

Techno-economic Analysis of Metal–Organic Frameworks for Hydrogen and Natural Gas Storage

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Supporting Information

ABSTRACT: A techno-economic analysis was conducted for metal–organic framework (MOF) adsorbents, which are promising candidates for light-duty vehicle on-board natural gas and hydrogen storage. The goal of this analysis was to understand cost drivers for large-scale (2.5 Mkg/year) MOF synthesis and to identify potential pathways to achieving a production cost of less than \$10/(kg of MOF). Four MOFs were analyzed with four different metal centers and three different linkers: Ni₂(dobdc) (dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate; Ni-MOF-74), Mg₂(dobdc) (dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate; Mg-MOF-74), Zn₄O(bdc)₃ (bdc²⁻ = 1,4-benzenedicarboxylate; MOF-5), and Cu₃(btc)₂ (btc³⁻ = 1,3,5-benzenetricarboxylate; HKUST-1). Baseline costs are projected to range from \$35/kg to \$71/kg predicated on organic solvent (solvothermal) syntheses using an engineering scale-up of laboratory-demonstrated synthesis procedures and conditions. Two alternative processes were analyzed to evaluate the cost impact of reducing solvent usage: liquid assisted grinding (LAG) and aqueous synthesis. Cost projections from these alternative synthesis approaches range from \$13/kg to \$36/kg (representing 34–83% reductions), demonstrating the large impact of solvent on the baseline analysis. Finally, sensitivity studies were conducted to identify additional opportunities for achieving MOF production costs of less than \$10/kg.

INTRODUCTION

Hydrogen (H₂) and natural gas (NG) are attractive gasoline alternatives owing to their potential for reducing greenhouse gas emissions, addressing dependence on foreign sources of fuel, and reducing the total cost of vehicle ownership. While H₂ has a high specific energy (energy per unit mass) relative to gasoline and NG has a specific energy comparable to that of gasoline, both H₂ and NG have much lower energy densities (energy per unit volume) than gasoline. This poses a significant challenge to conventional compressed gas storage. As transportation fuels, H₂ and NG are typically stored at 700 and 250 bar nominal working pressure, respectively.^{1–3} On a volumetric basis, H₂ at 700 bar requires 7 times greater storage volume and NG at 250 bar requires 3.5 times greater storage volume to yield the same energy content as a liter of gasoline. While this gap may be somewhat offset for a fuel cell vehicle with improved powertrain efficiency, increased on-board storage energy density is needed for both H₂ and NG to achieve an equivalent driving range with conventional vehicles. To address these challenges, the U.S. Department of Energy (DOE) has set 2020 technical targets for hydrogen storage systems cost (\$333/(kg_{H₂)), volumetric capacity (40 g_{H₂)/L), and gravimetric capacity (5.5 wt % H₂).⁴ Similarly, to be competitive with the incumbent technologies, the DOE Advanced Research Projects Agency—Energy (ARPA-E) developed NG storage targets for system cost (\$150/GGE), volumetric capacity (148 g_{NG}/L), and gravimetric capacity (31 wt % natural gas).⁵ Compressed}}

gas storage falls far short of the DOE cost and capacity targets due to the expensive and bulky pressure vessels, so alternative storage technologies are being explored.¹

One strategy to increase the volumetric capacity of alternative fuel vehicles (AFVs) is to bind H₂ and CH₄ to an adsorbent surface through a weak van der Waals interaction (physisorption).⁶ Metal–organic frameworks (MOFs) are one such class of adsorbents being considered. MOFs are high surface area materials containing a network of metal cations or clusters connected through bridging organic ligands. Owing to their high surface area and tunable surface chemistry, MOFs have received considerable attention as a material-based adsorbent option for natural gas and hydrogen AFVs and have shown potential for achieving high volumetric and gravimetric storage capacities.^{7,8} MOFs are able to store appreciable amounts of NG or H₂ at moderately low pressures (less than 100 bar).⁶ Low-pressure adsorbent-based fuel systems could reduce the cost of on-board tanks, the cost and technical difficulty of high-pressure compressors at the station, and the barriers to building a fuel delivery infrastructure.⁹ MOFs are generally considered to have the potential to improve volumetric and gravimetric density by physisorption through achieving a favorable balance of large surface area and

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Table 1. Chemical Names and Abbreviations for MOF Linkers Found in This Study

| linker | linker abbrev | MOF name | alternative MOF name (M = metal cation) |
|--------------------------------------|---------------------|-------------------------------------|---|
| 2,5-dioxido-1,4-benzenedicarboxylate | dobdc ⁴⁻ | M ₂ (dobdc) (M = Mg, Ni) | M-MOF-74 |
| 1,4-benzenedicarboxylate | bdc ²⁻ | Zn ₄ O(bdc) ₃ | MOF-5 |
| 1,3,5-benzenetricarboxylate | btc ³⁻ | Cu ₃ (btc) ₂ | HKUST-1 |

