Optimal design and sizing of HRES-powered electrochemical microsynthesis system

Weigu Wen, Zhihong Yuan\*

State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

\*Corresponding author’s E-mail: zhihongyuan@mail.tsinghua.edu.cn

Abstract

Under the context of carbon neutrality, chemical industry, as one of the dominant energy-intensive industries, necessitates high-penetration renewable electricity to reduce the emission of greenhouse gases and pollution. However, the conflict between the rigidity of the industry load and the intermittent nature of renewable energy sources is challenging. Therefore, leveraging microreactors in chemical production powered by renewable electricity, exploiting their flexibility and rapid start-up/shut-down features, has gained attention from academia and industry. This paper formulated a mixed integer linear programming (MILP) encompassing the electrosynthesis system (ESS) design and the corresponding hybrid renewable energy system (HRES). The optimized results reveal the optimal topology of the HRES-powered ESS. As a case study, the proposed model was implemented in the electrosynthesis of tetrabenzylthiuram disulfide (TBzTD) powered by solar and wind energy. The power transmission of the results suggests the flexible operation of microreactors to adapt to fluctuating weather conditions, which emphasizes the pivotal role of advancing electrochemical microreactor technology to facilitate HRES deployment within the electrochemical industry. Furthermore, to achieve competitive production, the technology parameters of the reactors are investigated, and the results imply that the current density and reactor cost are critical parameters, and improving them could dramatically decrease the production cost.

**Keywords**: HRES, MILP, microreactor, flexibility, TBzTD, mircrosynthesis

* 1. Introduction

Under carbon neutrality, renewable energy is called to attain clean, sustainable, affordable energy and mitigate greenhouse gas emissions (Papadis and Tsatsaronis, 2020). A rapid transition from conventional fossil energy to renewable energy in multiple sectors, including construction, industry, and transportation, is anticipated, given the current projection for dramatic climate change associated with fossil fuel usage. Within these sectors, chemical industry was the largest energy consumer (Yu et al., 2023). Furthermore, the majority of the energy for the chemical industry is supplied by fossil fuels and coal, causing massive CO2 emissions. Thus, increasing the renewable energy ratio in the total energy consumption while maintaining profit is urgent for chemical industry.

However, the intermittent nature of renewable energy sources (RES) conflicts with the rigid energy demand of the modern chemical industry. Hybrid renewable energy systems (HRES) incorporating multiple renewable and conventional energy sources are attractive solutions for power system reliability. Extensive research has addressed the fundamental issue of the optimal design and sizing of HRES, considering various renewable resources of the localities, the target users’ demands, and the investment with methods including state-of-art MIP solutions, heuristic algorithms, and machine learning (Thirunavukkarasu, Sawle, et al. 2023).

Although researchers explored many topology possibilities of HRES, most of the designs solely considered the characteristics of power sources and omitted the variant needs of the end users, while they have distinct energy consumption profiles. Standard models denote the end users’ demands by historical energy consumption data without specific descriptions, leading to the possibility of unbalanced electricity distribution. Furthermore, it is crucial for traditional chemical factories to keep stable operation conditions, and unpredicted loss of power supply is dangerous and unacceptable. Moreover, many chemical processes require high levels of pressure and heat, which are difficult to electrify and incompatible with renewable electricity.

To address the conflicts between conventional chemical processes and HRES, we take the advantage of operational flexibility and rapid start-up/shut-down features of electrochemical microreactors to substitute for traditional industry-scale reactors. Indeed, electrochemical microsynthesis can be operated with high energy efficiency under mild reaction conditions. In other words, the auxiliary units can be easily electrified (Noël and Cao et al. 2019). The flexibility and high electrified levels of the electrochemical synthesis system (ESS) imply a possible route for advancing HRES integration within the chemical industry. However, few have explored the possibility and design methods of combining HRES and ESS. Furthermore, the features of the systems departing from conventional chemical factories need further research. Thus, we formulated an MILP model encompassing the design of the ESS and the corresponding HRES to explore the optimum scale and the system's feasibility. The optimized results reveal the integrated system's topology and energy transmission characteristics.

* 1. Modeling and Optimization Formulation
     1. Configuration of HRES-powered ESS

The configuration of the HRES-powered ESS is shown in Figure 1. The system consists of two subdivisions: the energy supply section and the production section. The energy supply part contains PV panels, wind turbines, and battery storage to discharge complementary electricity when necessary. The critical module in production parts is the electromicroreactors that can transmute energy to substances through electrochemical reactions. Other modules, including syringe pumps and electric heaters, are auxiliary chemical engineering units for pumping and heating. The electricity converted by AC/DC or DC/DC converters will be transmitted to the reactors and other units through the DC bus line.



