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Estimating the Cost of Organic Battery Active Materials: A Case Study on Anthraquinone Disulfonic Acid

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0. Abstract

Redox-active organic molecules (ROMs) are an attractive alternative to the inorganic, charge-storing compounds typically used in modern batteries as they exhibit potentially superior electrochemical properties, a wide materials design space, and an abundance of raw constituent materials, which, in turn, may open pathways to inexpensive energy storage. However, as most of these molecules are not produced on a commercial scale, assessing the cost proposition of new ROMs is a challenging but critical task for projecting the economic viability of incipient battery technologies. Here, we evaluate different cost estimation methods, explain their application, and determine their practicality for newly developed materials. For this purpose, we use anthraquinone disulfonic acid as a benchmark material, as this compound has been proposed for redox flow batteries and is already produced on an industrial scale. Our results show that simple cost estimation methods are easy to apply but ultimately fail to provide reliable cost information due to their limited accuracy. In contrast, more advanced methods offer more consistent and precise cost estimates but depend on detailed process knowledge rarely obtainable for new organic molecules. Furthermore, our cost analysis proves the feasibility of ROMs at the costs necessary to enable grid storage technologies that meet established cost targets.

Keywords: techno-economic modeling, process modeling, redox-active organic molecules, 9,10-anthraquinone-2,7-disulfonic acid, Aspen, grid energy storage

1. Introduction

Rechargeable batteries are in the midst of a technological renaissance with applications varying from microelectronics to grid-scale energy storage.[1,2] While most commercialized secondary batteries rely on intercalation (e.g., lithium-ion), metal redox reactions (e.g., nickel metal hydride, vanadium redox flow), or inorganic phase transformations (e.g., lithium-sulfur, sodium-nickel chloride molten-salt) for charge storage,[2] redox active organic molecules (ROMs) offer an intriguing alternative due to the possibility for multi-electron transfer, improved power, mechanical flexibility, and high gravimetric capacity.[2–10] Furthermore, a broad design space is potentially accessible for ROMs as substituent groups can be introduced to tune physicochemical characteristics (e.g., redox potential, solubility), providing an elegant toolbox for engineering materials tailored for a particular battery system.[5,6] Finally, ROMs are especially attractive in supplanting several incumbent inorganic materials for batteries given that ROMs are comprised of earth abundant elements (i.e., hydrogen, carbon, oxygen, nitrogen, sulfur), and their cost is not determined by production rates of raw materials or materials reserves.[5,6]

While certain ROMs may offer cost benefits over inorganic alternatives, not all organic molecules are inherently inexpensive. The cost of an organic material depends on the synthetic route to produce the molecule and the costs of all precursors and reagents. Evaluating the cost of a novel ROM can be particularly challenging because, prior to validation as a battery material, the molecules of interest are rarely produced on the commercial scale and, typically, battery researchers do not engage in process design. Even if a ROM is commercially available through a specialty chemical supplier in small quantities (e.g., Sigma-Aldrich), these prices do not necessarily reflect chemical prices at the production scales required for mass battery manufacturing. Adding to the complexity of evaluating new molecule costs, literature estimates for chemical costs are limited and usually outdated, and attempts to extrapolate present-day chemical cost from historic data often leads to inaccuracies.[11] Moreover, while consultancy reports often provide valuable and accurate cost estimations, these reports are expensive and typically available for only widely produced chemicals, not novel ROMs.

Various modeling methodologies of differing complexity and accuracy exist to estimate the costs of new organic materials. The least information-intensive are step-counting methods, which consider the number of major process steps and chemical yields to estimate capital investment using algebraic correlations. While incredibly simple to implement, these methods typically result in the highest possible cost uncertainty. By contrast, the equipment list method, which requires creating a list of all major process equipment, can be very accurate but requires a significant amount of information

regarding the price of each component in the chemical plant and requires time-consuming calculations. Arguably, the most accurate and intensive estimation method is to implement the Aspen Process Economic Analyzer (APEA) software package, which requires a simulation of the entire chemical plant, including kinetic rates and thermodynamic properties. While this method can produce extremely accurate cost estimations, process flow diagrams are typically unavailable for new molecule synthesis, so the APEA method may be unrealistic to implement for many emergent organic materials.

Evaluating the aforementioned cost estimation methodologies for ROMs in battery applications requires a benchmark material to which all three methods can be applied. Thus, the benchmark material should be an established industrial compound with a well-known production process. Anthraquinone disulfonic acid (AQDS) is arguably the state-of-the-art active organic material for aqueous redox flow batteries (RFBs), due to its stability, solubility, and redox potential.[12,13] Similar anthraquinone derivatives have found application as positive electrode materials in several flow and enclosed batteries.[14] In general, grid storage batteries, such as RFBs, are expected to meet more stringent cost and performance targets than batteries for mobile applications (e.g., portable electronics, transportation) and long term capital cost targets have been outlined by the U.S. Department of Energy and other organizations [15]. As such, we compare the computed AQDS costs to recommended aqueous flow battery active material costs ($\leq \$5 \text{ kg}^{-1}$), which are derived from detailed techno-economic modeling [16,17] and could enable the Department of Energy installed system cost target of $\$150 \text{ kWh}^{-1}$ (for 4 hours of storage).[15]

AQDS provides a suitable benchmark because many water-soluble anthraquinone derivatives already have applications in the dye industry or as catalysts for the production of hydrogen peroxide.[18,19] Due to broad industrial implementation, a large amount of process knowledge exists for anthraquinone derivatives, as compared to other ROMs (e.g., TEMPO, viologens).[13,19–25] The AQDS production process (Figure 1) begins by distilling crude tar to isolate anthracene oil, which is then refined in several steps to produce anthracene ($\approx 1.5 \text{ wt\%}$ of crude tar) with approximately 95% purity.[26,27] In the next step, anthracene is oxidized to anthraquinone in air at elevated temperature. Finally, the anthraquinone is sulfonated with oleum (i.e., fuming sulfuric acid), yielding a mixture of anthraquinone-2-monosulfuric acid, anthraquinone-2,6-disulfonic acid and anthraquinone-2,7-disulfonic acid.[28–30]

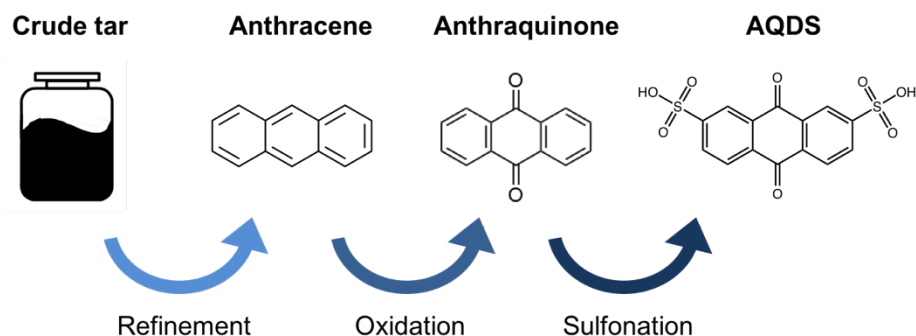


Figure 1: Schematic overview of the production process to generate AQDS from coal tar.

This study compares cost of AQDS estimated by the step-counting, equipment list, and APEA methods as a case study in evaluating cost prediction methods for new ROM-based battery materials. Each method is described in detail and then executed to estimate AQDS cost per unit mass ($\text{\$ kg}^{-1}$) as a function of production quantity; we also compare outcomes from each cost estimation method. For the information-intensive APEA method, relevant thermodynamic data unavailable in literature is estimated using density functional theory. Additionally, identifying reliable anthracene pricing is challenging, so AQDS cost is evaluated across a range of possible anthracene prices. Furthermore, we compare the AQDS cost per unit mass and capital expenditure when AQDS is synthesized in two steps (e.g., anthracene precursor), or in a single step (e.g., anthraquinone precursor). Ultimately, this study recommends the best routes for estimating costs of new ROMs and quantitatively evaluates the cost-effectiveness of AQDS in energy storage applications by comparing computed costs to a techno-economic informed target of $\text{\$5 kg}^{-1}$ for grid-scale flow batteries.[16] Although this work focuses on estimating AQDS cost, these methods are portable and can apply to a variety of charge-storing organic molecules, provided sufficient production process knowledge is available.