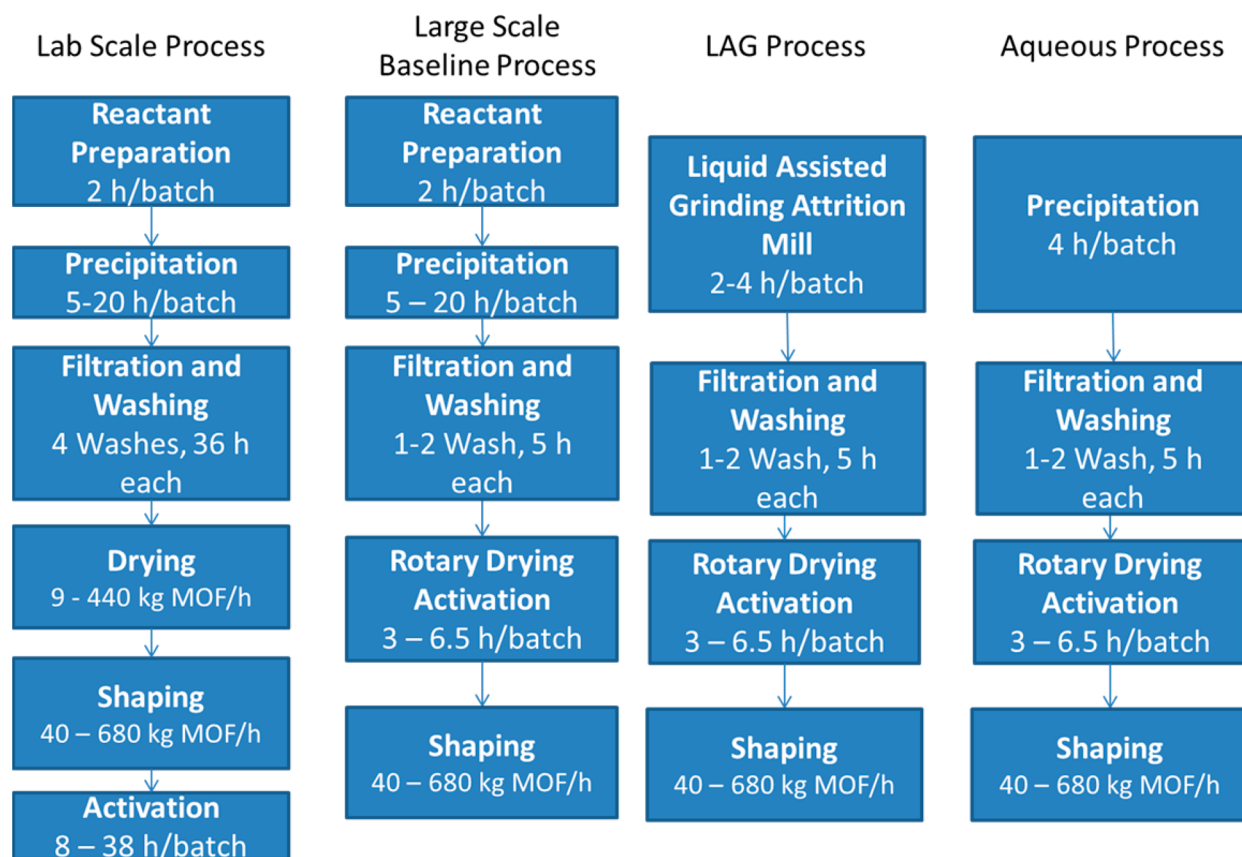


Figure 1. Block flow diagrams for each of the MOF synthesis processes. The processes described cover a range of options to produce MOFs. In this work, specific MOFs were linked with specific manufacturing processes (see Table 1). Times listed in each step are ranged across the four MOFs analyzed.

pore volume with high-affinity gas adsorption sites.⁶ BET surface areas for various MOFs can exceed 7,000 m²/g, while the pore volume can range from 0.043 to 4.40 cm³/g.^{10,11} ARPA-E technical targets for CNG vehicles include delivery rates (2.6 kW/L) and adsorbent gravimetric capacity (0.5 g_{NG}/g_{MOF}),⁵ and \$10/kg_{MOF} target for MOF production for use in NG vehicles.¹² Given the similarity in requirements between CNG vehicles and H₂ vehicles, it is expected that H₂ vehicles will need to achieve similar MOF production costs to be competitive. In fact, with the aforementioned DOE targets for H₂, one can determine that DOE's target H₂ storage system cost is approximately \$18/kg, setting an upper bound on MOF material costs.

To date, the majority of research efforts related to MOFs for NG and H₂ storage have been directed toward the development of new materials exhibiting improved adsorption properties with little regard for material or system cost. Indeed, conventional solvothermal MOF syntheses generally involve the reaction of hydrated metal salts with bridging organic ligands in expensive organic solvents at 100–150 °C.¹³ Recently, several alternative processing techniques have been explored to reduce or eliminate organic solvent usage. Liquid

assisted grinding (LAG) has been proposed, and recently demonstrated, and offers a pathway to reduced MOF costs by lowering synthesis times and dramatically reducing the amount of solvent needed.^{13–15} Aqueous synthesis routes for M₂(dobdc), which substitute water for the much higher priced organic solvents typically used, have been recently demonstrated and represent yet another alternative to conventional synthesis.¹⁵

In this work, detailed cost analyses [cost refers to production cost, including materials and manufacturing, but does not include a mark-up] were performed for four metal–organic frameworks that have promising adsorption properties for NG and/or H₂ storage: M₂(dobdc) (M = Mg, Ni), MOF-5, and HKUST-1.^{6,10,16,17} (See Table 1 for a summary of the linker abbreviations.) Following a brief discussion of the analysis methods used, the results are organized as follows. First, baseline costs are established using an engineering scale-up of laboratory-demonstrated solvothermal synthesis methods. Once the baseline is established, alternative synthesis approaches (LAG and aqueous) are analyzed. The purpose of this work is to demonstrate general MOF cost trends rather than to provide a detailed cost comparison between MOFs. To

Table 2. Synthesis Parameters for the MOF Synthesis Pathways Analyzed

| MOF identity | linker | linker solvent | metal salt | MOF solvent | synthesis method | yield, % |
|---|----------------------|--------------------------------------|--|--------------------------------------|------------------|----------|
| MOF-5 (Zn ₄ O(bdc) ₃) | H ₂ bdc | DMF ^a | Zn(O ₂ CCH ₃) ₂ ·2(H ₂ O) | DMF | solvothermal | 63 |
| HKUST-1 (Cu ₃ (btc) ₂) | H ₃ btc | DMF, EtOH, H ₂ O | Cu(NO ₃) ₂ ·2.5H ₂ O | DMF, EtOH, H ₂ O | solvothermal | 44 |
| Ni ₂ (dobdc) | H ₄ dobdc | DMF | Ni(NO ₃) ₂ ·6H ₂ O | DMF, MeOH | solvothermal | 69 |
| Mg ₂ (dobdc) | H ₄ dobdc | DMF | Mg(NO ₃) ₂ ·6H ₂ O | DMF, MeOH | solvothermal | 69 |
| MOF-5 (Zn ₄ O(bdc) ₃) | H ₂ bdc | DMF, CH ₃ NH ₂ | Zn(O ₂ CCH ₃) ₂ ·2H ₂ O | DMF, CH ₃ NH ₂ | LAG | 63 |
| Ni ₂ (dobdc) | H ₄ dobdc | DMF, CH ₃ NH ₂ | Ni(NO ₃) ₂ ·6H ₂ O | DMF, CH ₃ NH ₂ | LAG | 69 |
| Mg ₂ (dobdc) | H ₄ dobdc | DMF | Mg(NO ₃) ₂ ·6H ₂ O | DMF | LAG | 69 |
| HKUST-1 (Cu ₃ (btc) ₂) | H ₃ btc | DMF, EtOH, H ₂ O | Cu(NO ₃) ₂ ·2.5H ₂ O | DMF, EtOH, H ₂ O | LAG | 44 |
| Ni ₂ (dobdc) | H ₄ dobdc | H ₂ O | Ni(CH ₃ COO) ₂ ·4H ₂ O | H ₂ O | aqueous | 92 |
| Mg ₂ (dobdc) | H ₄ dobdc | H ₂ O | Mg(NO ₃) ₂ ·6H ₂ O | H ₂ O | aqueous | 92 |

^aDMF = dimethylformamide.

facilitate a thorough discussion of the cost drivers and potential savings, Mg₂(dobdc) is presented as a representative example. The trends observed for Mg₂(dobdc) also apply to the other three MOFs analyzed, and we expect these general trends to be similar for other MOFs. This work identifies potential pathways to reducing MOF costs to less than \$10/kg and identifies areas where the MOF research community can focus attention to address cost reduction.