Figure 1. Configuration of HRES-powered ESS

* + 1. Module models

The mathematical models of PV panels, wind turbines, and battery storage can be referred to by Maleki and Pourfayaz (2015) and Baruah and Basu (2021). The battery storage system can be charged when surplus energy is generated by PV panels and wind turbines and discharge to compensate for the loss of power supply under concurrent deficiency in solar and wind resources.

The electrochemical microreactors can drive reactions directly engaging electricity in relatively high efficiency under moderate reaction conditions. The flow rates of the reactors can also adjust in a particular range, enabling microreactors to be suitable modules for the HRES-powered ESS. The production output *M*Rec and the energy input *P*Recof the reactors are described in Eq. (1)-(3):

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Where *N*REC(t) represents the reactors working at time *t*, *N*REC,sys is the total number of reactors set in the ESS. Equation (3) reflects the system's flexibility with which the reactors can be shut down or started up during the time step (1 hour) with little cost, in contrast with traditional reactors. *P*Rec,S is the rated power input for one reactor and *m*Rec,S is the rated yield, both related to the current density, faraday efficiency and overpotential of the reactors and stable during the period.

* + 1. Integration of HRES and ESS

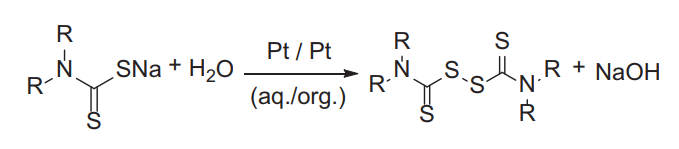
The optimization target is to minimize the annual average construction and O&M cost of the HRES-powered ESS while satisfying the specific market demand for the product, as shown in Eq (4) and (6). The energy supply and the production are integrated through energy balance. Eq. (5) indicates that generated electricity (*P*Gen) at *t* should always be larger than the load (*P*L). In contrast, a strict equation between the generation and load would be costly and unnecessary under various weather conditions. Excess energy can be sold to the grid or dealt with curtailing. The calculation of the cost of modules is listed in Eq. (7), in which *omi­* represents the O&M cost ratio for each module. CRF refers to the capital recovery factor calculated as . *n* is the lifetime, and *r* is the discount rate. *c* is the construction cost for each unit of the modules, e.g., 1 m2 PV panel or 1 kWh of battery storage.

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Combinations of the target function and module models formulate the optimization model of HRES-powered ESS, which determines the optimum portfolio of electricity generation, storage, transmission, and production. It should be noted that multiple energy sources may be added. The production part can also add more chemical units, such as separation and compression, integrated by energy and substance balance. The optimization model is generally compatible with various energy system topologies and chemical processes.

* 1. Case Studies and Discussion
     1. Parameters and data for a case study of Ningbo

The weather data is acquired from ERA5-Land hourly data of Copernicus Climate Change Service (C3S) Climate Data Store (CDS). Ningbo’s annual data for 2022 was retrieved. The optimization model was applied to an on-shore wind and solar-powered electrochemical process producing tetrabenzylthiuram disulfide (TBzTD) (Scheme 1), a low-toxicity substitute for wide-used accelerator tetramethylthiuram disulfide (TMTD). The reactors data is based on Zheng and Wang (2022). Although laboratory-scale data are applied here, it is possible to scale up microreactors by juxtaposing electrodes (numbering-up), which maintains efficiency and improves economic feasibility. Thus, we hypothesized that 100 laboratory-level microreactors could be integrated into one industry-scale reactor with minor performance degradation. For comparison, the selling price of TBzTD in China is approximately 3500 $/t. Average production prices lower than that are considered competitive, which require an annual average construction cost lower than 840,000 $.



Scheme 1. Routes of electrosynthesis of thiuram disulfides

* + 1. Results

Ningbo is a coastal city in China with abundant solar and wind energy resources. The optimized results of HRES-powered ESS for TBzTD indicate that to fulfill the production target, 24 electrochemical microreactors with corresponding auxiliary units were needed, along with 4197 m2 PV panel (rated power 120 W/m2) and three wind turbines (rated power 100 kW). The annual average cost is 1,086,872 $, which is 4,117 $/t TBzTD on average (including material cost) compared with 3,500 $/t selling price in China. The selling price implies that the HRES-powered ESS might be profitable, provided more advanced technology is used (the essential technology parameters are discussed below).