2. Methodology

2.1 Contributions to Manufacturing Cost

Estimating the production costs of organic active materials requires the compilation of all contributions to the final chemical cost, which is generally referred to as the “cost of manufacturing,” and incorporates plant construction, operation, depreciation of capital investment, and direct production (e.g., raw materials, utilities).[31] The initial capital investment required to build and operate a chemical plant is referred to as the capital expenditure (CAPEX) and consists of four major contributions: 1) inside battery limit (ISBL), 2) offsite battery limit (OSBL), 3) engineering costs, and

4) contingency costs. The ISBL includes all costs directly associated with constructing the chemical plant, such as equipment and installation. The OSBL includes contributions from additions or improvements to the site infrastructure, such as power lines, maintenance facilities, or pipelines. Engineering cost considers engineering design and other services, such as contractor fees, and the contingency costs account for the uncertainty associated with estimating the CAPEX. In our estimate, we assume the contingency cost is equivalent to 20% of the combined ISBL and OSBL.[32]

The operational expenditure (OPEX), which is comprised of fixed and variable costs, is defined as the cost associated with operating the chemical plant. The fixed OPEX includes labor, maintenance, and overhead. The operating labor costs are estimated from the number of shift positions required to operate the chemical plant and process type (e.g., batch or continuous).[32] Next, we assume a salary for laborers in a chemical plant of \$50,000 per year, a typical salary for a shift worker employed in the United States' Gulf Coast.[32] In practice, this number can be adjusted to incorporate differences in regional wage rates, inflation, work experience, and economic conditions. Additional labor costs for supervision and overhead are also included. Maintenance includes the cost of repairing or replacing plant equipment, and overhead includes administrative, research, and development costs. Additional labor, maintenance, and overhead costs are all estimated as fractions of the CAPEX or operating labor costs. The variable OPEX contributions considers raw material costs, estimated from the mass balance of the production process (kt/y) and prices (\$/kg), as well as the utility (e.g., electricity) and wastewater treatment costs that are proportional to production quantity.

We assume that AQDS is implemented directly into a flow battery after production, and, as such, do not consider the cost of packaging, shipping, sales, or product marketing. Further, property taxes, land lease, and environmental charges are neglected because these costs are generally small and can vary significantly with location.[32] In addition, we neglect licensing fees for the production process, assuming the chemical producer owns all relevant intellectual property rights. Finally, no capital charges are included because we anticipate equity financing, instead of debt financing, so no additional interest costs should arise.[32]

Considering the three cost estimation methods under investigation (step-counting, equipment list, and APEA), the former two are used to explicitly calculate the ISBL, from which many other cost contributions are calculated using the approximation principles outlined in Table 1. As such, acquiring an accurate ISBL estimate is of paramount importance for the step-counting and equipment list methods, since many other cost contributions are computed as fractions of the ISBL. For the APEA

method, all costs are computed automatically from the process steps, production quantity, and material specifications.

Table 1: Overview of cost contributions to the total cost of manufacturing, as well as typical estimation methods.[32–34]

Cost	Description	Estimation
Inside Battery Limit (ISBL)	Purchasing and installation of process equipment that comprises the plant	Step-counting, equipment list
Offsite Battery Limit (OSBL)	Costs of improvements to the infrastructure	40% of the ISBL when no details of the site are available (applies to all included cases)
Engineering Costs	Cost of detailed engineering and other engineering services	Small projects: 30% of ISBL + OSBL Large projects: 10% of ISBL + OSBL
Contingency	Model uncertainty	Minimum: 10% of ISBL + OSBL Typical: 20% of ISBL + OSBL
Labor	Operating labor, supervision, management, and overhead	Operating labor algorithm[32], Supervision and management: 25% of operating labor Overhead: 40-60% of operating labor + supervision (we use 50%)
Maintenance	Repairing or replacing equipment with associated labor	3% of ISBL
Overhead	General administrative, R&D, sales, and marketing	65% of labor and Maintenance + 2% CAPEX
Raw Material Costs	Raw materials consumed by the process	Mass balance on production process, raw material costs
Utilities	Fuel, process steam, electricity etc.	10% of OPEX
Waste Treatment	Waste disposal	Wastewater treatment: \$1.5 per metric ton Solid waste: \$50 per metric ton

2.2 ISBL Estimation Methods

As previously mentioned, several cost contributions are typically estimated as a proportion of the ISBL, therefore the accuracy of the ISBL estimate has a large influence on the accuracy of the entire estimate.[32] The Association for the Advancement of Cost Estimating International (AACE) defines five classes of cost estimates (Table 2) characterized by accuracy and the amount of information (or effort) required to create the estimate.[35] Typically, Class 5 estimates, which carry the highest degree of uncertainty, are based on existing chemical plant cost information. Given that chemical plants do not exist for new battery materials, we investigate step-counting methods that promise the fastest route to estimating the ISBL. From process flow diagrams (PFDs) available in peer-reviewed and patent literature, sufficient information is available to perform Class 4 and Class 3 estimates. The equipment list method for estimating ISBL is typically considered to be Class 4, whereas the APEA represents a Class 3 method. The frameworks of the equipment list and APEA methods are sufficiently flexible that either method could offer as high as a Class 2 designation, provided sufficient process information is available. In the present analysis, considering the paucity of accessible process information on the

public domain, we conservatively label the equipment list and APEA methods as Class 4 and Class 3 estimates, respectively.

Table 2: Cost Estimate Classification Matrix for Process Industries defined by the AACE.

Estimate Class	Project Maturity	Methodology	Expected Accuracy
5 - Order of Magnitude	0-2%	Capacity factored, parametric models, judgment or analogy	-50% to +100%
4 - Preliminary	1-15%	Equipment factored or parametric models	-15% to +50%
3 - Definitive	10-40%	Semi-detailed unit costs with assembly level line items	-10% to +30%
2 - Detailed	30-75%	Detailed unit cost with forced detailed take-off	-5% to +20%
1 - Check	65-100%	Detailed unit cost with detailed take-off	-3% to + 15%

2.3 Step-Counting Methods

Several authors have proposed step-counting methods to estimate the ISBL of chemical plants.[36–38] While each method differs slightly in implementation, step-counting methods generally require structuring the production process into major steps and subsequently correlating the number of process steps with total capital investment. As such, step-counting methods are extremely easy to implement and only require basic knowledge of how a chemical is produced. In this work, we will focus on the Bridgewater method, the most widely-applied step-counting method.[39] Other common step-counting methods include the Taylor and Viola methods. The Taylor method requires detailed knowledge of process conditions that are typically unknown for a newly proposed material, making it unsuitable for chemicals not yet produced on a large scale. Further, with the amount of information required to engage the Taylor method, an equipment list or APEA estimate could be made with much greater accuracy. The Viola method requires historical cost curves and thus is inapplicable for new materials when historical cost information is unavailable, such as the case here.