METHODS

MOF Cost Calculation Methods. A process-based cost estimation methodology was used to assess the production cost of four representative MOFs: Mg₂(dobdc), Ni₂(dobdc), MOF-5, and HKUST-1. This process-based methodology mimics the actual steps of production and determines final cost by summing the individual costs incurred in each manufacturing step (i.e., synthesis, filtration, and drying) of the process. A brief description of the approach follows.

For each identified step in the production process, a cost is tabulated based on the materials used in that step, the cost of the capital equipment for the step, and the machine and labor operational time to complete each step. Price quotes for each of the chemical reagents and the necessary capital equipment are collected from suppliers. Operational time calculations are determined from detailed mass and energy balances (including reaction kinetics and yield) for the system along with product information on equipment and reaction cycle times, and standard operating procedure (SOP) for chemical operations. Standard labor and manufacturing rates, as well as utility prices, are used to determine the final manufacturing cost of the product.¹⁸ Cost is assessed at a range of MOF annual production rates, from 50,000 kg_{MOF}/year to 2.5 million kg/year. Each projected MOF cost correlates to a production facility optimized for that level of production: MOF costs are not merely the costs from a large facility operated at lower than design capacity. At a nominal level of 50 kg_{MOF} per vehicle storage system, this correlates to 1,000 systems per year and 500,000 systems per year, respectively.

For standardized materials and devices, price quotations from industry as a function of annual order quantity form the basis for financial estimates. A learning curve formula is then applied to the available data gathered from industry to provide price estimates between the quotation data points.

When nonstandard materials and devices are needed, costs are estimated based on detailed DFMA style models developed for a specific, fully defined, manufacturing process train. In this approach, the estimated capital cost, C_{Est} , of a manufactured device is quantified as the sum of materials costs, C_{Mat} , and the manufacturing costs, C_{Man} . Given that, in a chemical process, no tooling or assembly is usually required, these costs are not considered in the technical economic analysis. However, a contingency cost was added, which increases the manufacturing cost by 10%:

$$C_{Est} = C_{Mat} + C_{Man} \quad (1)$$

The materials cost is derived from the amount of raw materials needed to make each intermediate or chemical product, based on the system physical design (material, geometry, and manufacturing method). The manufacturing cost is derived from a specific design of a manufacturing process train necessary to make all parts.

Models were iteratively developed with the technical analysis informing the cost analysis. Process designs were created for each system analyzed. Designs were iterative and further assumptions were made to reduce costs, which then further adjusted the process designs. Generic design descriptions for various synthesis methods are provided below.

Analyzed Production Methods. The manufacturing process for the baseline cost assessment for all four MOFs (Ni₂(dobdc), Mg₂(dobdc), MOF-5, and HKUST-1) is defined in Figure 1 as the Industrial Baseline Process. This process is based on laboratory-scale synthesis but has been modified to translate the steps to standard operations conducted in large production facilities. Thus, the Industrial Baseline Process is intended to represent the cost if the proven laboratory-scale synthesis was transferred directly to scale-appropriate unit operations. The remainder of this section will describe what assumptions were made to scale-up laboratory-demonstrated synthesis. Following the description of the laboratory to industrial scale-up, the rationale and assumptions used for aqueous synthesis and liquid assisted grinding will be described.

Laboratory Methods. A generalized laboratory-scale solvothermal synthesis is based on previously reported syntheses,^{17,19} as described here briefly:

- (1) The metal salt and linker are separately dissolved in organic solvents at less than 5 wt % solid to solvent ratio.
- (2) The two solutions are combined in a precipitation reaction to form the MOF particles, typically at elevated temperature (80–120 °C) and 1 atm pressure for 18–20 h. [Tranchemontagne et al. have demonstrated a successful room-temperature synthesis. Further, HKUST-1 was modeled at 25 °C, as described in the laboratory methods.]
- (3) The products are separated from the mother liquid by centrifugation.
- (4) Products are washed multiple times in DMF and then methanol (20 mL volumes each time).
- (5) The product MOF is dried in several stages over the course of 31 h.

The cost analysis for MOF synthesis at 2.5 Mkg/year that follows is based on assumed reaction conditions and process steps demonstrated at laboratory scale, as described above. However, laboratory procedures are not well-suited to high production rates, so three variations on the laboratory procedures were also examined: industrial-scale MOF synthesis in organic solvents, synthesis in water, and synthesis using liquid assisted grinding (LAG). Figure 1 summarizes the approaches for each of these four processes with justification for departures from the laboratory-scale synthesis described below. Table 2 further identifies specific parameters in each approach.

Industrial-Scale Solvothermal Methods. The Industrial Baseline process is based on reaction conditions and the process steps

Table 3. Laboratory vs Industrial Baseline Synthesis Process Conditions^a

| | unit | laboratory values | Mg ₂ (dobdc) industrial baseline synthesis assumptions |
|-----------------------------------|------|-------------------|---|
| molar yield | % | 69 | 69 |
| linker:metal salt molar ratio | | 0.5:1 | 0.5:1 |
| precipitation reactor pressure | bar | 1 | 1 |
| precipitation reactor temperature | °C | 25–120 | 120 |
| precipitation reaction time | h | 18 | 20 |
| washing steps | | 5 | 2 |
| wash fluid | | DMF/methanol | DMF |
| drying time | h | 31 | 6.5 |

^aFull process conditions for all four analyzed MOFs can be found in [Supporting Information](#).

