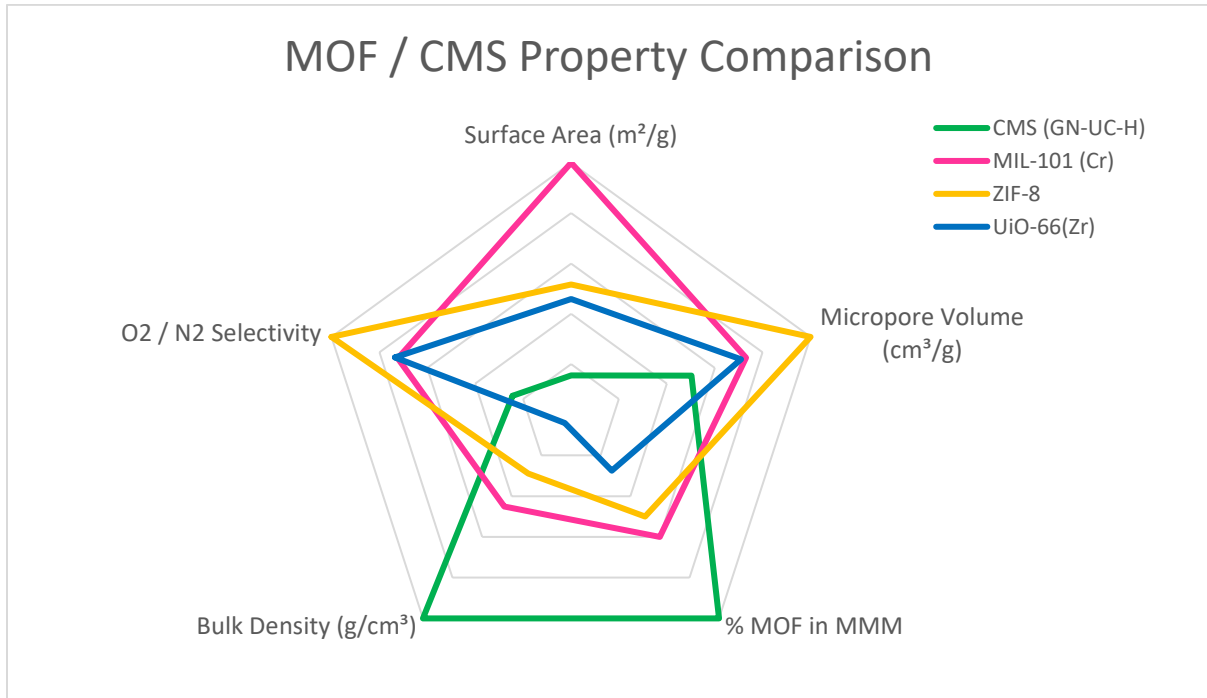
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