The Bridgewater method requires identification of the number of major process steps, determined from laboratory synthesis steps (i.e., Figure 1) or a PFD. The “major process steps” are defined as groups of several process units that together perform one function. As a practical example,

“separation” can typically be regarded as a major process step, incorporating a distillation column, heat exchangers, and condensers required to perform the task. The Bridgewater method utilizes the correlation in Equation (1), where N is the number of process steps, Q is the production capacity (metric tons per year), and s is a conversion factor defined as the ratio of product mass to reactor feed mass. The prefactor (397043) and exponent (0.3) in Equation (1) are updated according to the Chemical Engineering Plant Cost Index (CEPCI) of 2015 for a chemical plant operating on the US Gulf Coast.[40]

$$C = 397043 \cdot N \cdot \left(\frac{Q}{s} \right)^{0.3} \quad (1)$$

2.4 *Equipment List Method*

Another common method for ISBL estimation for a chemical process is to generate a list of major process equipment and directly compute the associated capital cost. For simplicity, we refer to this as the equipment list method. When available, the costs of equipment can be collected from vendors, price databases (e.g., Aspen ICARUS), or published cost correlations, which are mathematical relations that estimate equipment cost based on production volume. For our equipment list estimate, we use published cost correlations because vendor catalog prices are not publicly available; we also reserve price databases for our APEA estimate. Generally, the equipment list method requires significantly more information to estimate the ISBL than step-counting methods, but the complexity of the equipment list model can be easily updated over time as additional details of a production process are unveiled.[32–34]

Beyond the capital investment of purchasing equipment, installation costs must also be considered to determine the ISBL. Two common factorial methods are used to estimate installation costs from equipment purchasing costs. First, the Lang method multiplies the cost of each piece of equipment using a factor determined by the plant size, providing a rough approximation of installation costs.[41] A second set of multiplicative factors, proposed by Hand, are more detailed, varying with the equipment type.[42] In this work, we implement the Hand factors due to their improved accuracy. Both the Lang and Hand methods account for engineering costs, and, as such, engineering costs are not double counted when compiling the final CAPEX. Also note that installation cost factors must be updated to account for price increases over time that include inflation and increases to wages and transportation costs. Finally, most equipment and installation cost correlations assume carbon steel as

the construction material, and alternative materials will require additional materials-specific multiplicative factors.[32,33]

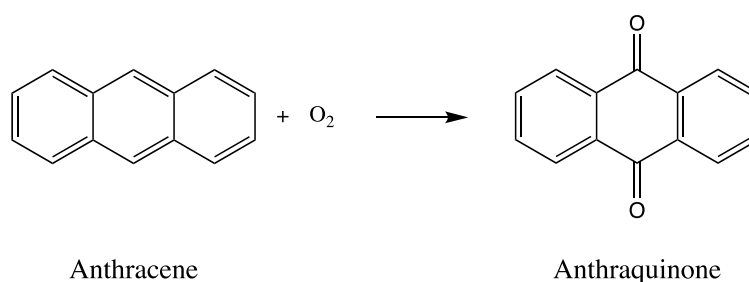
2.5 Aspen Economic Analyzer

The third and final method investigated in this work is a cost simulation of a chemical plant with the APEA, a package included within the industry-standard process simulation software Aspen Plus. The APEA estimates the CAPEX using proprietary models and correlations, and specifications not explicitly included in the APEA database are computed automatically from the process simulation. The APEA also automatically computes the OPEX from the mass and energy balance of the process simulation. Generating an APEA cost estimate begins with an entire simulation of the production process in the Aspen Plus software, and each process unit must be mapped to a specific equipment type. For example, a heat exchanger can be mapped as a tube and shell or U-tube design. Once the mapping is complete, the APEA calculates the CAPEX and OPEX.[32,43] The major challenge associated with the APEA method is the large amount of detailed process information required for the simulation to converge. At a minimum, a simplified PFD with operating conditions is required, and this level of knowledge is likely unavailable for new organic battery materials. Additionally, new materials are unlikely to exist within the Aspen materials database, and the relevant thermodynamic information (i.e., enthalpy of formation) required to manually specify new materials properties may be unknown necessitating additional experimentation.

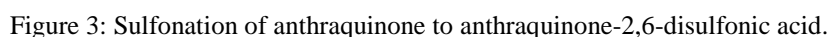
3. Cost Modeling and Results

3.1 Production of AQDS

Two industrially relevant oxidation processes exist for producing anthraquinone from anthracene: oxidation via chromic acid or direct oxidation with air.[44] In this work, we investigate anthracene oxidation in air (Figure 2), which offers both high yield and high purity (99.6%).[45] We assume that the anthraquinone product obtained from direct oxidation in air is of sufficient purity as to enable direct use in the subsequent sulfonation reaction.



The sulfonation of anthraquinone occurs with oleum (balance sulfuric acid), yielding a mixture of anthraquinone-2-sulfonic acid, anthraquinone-2,6-disulfonic acid, and anthraquinone-2,7-disulfonic acid (Figure 3).[19] We assume the various sulfonated anthraquinone derivatives are all adequate for implementation in a battery,[12] and, therefore, no additional steps are required to separate the various sulfonated products. Additionally, the anticipated yields of 28.3% anthraquinone-2,7-disulfonic acid, 60.6% anthraquinone-2,6-disulfonic acid, and 2.7% anthraquinone-2-monosulfonic acid indicate that the quantity of monosulfonic acid derivative in the product mix is almost negligible.



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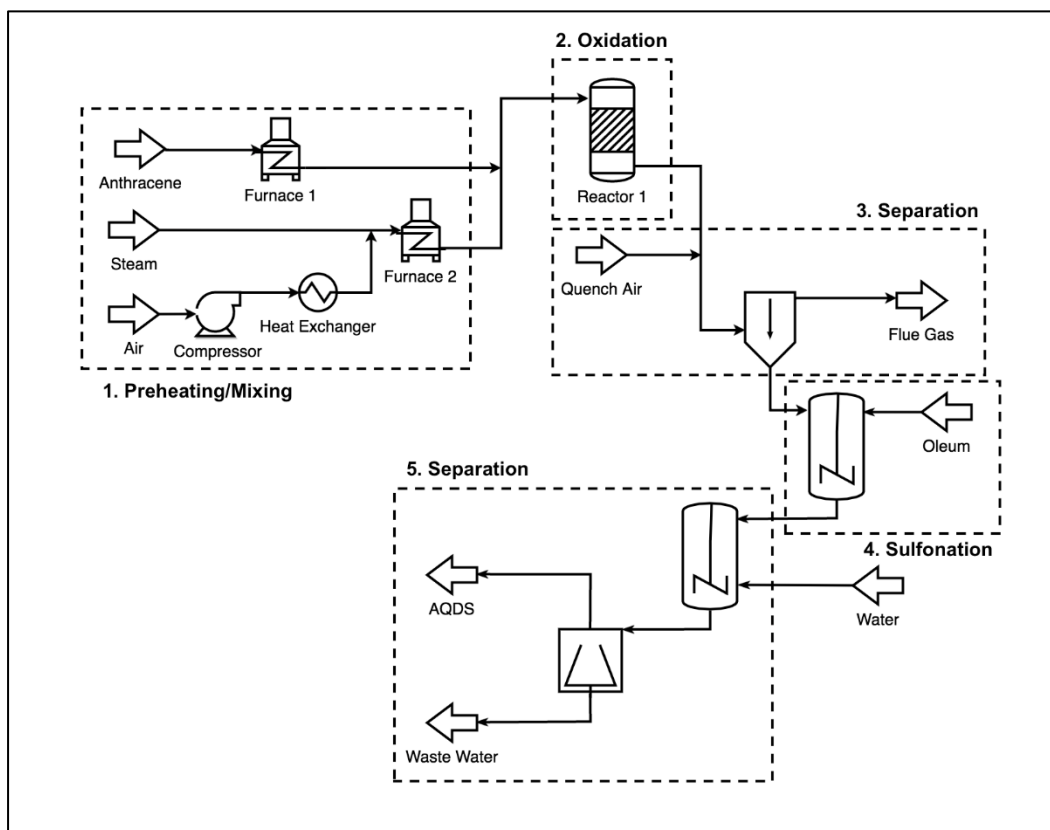


Figure 4: Process flow diagram of the production process of AQDS from anthracene.