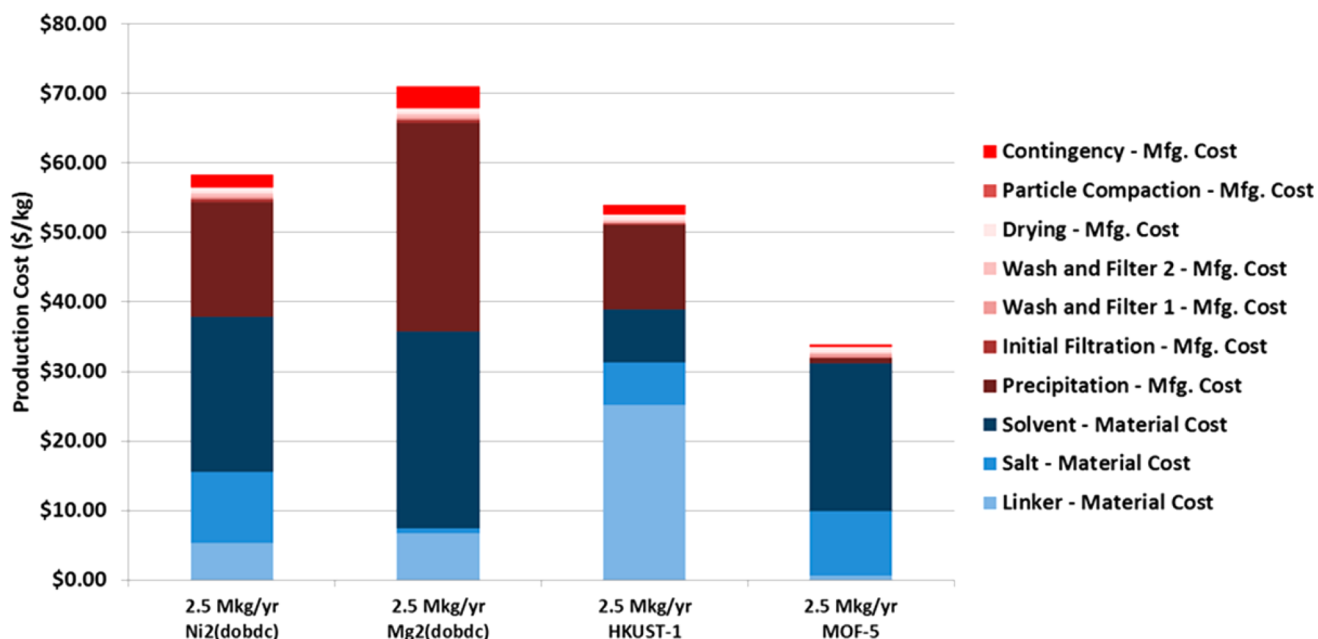


Figure 2. Baseline total cost of four MOFs manufactured at 2.5 million kg/year by solvothermal synthesis methods. Material cost contributions (linker, metal salts, and solvents) are shown as shades of blue while manufacturing costs for each step are shown as shades of red.

described in the previous section with minor modifications based on engineering judgment. At the industrial scale, it is assumed that the drying and vacuum activation steps can be combined using a rotary dryer. Additionally, a rotary dryer would provide the capacity to combine drying and activation into one step and obviate the liquid–MOF mixing step required for a spray dryer. Furthermore, the rotary dryer has the potential to decompose and/or sublime excess organic ligands that might remain in the framework pores after the filtration/wash step. This contaminant cleansing effect is expected to be more effective than that achievable in a spray dryer or belt dryer, due to the much longer residence time at temperature. A comparison of generalized laboratory-scale solvothermal reaction conditions and our assumed industrial-scale solvothermal reaction conditions is summarized in [Table 3](#). Metal precursors were generally selected for scale-up from demonstrated laboratory-scale solvothermal syntheses. One departure was for Mg₂(dobdc) and Ni₂(dobdc). In a typical solvothermal synthesis, Mg₂(dobdc) and Ni₂(dobdc) are prepared from Mg(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O, respectively; however, we assumed that the same synthesis demonstrated by Tranchemontagne et al. for Zn₂(dobdc) using Zn acetate is valid for Mg₂(dobdc) and Ni₂(dobdc) using magnesium nitrate (Mg(NO₃)₂) and nickel nitrate (Ni(NO₃)₂) salts, respectively.¹⁷ This is expected to be a valid assumption because of the similarities between these metal salts. Caskey et al. reported reaction temperatures of 120 °C for Mg₂(dobdc).¹⁹

For solvothermal synthesis, the linker and metal salt are separately dissolved in organic solvents, and the two solutions are combined in a precipitation reactor. Reaction times range from 5 h (MOF-5) to 24 h

(HKUST-1), depending on the individual MOF being synthesized. Solid precipitation of the MOF occurs with the solids fraction estimated to be approximately 2.5% by weight of the solution. The solids are filtered and washed. Multiple washes are used to clean excess reagents from the solids followed by a rotary dryer to completely dry the solid MOF. The dry MOF powder can then be compacted into a usable shape (e.g., pellets) and undergo a heated activation step. Once activated, the MOF is ready for use in the on-board NG or H₂ storage system.

Liquid Assisted Grinding Method. Liquid assisted grinding is a high-volume chemical synthesis technique for preparing coprecipitates in a minimum of solvent that has been demonstrated for preparing MOFs, including HKUST-1.¹⁴ The role of the solvent depends on the particular reaction: in some cases, it acts as a lubricant and energy transfer medium, while in others it acts as a catalyst. Selection of appropriate solvent ratios and solvent mixtures is an active area of research for LAG synthesis.^{20–22} Based on advice from experts in LAG manufacturing,²⁰ we assume that the solvent is a 1:1 mass mixture of DMF and methylamine, and that 7.5 wt % (solvent to MOF) is sufficient to wet the solid reactants when added together with the MOF precursor salts in a high-energy attrition mill. The mill imparts mechanical energy sufficient to overcome the activation energy of the chemical reaction.^{23–25} LAG may also be a useful means of tuning or controlling surface area and pore volume;²⁴ however, this analysis assumes that the MOF surfaces remain unchanged by the preparation method. The LAG method was modeled only for MOF synthesis, not for linker synthesis.