3.2 Anthracene Price Range

In this work, we assume that building a plant to generate AQDS from crude tar is impractical for a battery manufacturer, considering that crude tar offers many more valuable products than anthracene. As such, we take anthracene as our initial precursor in the process model meaning that an anthracene price must be assumed. A reliable anthracene price is not readily available in the public domain, so we estimate upper and lower bounds based on the pricing of other crude tar derivatives and assume that anthracene prices will lie within this range. As a lower bound, we assume that anthracene price will not be lower than the price of naphthalene (\$0.84 kg⁻¹), the largest component of crude tar (10%) [27,46], and, as an upper price limit, we consider the average price of cresol derivatives (\$5 kg⁻¹) from crude tar.[47] Aside from the upper and lower price bounds, we also assume a nominal anthracene price of \$2 kg⁻¹. [27,47]

3.3 Bridgewater Method

The production process for AQDS is comprised of five major steps, identified by the dashed boxes within Figure 4. We consider an upper bound on AQDS production rate (Q) of 3.4×10^4 metric tons

per year, which is equivalent to the total global annual production of anthraquinone,[45] and a lower bound of 300 metric tons per year. Required quantities of raw material inputs can be back-calculated from the production rates and typical reaction yields. We calculate the conversion factors to be $s = 0.335$ and $s = 0.334$ for the oxidation and sulfonation reactions, respectively. Equation (1) calculates the ISBL, and we estimate the remaining CAPEX and OPEX contributions from the guidelines in Table 1.

The Bridgewater estimate follows the behavior of a typical cost curve (Figure 5a): at low production volumes, the CAPEX increases more rapidly than at high production volumes, therefore, as production quantity increases, the rate of CAPEX increase slows. The OPEX (Figure 5b) increases nearly linearly with production quantity since the major OPEX contribution is the raw material cost (e.g., anthracene). The small deviation from linearity in the OPEX at low production quantities originates from fixed OPEX estimates that are derived as fractions of the ISBL (i.e., maintenance); the ISBL increases relative to the variable OPEX at low production volumes. Generally, we find that the Bridgewater method estimates CAPEX values are significantly higher than the equipment list or APEA methods, but the OPEX estimates are quite similar. Discrepancies among the three methods will be discussed in detail later.

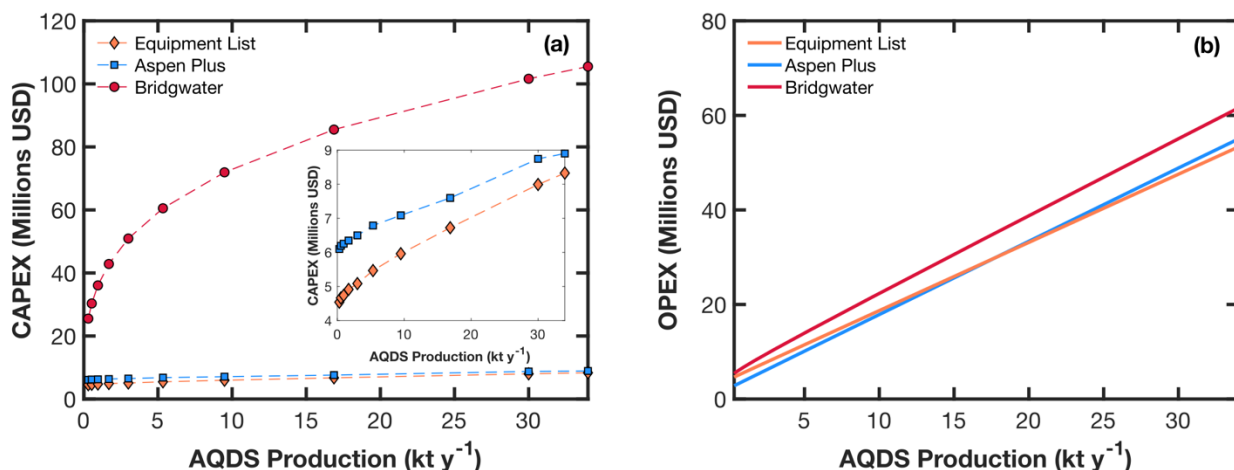


Figure 5: (a) CAPEX and (b) OPEX estimates from the Bridgewater, equipment list, and APEA methods. OPEX estimates assume an anthracene price of \$2 kg⁻¹. OPEX estimates for higher (\$5 kg⁻¹) and lower (\$0.84 kg⁻¹) anthracene prices may be found in the appendix Fig. A1.

Once the CAPEX and OPEX have been calculated, the AQDS cost per unit mass (\$ kg⁻¹) can be determined; we estimate linear depreciation of the CAPEX over 16 years, which is a typical estimate for the petroleum refining industry.[48] For small production rates, AQDS cost decreases rapidly with increasing production rate, while at high production rates, the AQDS cost reaches a minimum plateau

dictated by the variable OPEX (Figure 6). Accordingly, the sensitivity of AQDS cost to the price of the anthracene precursor increases as production quantity rises.

The Bridgewater estimate for AQDS cost is largest across all production volumes when compared to the equipment list and APEA methods, especially at low production volumes where the cost estimate is $\approx 67\%$ larger. Despite the large disparity between the Bridgewater method and the more-refined estimations, the Bridgewater results for AQDS cost are within the specified error range (-50% to +100%) of a Class 5 estimate, when compared to the more reliable equipment list or APEA methods. Thus, we confirm the major drawback of the Bridgewater method: low accuracy due to a minimal set of input variables. Additionally, the Bridgewater method does not provide clear guidelines for determining the major steps of a production process, and consequently, dividing a process into major steps is determined at the discretion of the individual engaging the analysis. Variability in user-identified process steps implies added uncertainty in the critical ISBL estimations. Finally, the prefactor and exponent in the Bridgewater equation are derived from cost correlations for petroleum processing plants, and thus, the correlations may not be representative of other processes.

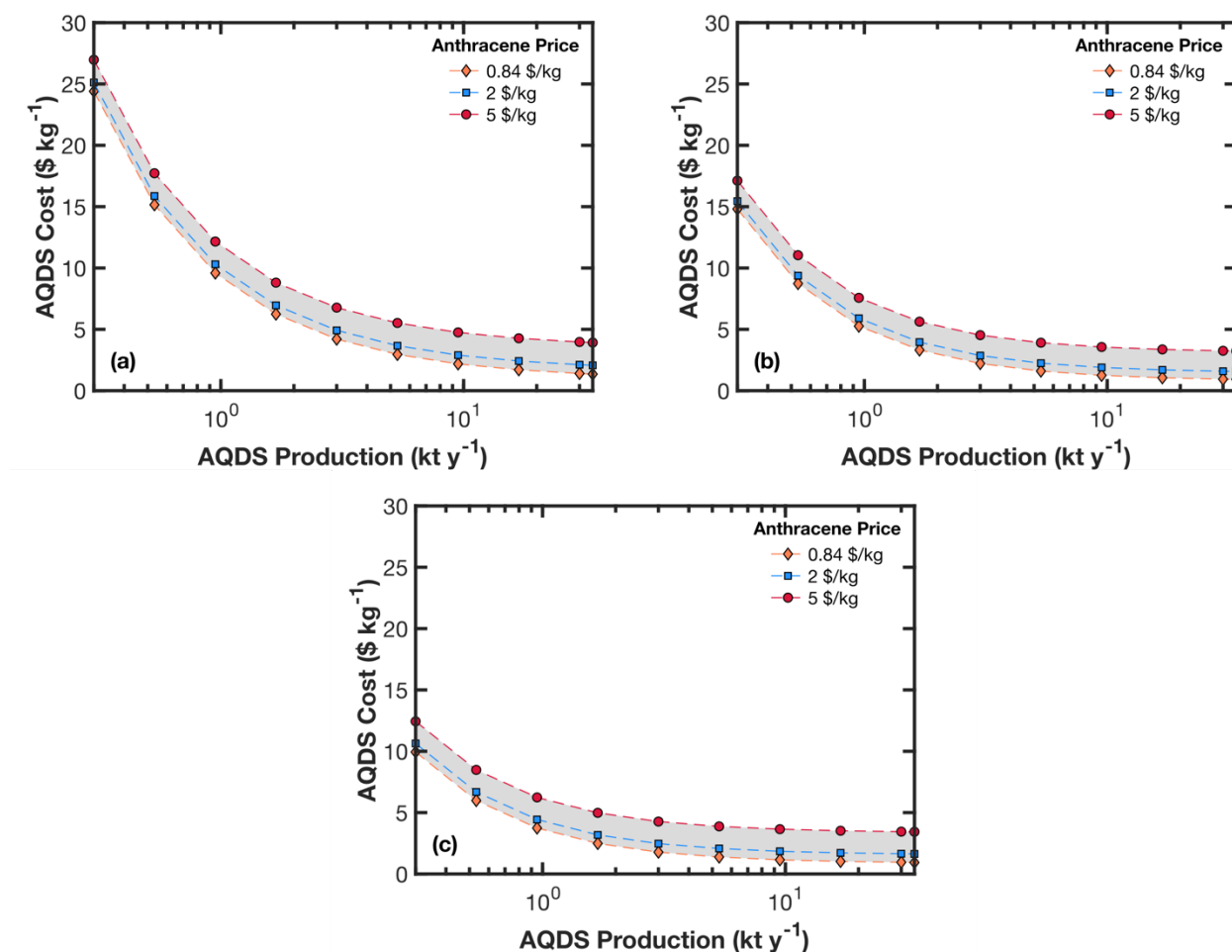


Figure 6: AQDS cost (\$ kg⁻¹) as a function of production quantity calculated from the (a) Bridgewater, (b) equipment list, and (c) APEA methods for various anthracene prices. The gray region represents the feasible range of AQDS costs. Dashed lines only serve as visual aids.

3.4 Equipment List Estimate

Lists of major equipment required for a chemical process can be determined from a process flowsheet diagram (Figure 4). Correlations (Equations (2) and (3))[32,33] are then used to estimate equipment prices (C_p), where S is a sizing parameter and K_{1-3} are equipment-specific constants.

$$C_p = a + b \cdot S^n \quad (2)$$

$$\log C_p = K_1 + K_2 \log S + K_3 (\log S)^2 \quad (3)$$

Determining a sizing parameter is an equipment-specific activity, where S relates to a key attribute of the equipment; for example, the sizing parameter for a heat exchanger is defined by the surface or exchange area of the device[33]. An overview of the equipment specific parameters employed in this work are available in the Appendix.[33]

Battery materials, or other specialty chemicals, are produced in much smaller quantities than commodity petrochemicals, and equipment cost correlations, such as those in Equations (2) and (3) are typically generated for chemicals with extremely large production quantities. As such, the production quantities for specialty chemicals can lie outside the valid range for a given correlation, and typical chemical engineering equipment cost correlations may not be suitable when considering the production of a new chemical. Alternative sources of cost correlations, such as bioengineering publications[49], are considered in the present work, but these correlations may only be valid for small production quantities and are unavailable for all equipment types. To confirm the validity of our selected equipment cost correlations, we compare the calculated cost with values from the APEA, which are in good agreement, lending confidence to the cost correlation methodology. Equipment sizes for this estimate are determined from the later APEA simulation.

The equipment list estimates the lowest CAPEX (Figure 5a) of all three methods considered but is in reasonable agreement with the APEA method. The form of the CAPEX estimate mirrors the behavior observed in the Bridgewater method; the rate of increase in CAPEX slows with higher production quantity. As production quantity grows, the deviation between the equipment list and APEA CAPEX estimates decrease. A possible explanation for the improved agreement between the two methods is that, for the equipment list, some of the lower production quantities are outside the intended correlation range; near these limits, the correlation accuracy tends to decrease. Nonetheless,

the difference between the equipment list and APEA estimates are within the anticipated accuracy range of a Class 3 estimate (-10% to +30%).

The equipment list OPEX estimate (Figure 5b) is in excellent agreement with the other estimation methods under consideration, adding confidence to the ISBL-derived cost component guidelines in Table 1. The small differences in slope and intercept are likely due to differences in utility and fixed OPEX costs. The AQDS cost per unit mass (Figure 6b) generally follows the same trends as the Bridgewater and APEA methods, decreasing steadily with production volume and achieving a plateau dictated by the variable OPEX. The equipment list estimates are less sensitive to changes in production quantity than the Bridgewater estimates, likely due to the more detailed CAPEX calculation. At high production volumes, the equipment list method estimates nearly identical AQDS costs as the other two methods, owing to the excellent agreement in OPEX cost at high production volumes among the three methods.

3.5 *Aspen Process Economic Analyzer*

As previously mentioned, the APEA cost estimate requires a steady-state simulation of the AQDS production process, based on the diagram in Figure 4. Given that anthraquinone is a molecule of interest for major industrial processes, the Aspen materials database contains thermodynamic and physical information for all relevant species in the production of AQDS, except for the final sulfonated anthraquinone derivatives. The enthalpies and entropies of formation for these compounds are unknown, and, as such, we used density functional theory to calculate the missing thermodynamic quantities. The enthalpy and entropy of formation of anthraquinone-2,7-disulfonic acid and anthraquinone-2,6-disulfonic acid were calculated using QChem incorporating density functional theory with the 6-31+G(d) basis set and the B3LYP exchange-correlation functional. The molecule was first subject to a geometry optimization, followed by a frequency calculation, and a single-point energy calculation [50].

3.6 *Mapping*

Once a simulation of the production process is created, each piece of equipment in the production process must be mapped to a specific equipment type. A simple pipe connection is assumed to sufficiently serve as the mixer blocks, which does not incur additional equipment costs. The compressor block is defined as a centrifugal compressor, and we also assume the use of tube and shell heat exchangers. Due to the elevated temperature of the anthracene oxidation reaction, we implement a fired reactor for the oxidation step. The separator block is assumed to be a vertical vessel since the

liquid phase anthraquinone product can simply be separated from the gas phase by settling at the bottom the vessel. While two separate blocks simulate anthraquinone mixing with oleum and subsequent sulfonation reaction, we map both blocks together as a mixed vessel (continuous stirred tank reactor) for the cost estimate. Finally, we assume that AQDS separation from the liquid waste stream is performed in a disk centrifuge.

3.7 Results

As with the equipment list estimate, the APEA CAPEX estimate is much lower than the Bridgewater calculation (Figure 5a) and follows the same functional form. Further, the APEA estimate is in particularly good agreement with the equipment list estimate. The APEA OPEX estimate (Figure 5b) also in agreement with the other two OPEX estimates; again, the larger deviation between the Bridgewater and APEA OPEX at low production quantities is due to the higher CAPEX estimate of the Bridgewater method. The OPEX agreement between the APEA method and the other estimates adds confidence to the OPEX calculation guidelines from Table 1. Further, the AQDS cost per unit mass (Figure 6c) is generally lowest with the APEA estimate, caused by the low CAPEX and OPEX estimate, but approaches similar limiting cost at high production quantities. Of the three methods considered, the APEA is believed to be the most accurate, offering Class 3 certainty.