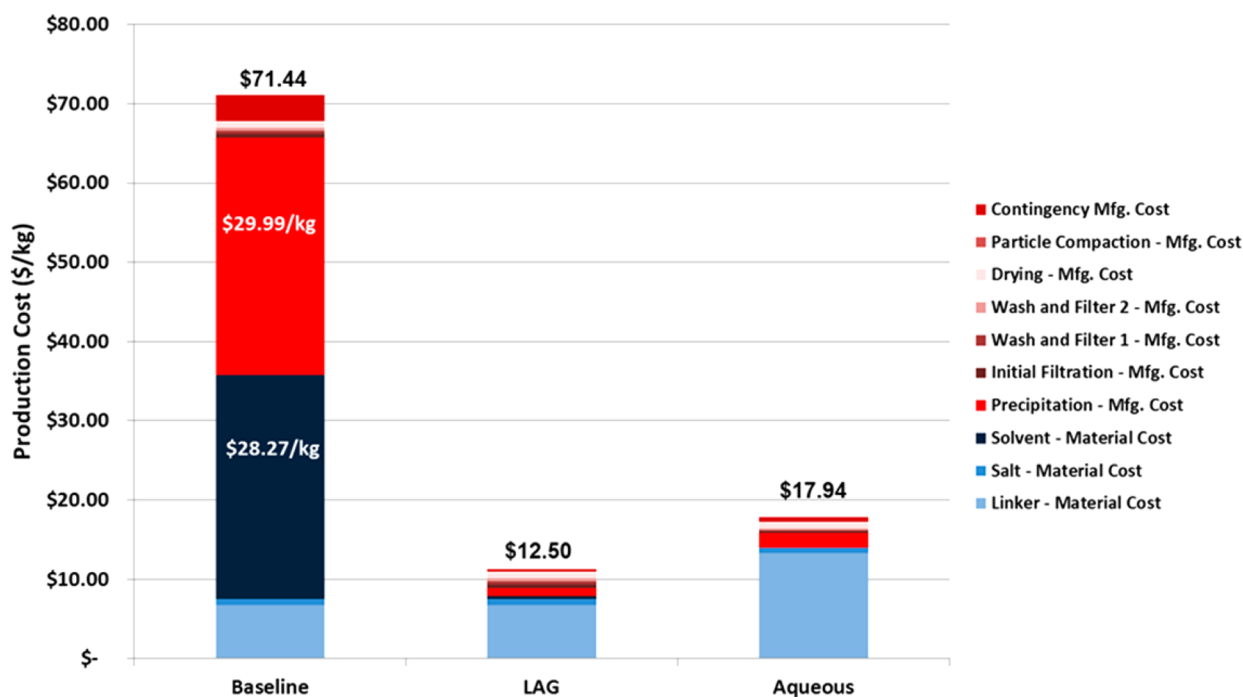


Figure 3. Detailed cost breakdowns for the synthesis of $\text{Mg}_2(\text{dobdc})$ by the baseline industrial-scale solvothermal, LAG, and aqueous synthesis methods with reported yields. Material costs are represented by shades of blue while manufacturing costs are represented by shades of red. Yields are 69%, 69%, and 92% for the baseline, LAG, and aqueous methods, respectively.

In the following LAG analysis, ball milling units replaced the precipitation reactor used in solvothermal methods, while the remaining steps of the solvothermal process remained the same. Likewise, reported solvothermal yields (see Table 1) were maintained for LAG calculations.

Aqueous Solution Chemistry. Aqueous synthesis routes have been demonstrated for $\text{Ni}_2(\text{dobdc})$ and $\text{Mg}_2(\text{dobdc})$ with yields above 90%.^{15,26} Aqueous synthesis is modeled as a one pot synthesis with the metal salt and linker dissolved together in deionized water in a precipitation reactor and held at reflux. The filtration, washing, drying, and activation steps are similar to solvothermal synthesis.

Linker Synthesis. Price quotes were obtained for the linkers for MOF-5 (H_2bdc) and HKUST-1 (H_3btc). However, the linker for $\text{M}_2(\text{dobdc})$ (H_4dobdc) is not produced commercially on an industrial scale. Consequently, a process-based cost estimation analysis was conducted to estimate the cost of H_4dobdc , based on scale-up of a patent production process.²⁷ The modeled manufacturing process involves using a precipitation reactor to produce the linker, which is then filtered and washed before running the powder through a rotary dryer. Reactants, material usages, reaction times, and yields were based on the experimental values described in the patent. Price quotes or estimates were obtained for the raw materials as well as all required capital equipment. The total cost of production of H_4dobdc , as well as the raw materials costs for H_4dobdc , can be found in the Supporting Information along with other MOF raw material costs.

RESULTS

Cost results comparing four MOFs ($\text{Ni}_2(\text{dobdc})$, $\text{Mg}_2(\text{dobdc})$, MOF-5, and HKUST-1) manufactured by the baseline solvothermal synthesis are presented in Figure 2. The cost to manufacture each MOF was calculated based on the respective materials, process conditions, and times presented in Table 3. Cost results presented in Figure 2 are based on the solvothermal synthesis and the Industrial Baseline Process diagrammed in Figure 1. Material costs reflect the costs of raw materials (salts, linkers, and solvents), while manufacturing costs reflect the cost of machinery amortized over equipment

lifetime as well as process energy, utilities, labor, and facility costs. Solvent costs dominate the material costs for solvothermal synthesis for almost all of the MOFs listed. HKUST-1 is the single exception due to the exceptionally high linker price. [There is the potential to lower the linker price by manufacturing an appropriate HKUST-1 linker rather than purchasing a commercial linker. This would offer potential cost reductions through the advantage of economies of scale as well as removing a layer of cost mark-up.] Material costs also contribute more to the total production cost than manufacturing costs for all cases. (Material cost details can be found in Supporting Information Table S4.)

Figure 3 shows cost breakdown comparisons for the three industrial-scale synthesis methods analyzed, as applied to $\text{Mg}_2(\text{dobdc})$. This material serves as a representative MOF to illustrate cost trends. Yields for the baseline method and LAG are taken from laboratory yields reported by Tranchemontagne et al.,¹⁷ while aqueous yields are reported by Cadot et al.¹⁵ Costs are divided between materials and manufacturing costs and are further segregated by the processing steps shown in Figure 1. Linker costs do not vary between the baseline and LAG methods, except where the yield varies. Aqueous synthesis has a slightly higher linker cost than the LAG or baseline methods, owing to the variation in the stoichiometric requirements of linker to salt listed in the laboratory procedures (see Table S4 in Supporting Information). As a result, linker costs contribute \$6.74/kg for both the baseline and LAG synthesis, while the linker costs for aqueous synthesis is \$13.28/kg. The linker cost contribution in the aqueous synthesis methods could be reduced by up to 33% if the linker-to-metal ratio was reduced to the stoichiometric theoretical limit of 2 linkers per metal atom. The solvent and manufacturing costs are dramatically different between the baseline, LAG, and aqueous methods. Total organic solvent usage is reduced from approximately 95 wt % to 7.5 wt % in

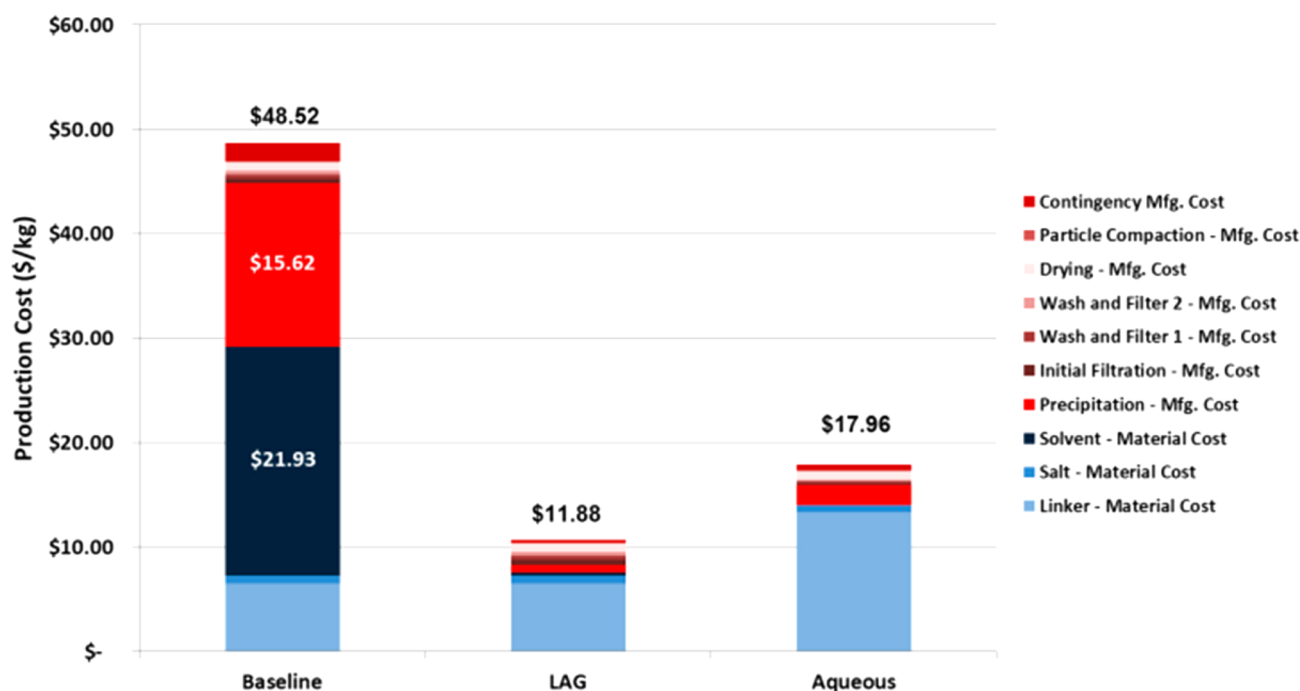


Figure 4. Detailed cost breakdowns for synthesis of Mg₂(dobdc) by the baseline industrial-scale solvothermal, LAG, and aqueous synthesis methods at 92% yield. Material costs are represented by shades of blue while manufacturing costs are represented by shades of red. Aqueous linker costs are higher than LAG and baseline methods due to the higher salt:linker ratios used in the aqueous method.

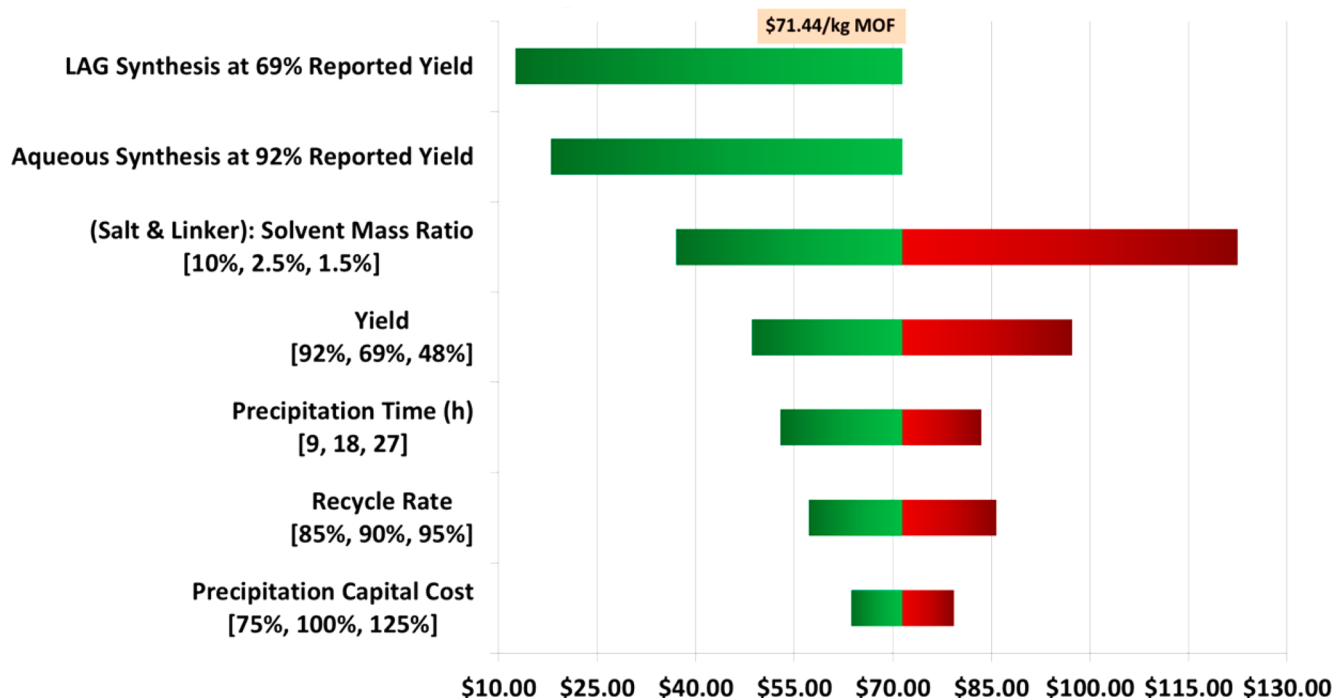


Figure 5. Tornado chart showing parameter sensitivity for Mg₂(dobdc). Costs are taken at reported yields so as to identify the most significant factors including the need for optimization.