4. Discussion

4.1 Comparison of Cost Estimation Methods

Each of the three cost estimation methods explored in this paper, the Bridgewater, equipment list, and APEA methods, exhibit unique advantages and disadvantages. The Bridgewater method is the easiest to implement but is also the most inaccurate. The equipment list allows for a detailed accumulation of equipment costs, which can be continuously adapted throughout the growth of a project, but identifying reliable equipment prices poses a major challenge. Finally, the APEA estimate is detailed and offers the best accuracy, but this method is time consuming and requires many process details to converge the process simulation and cost estimate. Generally, the equipment list and APEA methods are in good agreement, estimating CAPEX much lower than the Bridgewater method.

The Bridgewater method may offer a reasonable order-of-magnitude estimate for a chemical cost, but its broad inaccuracy limits practical usefulness. Challenges for the Bridgewater method originate from ambiguous determination of the number of major process steps and historic correlations based on chemicals with very large production quantities, which may not extend to specialty chemicals, such as battery materials. Additionally, the Bridgewater method accounts for the cost of each process step

equally; if a process contains some or all particularly inexpensive or expensive process steps, then the Bridgewater method will be even more inaccurate. We hypothesize that the Bridgewater method will offer the best accuracy for chemical processes with many process steps, where, on average, expensive and inexpensive steps balance the cost estimate. Given that the production of AQDS is a relatively straightforward process requiring relatively inexpensive equipment, the Bridgewater method is unsuitable for the CAPEX estimate.

The equipment list CAPEX estimate offers the greatest transparency and flexibility of all methods considered because the cost correlations for each piece of equipment can be individually specified and the estimate can be updated easily as new equipment pricing information becomes available. Generally, the method is dependable and easy to implement, provided reliable equipment pricing can be identified. Cost correlations are only available for a limited number of equipment types, and, for specialty chemicals, relevant production quantities will likely lie outside the valid range for a given correlation. Additionally, equipment vendors are unlikely to provide price information without a non-disclosure agreement. Even if vendor price information is available, single quotations for a particular equipment size cannot be applied to a cost analysis as a function of production quantity, since equipment size must scale with quantity. Furthermore, the equipment list method necessitates that the required process equipment is known, which may not be the case for a new material synthesized only at laboratory scale.

The APEA arguably offers the most trustworthy and accurate cost estimate of the three methods explored. The primary advantage of the APEA is the ability to tether the cost estimate with a simulation of the entire chemical production process, allowing for interpolation of unknown process parameters and automatic sizing of equipment. Furthermore, the software contains a database with a wide range of equipment cost correlations, so the APEA method applies rigorously to a broad variety of processes. The cost correlations included within the APEA, however, are proprietary, and, therefore, the APEA is much less transparent than manually constructing an equipment list. Additionally, identifying relevant thermodynamic data for new chemicals required to implement the Aspen process simulation can be difficult. Finally, the Aspen software package is expensive and converging a simulation requires a high degree of user expertise, both of which may deter future users.

4.2 *AQDS Cost*

Considering the cost estimation results from all three methods, AQDS can achieve or surpass the benchmark price of \$5 kg⁻¹ across the range of realistic anthracene prices (\$0.84 kg⁻¹ to \$5 kg⁻¹),

provided that the production quantity is sufficiently high. Figure 7 directly compares AQDS cost, assuming \$2 kg⁻¹ anthracene price, for the three cost estimation methods. Similar figures assuming anthracene prices of \$0.84 kg⁻¹ and \$5 kg⁻¹ are provided in the appendix (Figure A1). At large production quantities, all three methods converge to the same AQDS cost, which is dictated by the variable OPEX. Given the good agreement among the three methods at high production quantities, we suggest that the variable OPEX, as calculated by any of the methods, offers a suitable estimate for the lower bound of the cost of a new material.

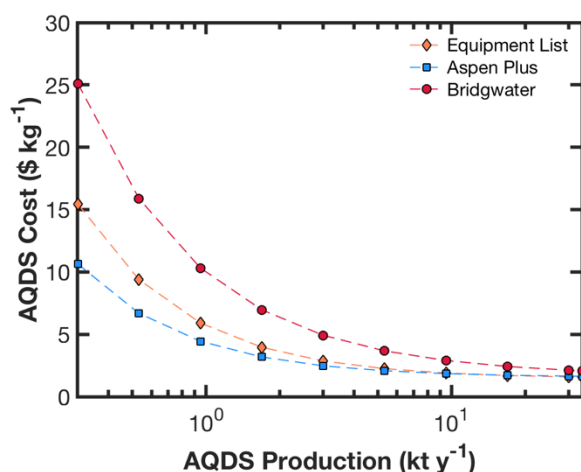


Figure 7: AQDS costs (\$ kg⁻¹) as a function of production quantity for the three estimation methods, assuming \$2 kg⁻¹ anthracene price.

We next consider the relative contributions of the CAPEX, fixed OPEX, utilities, and raw materials to the APEA estimate (Figure 8, \$2 kg⁻¹ anthracene price). The CAPEX and fixed OPEX both decrease with production quantity, with fixed OPEX as the dominant cost contribution at low production quantities. Since raw materials are defined as variable operating costs, they contribute as a constant value to the chemical cost per unit mass regardless of production quantity; we assume no price discount with increasing purchase volume of raw material. At high production quantities, raw materials dictate the chemical cost, since utility costs are quite small in comparison (Figure 8). This finding reinforces the notion that the lower bound cost for a new chemical may be estimated from just the cost of the raw materials, assuming the raw materials dominate the variable OPEX (i.e., not utilities).

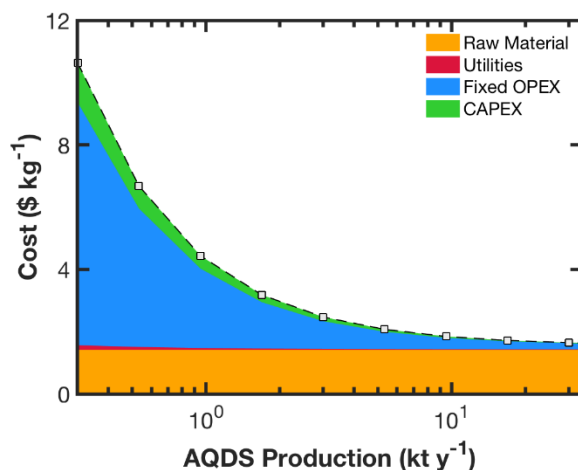


Figure 8: Contributions to AQDS cost per unit mass as a function of production quantity for the APEA estimate, assuming \$2 kg⁻¹ anthracene price.

4.3 Changing Precursors and Minimizing CAPEX

Although the raw material cost dictates total AQDS cost per unit mass at high production quantities, the CAPEX plays a pivotal role in decision-making when embarking on new product development. The CAPEX represents a cost barrier to beginning production of a new material, and certain companies may be unwilling to invest enormous capital for an unproven process. The CAPEX can be reduced by shrinking the number of process steps, which can practically be achieved by using a higher value chemical, in this case anthraquinone, as the starting reagent. In our case study, anthraquinone is anticipated to be more expensive than anthracene, however, producing AQDS in a single step from anthraquinone will require a substantially smaller CAPEX (Figure 9a) across all production quantities. We estimate a nominal anthraquinone price of \$4.40 kg⁻¹ [45], with lower and upper price bounds of \$2.50 kg⁻¹ and \$5.50 kg⁻¹, respectively, to engage the OPEX estimate (Figure 9b). OPEX estimates for producing AQDS directly from anthraquinone vary significantly with anthraquinone price. Due to the lower CAPEX associated with this process, the raw material cost is a larger fraction of the total OPEX; fixed OPEX and utility costs are smaller than the case of AQDS production from anthracene. The smaller CAPEX, when producing AQDS from anthraquinone, yields a lower AQDS cost at small production volumes and a weaker cost dependence on production volume (Figure 10). Interestingly, the plateau in AQDS cost at high production volume is only marginally larger than using anthracene as the starting material, and the processes with either precursor achieve the \$5 kg⁻¹ target cost at ca. 1 kt annual production. As such, AQDS production from anthraquinone is likely the most sensible route.