LAG, resulting in a reduction of \$27.87/kg_{MOF} for solvent cost. Organic solvents are eliminated altogether in the aqueous synthesis, resulting in a cost reduction of \$28.27/kg_{MOF} for solvent costs. Manufacturing costs are also lower for LAG and aqueous synthesis methods. LAG methods reduce the cost of MOF manufacturing through a reduced reactor volume and reduced operation times. The combined reductions in volume and operating times reduce the number of simultaneous

production lines required, resulting in a manufacturing cost reduction of \$31.92/kg. Aqueous manufacturing methods similarly reduce process operation time, which also reduces the number of simultaneous production lines required, resulting in a manufacturing cost reduction of \$31.52/kg.

Cost Comparison at Common Yield. Yields above 90% have been demonstrated by Das et al., and it is reasonable to expect all future MOFs will reach that approximate level when

fully optimized.²⁸ Consequently, the MOF cost analysis was repeated with all four MOFs and three synthesis routes at 92% yield, so as to highlight fundamental differences, while eliminating yield-based differences, due to different levels of MOF process optimization. Figure 4 shows cost breakdowns for materials and manufacturing compared for the three industrial-scale synthesis methods at 92% yield. Both the baseline and LAG costs are lowered due to increasing the yield from 69% to 92%. Material costs (primarily linker and metal salt) are lowered by increased yield, but gains are modest due to the high reactant recycle rates assumed in the baseline process. Manufacturing costs are reduced more significantly by increased yield, owing to the lower capital expenditures for a given production rate.

Sensitivity Analysis. Sensitivity studies were conducted to further examine cost drivers beyond simple materials and synthesis methods and to identify areas for future research that will further lower costs. Five parameters (shown in Figure 5), in addition to LAG and/or aqueous methods, were varied to determine which factors may have the largest impact on cost reduction. Switching processing from solvothermal to LAG or aqueous syntheses had the largest impact, as both approaches significantly reduce solvent cost. The next most influential parameter to the baseline cost is the mass ratio of salt-and-linker to solvent. This ratio, set at a baseline value of 2.5%, leads to high solvent usage and high reactor volume, and ideally would be much higher in a practical, compact, and cost efficient future plant. However, the ratio is limited by the inherent solubility of salt and linker in the solvent. Further research is required to explore solubility limits and to possibly find future low-cost solvents with greater solubility characteristics. Predictably, yield is also a large cost driver, and any cost-effective production site will seek to maximize yield. By “stacking” and adjusting certain parameters from the sensitivity (as shown in Figure 6), a pathway to reducing the price of the MOF can be identified. Both LAG and aqueous routes, in combination with other improvements, hold promise to approach or be better than the \$10/kg_{MOF} target. It is worth noting that adoption of the LAG or aqueous pathways alone is almost enough to reduce the cost of producing MOF below \$10/kg. In fact, the LAG method reduces the cycle time and the organic solvent usage so much that increasing the yield by 23% has little effect on the overall production cost.

DISCUSSION

Solvent costs (even while assuming a solvent recycle rate of 90%) are a driving cost parameter of the industrial solvothermal baseline production method and account for more than 79% of the material costs for Mg₂(dobdc), 60% for Ni₂(dobdc), 69% for MOF-5, and 40% for HKUST-1. Achievement of high solvent recycle rates is, therefore, crucial, and the 90% recycle rate assumed for all materials (solvent, unreacted salt, and unreacted linker) in this analysis has not been publically demonstrated. Lowering the recycle rate would naturally raise the cost of production, as is further illustrated in Figure 5. Further research is needed to determine if such high recycle rates of organic solvents are feasible without affecting product quality.

Not surprisingly, reducing solvent usage will also be necessary in order to produce large quantities of MOF at low costs. LAG and aqueous methods lead to significantly lower materials and manufacturing costs compared to solvothermal methods. At 92% yield, Mg₂(dobdc) produced by LAG shows a

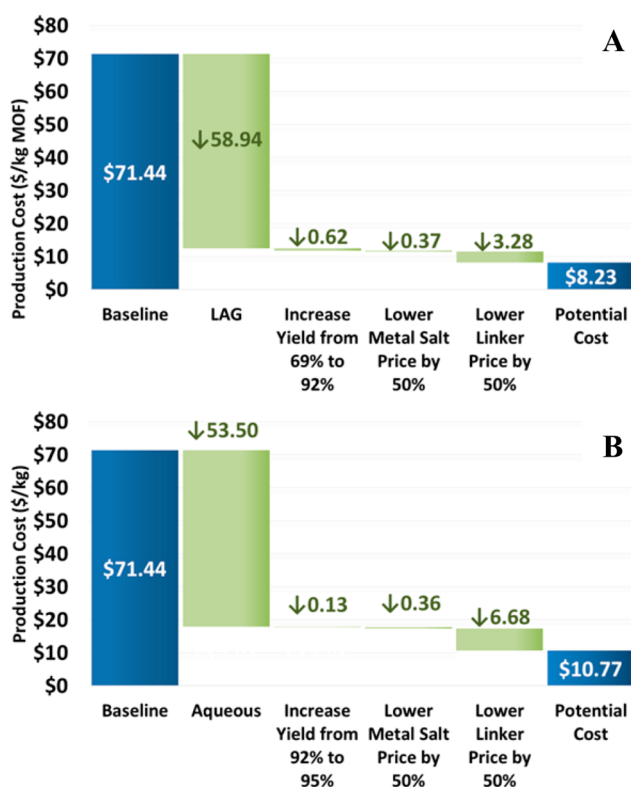


Figure 6. Waterfall charts for Mg₂(dobdc) showing the potential costs of utilizing (A) LAG and (B) aqueous methods with reduced material prices to lower MOF costs.

74% decrease in material costs (with 99% of the decrease being directly attributed to the solvent cost contribution) and an 84% decrease in manufacturing costs when compared to the baseline solvothermal synthesis method. These steps alone almost achieve the ARPA-E target price of \$10/kg_{MOF}, and only require an additional \$1.88/kg savings to make the target price.