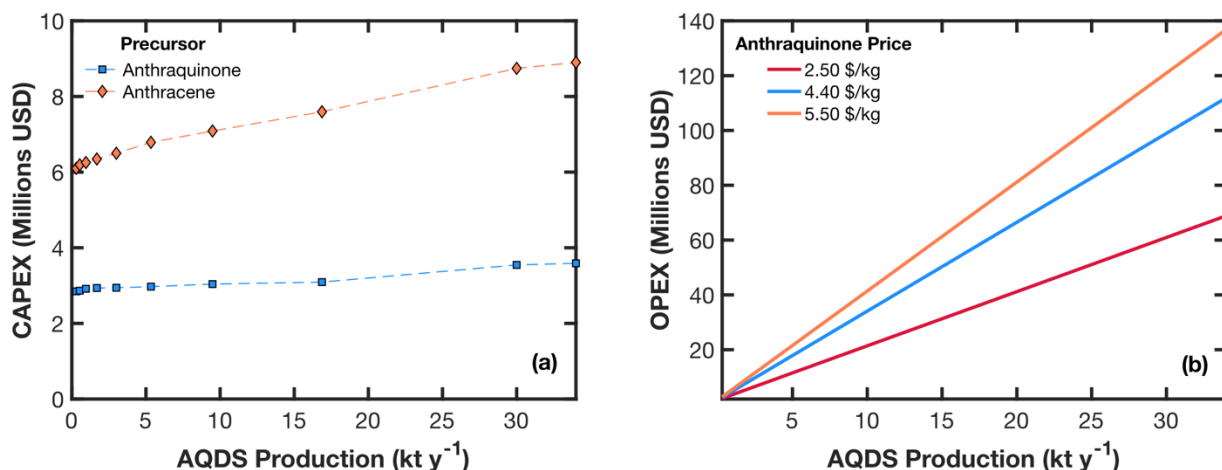


Figure 9: (a) CAPEX and (b) OPEX estimates for production AQDS directly from anthraquinone. Calculations are carried out using the APEA method.

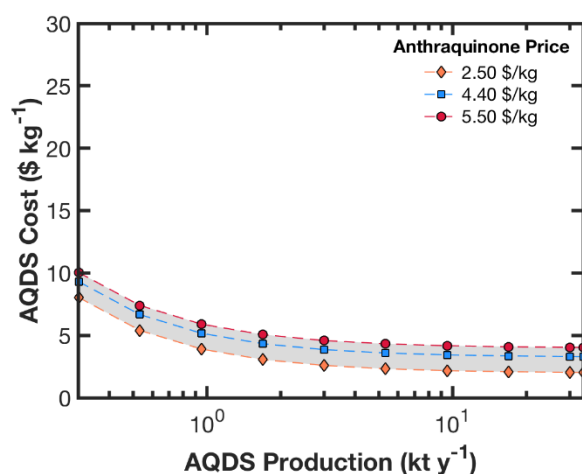


Figure 10: AQDS cost (\$ kg⁻¹) as a function of production quantity when produced directly from anthraquinone. The gray region represents the feasible range of AQDS costs. Dashed lines only serve as visual aids.

4.4 Energy Storage Capacity

We have illustrated that our case study molecule, AQDS, can achieve costs below \$5 kg⁻¹ when produced from either anthraquinone or anthracene. Achieving this low cost, however, requires at least moderate production volumes (≥ 1 kt per year from APEA estimates). The total charge storage capacity (Figure 11a) is calculated by converting the mass production quantity of AQDS to a mole production quantity and multiplying by the theoretical two-electron charge storage capability per molecule [22]. From the charge capacity, we can estimate the theoretical energy capacity for different battery cell potentials (Figure 11b).

The energy capacities shown in Figure 11b are quite large, and to put these values in perspective, we will assume a target cell potential of 1.5 V for an aqueous flow battery. To achieve the target active

material price of $\$5 \text{ kg}^{-1}$, an AQDS production quantity of $\geq 1 \text{ kt}$ per year is required, which corresponds to an energy capacity of $\approx 100 \text{ MWh}$ for a 1.5 V battery. The largest pumped hydro energy storage site in the world is Bath County, Virginia, USA, which contains $\approx 31000 \text{ MWh}$ capacity.[51] For further comparison, the largest sodium-sulfur grid battery installation in Japan has $\approx 245 \text{ MWh}$ capacity[52], and, in the US, the state of Massachusetts recently pledged to purchase 200 MWh of storage capacity by 2020.[53] Thus, while 100 MWh is only a fraction of the largest energy storage installation in the world, supplying enough grid batteries to warrant AQDS production rates necessary to achieve the $\$5 \text{ kg}^{-1}$ target price would require a dominant market position. Furthermore, producing 100 MWh of storage with AQDS synthesized from an anthraquinone precursor would require $\approx 1.8\%$ of the world's entire production of anthraquinone (34 kt per year [44]).

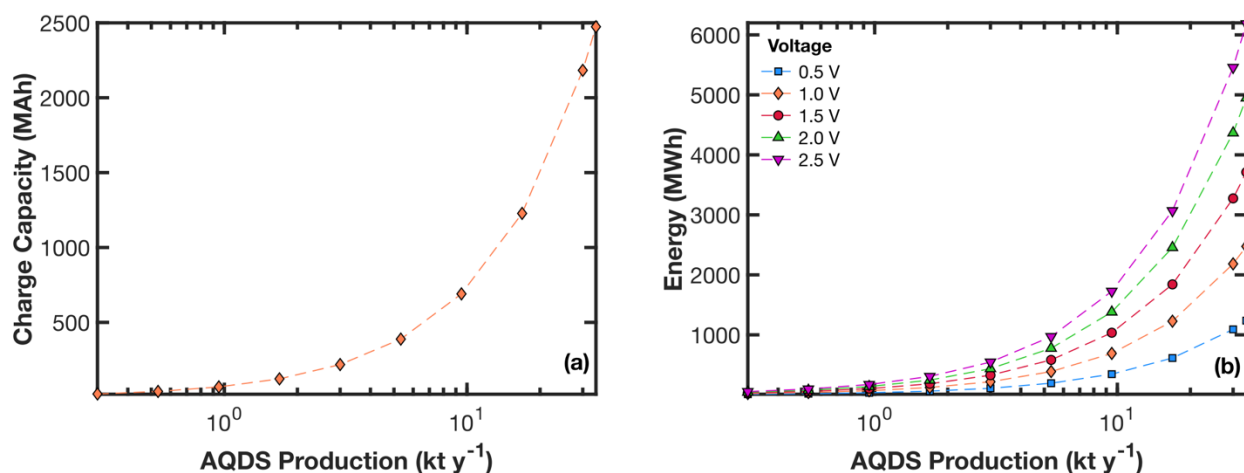


Figure 11: (a) Charge storage capacity (MAh) as a function of AQDS production quantity. (b) Theoretical energy storage capacity (MWh) as a function of AQDS production quantity and battery cell potential.

5. Conclusion

The different cost estimations detailed in this paper for AQDS demonstrate that organics can offer an inexpensive alternative to inorganic active materials, provided sufficiently large production quantities can be reached. At the highest considered production quantity of $3.4 \times 10^7 \text{ kg}$ per year, the prices for AQDS are estimated in the range of $\$0.92 \text{ kg}^{-1}$ (for the equipment list estimate and a low anthracene price of $\$0.84 \text{ kg}^{-1}$) and $\$3.92 \text{ kg}^{-1}$ (for the Bridgwater estimate and a high anthracene price of $\$5 \text{ kg}^{-1}$) confirming that the ROM cost target of $\$5 \text{ kg}^{-1}$ is achievable irrespective of the used estimation method. A major challenge in developing a reliable cost estimation is the lack of available cost and process information. For example, our assumption that the various sulfonated anthraquinone

derivatives offer similar electrochemical storage capabilities has the potential to skew these results up a factor equal to the inverse of the yield of the best-performing derivative. Accounting for the actual impact on cost would require further details of process design, both kinetic and thermodynamic, and we defer this investigation for future work. From the three investigated estimation methods, the APEA and the equipment list method provide the highest level of accuracy, yet process information and assumptions must be applied to novel materials emerging from laboratories around the world. We find step counting methods to be too inaccurate for initial estimates. In addition, at high production quantities the raw material costs determine the costs of the chemical, and the depreciation of the CAPEX does not play a major role. The techniques and methods detailed in this paper provide a toolkit for researchers to estimate the future chemical costs of novel compounds which seek to enable low-cost, grid-level energy storage.

6. Acknowledgements

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Appendix

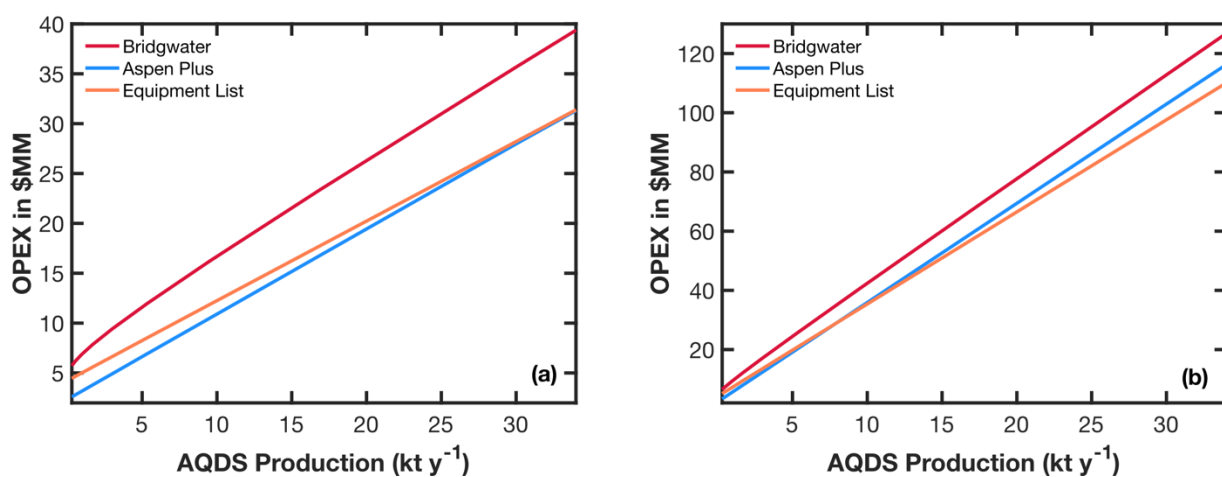


Figure A1 OPEX for different estimation methods and an anthracene price of (a) \$0.84 per kilogram and (b) \$5 per kilogram

Table A1 Correlation parameters for equation (2) [32]

Equipment Type	Unit of S	Lower Bound of S	Upper Bound of S	a	b	n
Box Furnace	MW	30	120	43,000	111,000	0.8
Centrifugal Compressor	kW	75	30,000	580,000	20,000	0.6
Cone roof tank	m ³	10	4,000	5,800	1,600	0.7

U-tube shell and tube heat exchanger	Area, m ²	10	1,000	28,000	54	1.2
Jacked agitated tank	m ³	0.5	100	61,500	32,500	0.8

Table A2 Correlation parameter for equation (3) [33]

Equipment Type	Unit of S	Lower Bound for S	Upper Bound of S	K1	K2	K3
Atmospheric Disc Centrifuge	Diameter, m	0.5	1	4.3612	-0.1236	-0.0049

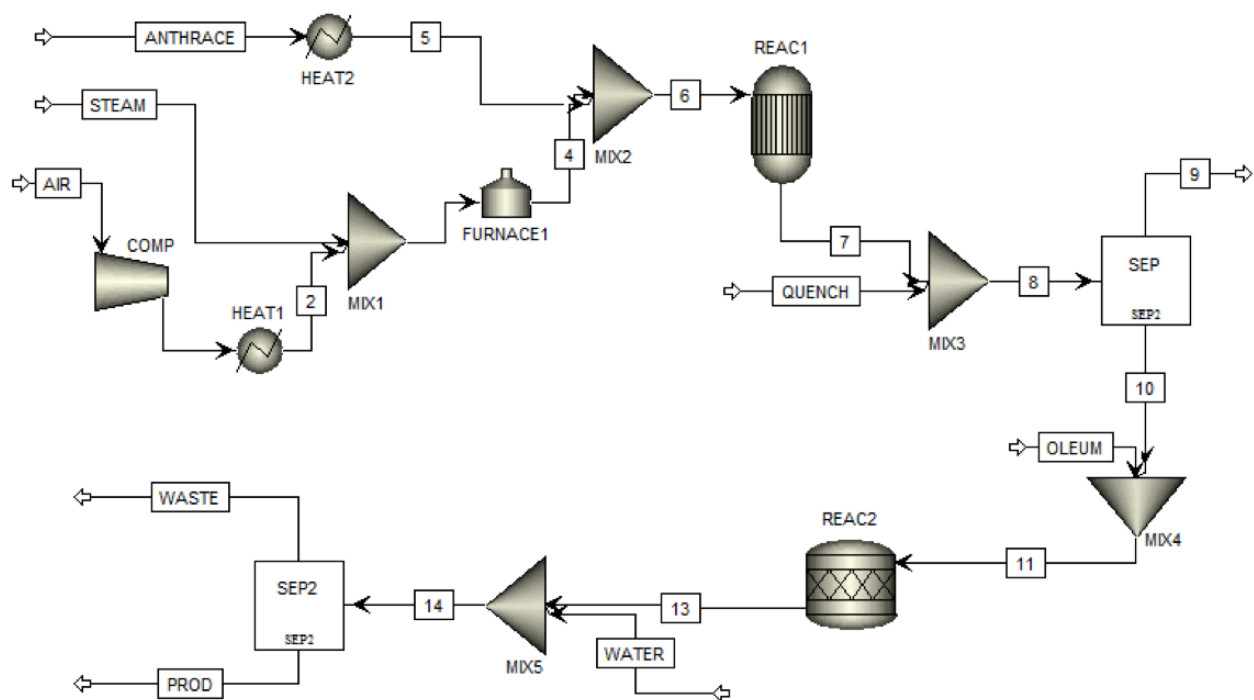


Figure A2. Simulation of the AQDS production process in Aspen Plus.

Table 3 Overview of the mapped equipment

Equipment	Mapped Component	Explanation
Compressor	Centrifugal Compressor	Default component type of the APEA
Heat Exchanger	Tube and Shell Heat Exchanger	Most common heat exchanger type for oil refineries and large chemical processes
Oxidation Reactor	Fired Reactor	Fired reactor type to achieve the necessary reaction temperature
Separation Block 1 (Anthraquinone from waste gases)	Vertical Vessel	Separation of the liquid phase from the waste gases by settling to the bottom of the vessel
Mixer (Anthraquinone and Oleum)	Mixed Vessel (mapped together with sulfonation reactor)	Mixing and chemical reaction take place simultaneously
Sulfonation Reactor	Mixed Vessel (mapped together with Mixer)	Mixing and reaction take place simultaneously
Mixer (reaction product with water)	Mixed Vessel	
Separation Block 2 (AQDS from liquid waste stream)	Disk Centrifuge	For continuous separation of solid from liquid streams a centrifuge is necessary (filters only possible for batch processes)