The aqueous solution chemistry for Mg₂(dobdc) yields large material cost savings (up to 52%) and leads to a large reduction in total cost (up to 63%). Additional cost reduction opportunities exist through temperature and processing time optimization. The aqueous synthesis procedure requires the synthesis reactor contents to be held at reflux for 1 h. Maintaining reflux for such a large volume consumes a large amount of energy. As such, large and expensive heaters are required for the aqueous synthesis route, though the capital cost is less of an impact than the energy requirements. Optimization of the manufacturing process steps is a viable cost reduction strategy. Reducing the reflux time to 30 min would reduce the MOF cost by only ~2%. However, increasing the salt-and-linker:solvent ratio (currently at less than 3% for the baseline synthesis of Mg₂(dobdc)) to 10% offers a price reduction of approximately 50% in the baseline synthesis method.

CONCLUSIONS

The results of this study identify cost drivers and highlight two potential pathways to significantly reduced MOF production cost at an industrially relevant scale. Four MOFs were examined with generally similar cost trends thereby suggesting widespread applicability of the findings. Furthermore, these results quantify the impact of two synthesis alternatives (LAG and aqueous) to the traditional solvothermal approach (see

Table 4. Comparison of MOF Production Prices for 50,000 Systems Per Year at Reported Yields^a

| | | thermosolvent | LAG | aqueous | potential cost | |
|--------------------|-------------------------|---------------|---------|--------------|----------------|--------------|
| | | | | | LAG | aqueous |
| total cost | Ni ₂ (dobdc) | \$58.69 | \$20.55 | \$19.41 | \$12.11 | \$12.58 |
| | Mg ₂ (dobdc) | \$71.44 | \$12.50 | \$17.94 | \$8.23 | \$10.77 |
| | MOF-5 | \$34.76 | \$13.85 | not analyzed | \$8.34 | not analyzed |
| | HKUST-1 | \$53.75 | \$35.73 | not analyzed | \$17.62 | not analyzed |
| material cost | Ni ₂ (dobdc) | \$38.28 | \$17.24 | \$13.66 | \$9.05 | \$6.83 |
| | Mg ₂ (dobdc) | \$36.11 | \$9.09 | \$14.13 | \$5.10 | \$7.05 |
| | MOF-5 | \$32.09 | \$11.20 | not analyzed | \$5.95 | not analyzed |
| | HKUST-1 | \$38.67 | \$32.93 | not analyzed | \$15.38 | not analyzed |
| manufacturing cost | Ni ₂ (dobdc) | \$20.41 | \$3.31 | \$5.75 | \$3.06 | \$5.75 |
| | Mg ₂ (dobdc) | \$35.33 | \$3.41 | \$3.81 | \$3.15 | \$3.71 |
| | MOF-5 | \$2.67 | \$2.65 | not analyzed | \$2.39 | not analyzed |
| | HKUST-1 | \$15.08 | \$2.80 | not analyzed | \$2.24 | not analyzed |

^aPotential cost values show the lowest potential price as described in the water fall charts in Figure 6.

Table 4). Implementation of LAG or aqueous synthesis is projected to lead to greater than 50% MOF cost reduction. When combined with other improvements, the projected costs approach the \$10/kg ARPA-E target for natural gas storage. These low-cost MOFs would be invaluable in helping to achieve the DOE targets for a low-cost H₂ storage system, as well as for many other potential MOF applications.

Both LAG and aqueous methods offer significant cost reductions, achieved primarily by reducing the use of organic solvent and, subsequently, manufacturing costs. Both methods are projected to achieve similar cost reductions, suggesting that both LAG and aqueous solution chemistries merit further process evaluation. Ultimately, the selection of synthesis method will be determined by which method fits best with a particular MOF. The possibility of combining LAG and aqueous methods into a single production method is worth further investigation.

It is also recognized that a fully continuous synthesis operation has the potential for further cost opportunities. For direct comparison and extension from laboratory-scale, the scope of this analysis was based on a large-scale batch synthesis with certain steps that could be implemented with a pseudocontinuous operation such as drying and shaping. A future study should be conducted to evaluate each process step to determine the most suitable approach between continuous and batch processing since certain batch process operations may still be optimal.

As solvent costs are a significant cost contributor, demonstration of high solvent recycle rates ($\geq 90\%$) is crucial to achieving even the moderate to high cost projections made within the analysis for solvothermal syntheses. This will be particularly important for MOFs that may not be amenable to aqueous or mechanochemical syntheses. Studies to minimize solvent usage are also recommended to both reduce material cost and reduce the size of reactors (and thereby reduce manufacturing cost).

Finally, after solvents, linker costs are a large contributor to MOF costs. Overall process optimization may further lower the total MOF cost by improving the process yield. In addition, for Mg₂(dobdc) and Ni₂(dobdc), we note that analogous MOFs recently synthesized using a less-expensive isomer of the dobdc⁴⁻ linker, specifically 4,6-dioxido-1,3-benzenedicarboxylate, can be expected to significantly reduce MOF cost, while also boosting the H₂ and possibly NG storage capacities.⁷ The production methods described here have used fairly low

temperatures (20–120 °C), with little consideration for pressure optimization, and only one examination of synthesis reaction time. Each of these parameters can have a significant effect on yield and (perhaps redundantly) cycle time. Cost estimates were largely projected for all MOFs with a 92% yield based on the assumption that process optimization could achieve that performance level, although this may not have been demonstrated for all MOFs.

More than 20,000 different MOF compounds have been reported in the literature and that number continues to grow. Existing and newly identified materials should have their costs and manufacturing processes critically assessed so as to identify cost drivers. Such assessments can then lead to process optimization, higher yields, lower material costs, and simplified synthesis. In addition, increases in MOF adsorption performance can also reduce the material quantity required within the system and lead to lower overall cost. Pursuing the recommendations outlined within this techno-economic analysis provides a pathway for researchers to achieve DOE and ARPA-E cost targets for MOFs in the future. The results of this analysis are expected to be generally valid for other MOFs and highlight avenues of investigation for the R&D community to address MOF costs.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.6b02510.

Material price tables, reaction conditions, and expanded data set for baseline production costs (PDF)

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Notes

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ABBREVIATIONS

- AFV = alternative fuel vehicles
DMF = dimethylformamide
DOE = Department of Energy
EtOH = ethanol
H₂ = hydrogen
LAG = liquid assisted grinding
MeOH = methanol
MOF = metal organic framework
NG = natural gas

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