The electricity generation and consumption of modules are derived from the results, and the energy flow on specific days in February is shown in Figure 2. PL represents the reactors’ and auxiliary units' consumption in the figure, and Ppv and Pwt represent energy supply. Attributed to the advantages of microreactors, extra flexibility existed in the HRE-powered ESS since reactors can frequently shut down and restart to track the weather conditions and reduce the need for large-scale energy storage, leading to lower construction costs. As in Figure 2(a), when both solar and wind energy were insufficient from 8th to 10th, instead of enlarging the scale of battery storage for stable operations, the production output was dialed down at night and even shut down. Similar flexibility can be observed on the 12th day when the load follows the fluctuation of wind energy (Figure 2(b)). Due to reactors' flexibility, the state of charge (EB in Figure 2) remains nearly constant for over half the period, prolonging the battery lifetime and reducing O&M cost by reducing charge and discharge recycle times.



Figure 2. Electricity transmission of the system in February (a) 8th to 10th, (b) 12th to 13th

* + 1. Reactor parametric investigation

To assess the crucial reactor parameters for competitive TBzTD production, we analyze the Faraday efficiency (FE), current density, and reactor cost of the electrochemical microreactors and their impact on the average annual cost. Figure 3(a) shows the influence of FE and current density with the cost of reactors set to 20 $/cm2. Total cost descends rapidly when the current density rises from 1 mA/cm2 to 10 mA/cm2, indicating the paramount impact of current density in this range. When current density exceeds 10 mA/cm2, the descent is mild, suggesting that current density is less crucial. The ascent of FE shows a more critical impact on the cost with the current density below 10 mA/cm2 than in the high current density situation. This trend is comprehensible for the product of FE and current density represents the efficient current of the main reaction; thus, when the current density is sufficiently high, FE can be lower. The competitive annual average cost marked in the figure (bold dashed line) suggests that under other given conditions, FE higher than 85% and current density larger than 25 mA/cm2 are requisite.

Figure 3(b) shows the analysis of current density and reactor cost with the FE set to 75 %. The original cost of the reactors (20 $/m2) is relatively high due to the Pt anode. If the electrode could be replaced by non-noble metal, a dramatic drop in the reactor cost might be expected. Reactor cost significantly impacts current density lower than 10 mA/cm2 due to many reactors being applied. Along with the increase in current density, reactors’ production rate increases and fewer reactors are needed, diluting the impact of reactor cost. Competitive production can be achieved when the reactor cost is lower than 5 $/cm2 and the current density is higher than 15 mA/cm2. It can be inferred that the descent of reactor cost is more critical than the improvement of FE with high current density. Furthermore, high FE characterizes electrochemical microreactors. Therefore, future work on electrochemical microreactors should concentrate on improving current density and replacing the noble metal electrode.



Figure 3. Effects of electrochemical reactor parameters on construction cost. (a) Effect of Faradaic efficiency and current density (b) Effect of reactor costs and current density

* 1. Conclusion

To address the conflict between the variability of renewable energy sources and the rigidity of load in the chemical industry, we formulated a MILP model to design and optimize HRES-powered ESS, exploiting the flexibility of electrochemical microreactors. The optimization results revealed the optimal topology of the systems that could be referenced for investors and policy-makers. The system's electricity generation, storage, and transmission were acquired for further analysis. The energy flow showed microreactors' superiority of the rapid start-up/shut-down characteristics to adapt to renewable energy sources, which is impractical for conventional chemical factories at a reasonable cost. Current technology is infeasible to sustain a profitable HRES-powered ESS. Thus, we investigated the requisite reactor parameters for the competitive production of TBzTD. Analyses show that current density is the decisive parameter. The current density reaching above 10 mA/cm2 can dramatically reduce the cost of production, while FE is less crucial considering the already high efficiency of electrochemical microreactors. The cost of the reactors is also significant due to the difficulty of applying Pt electrodes on a large scale. Replacement of the Pt electrodes with non-noble metal can drastically lower the total construction cost, hence the selling price. The analyses imply that future work might focus on raising the current density above 10 mA/cm2 and decreasing the reactor cost to 5 $/cm2.

Further expansion of the HRES-powered ESS would be explored, including more chemical engineering units and varieties of renewable sources to resemble more complicated practical processes and enhance the adaptation of different sites. Expanding the model will increase the number of variables, resulting in longer CPU time, and oversized models are infeasible for commercial solvers, calling for advanced algorithms for large-scale MILP. In addition, the system's design is based on historical weather data. For installed systems, weather conditions are uncertain due to inaccurate weather forecasts, requesting system operation control under uncertainty to involve the systems' flexibility fully.

References

Papadis Elisa, George Tsatsaronis. 2020. Challenges in the Decarbonization of the Energy Sector. *Energy* 205: 118025.

Zhipeng Yu, Jin Lin, Feng Liu, Jiarong Li, Yuxuan Zhao, Yonghua Song, Yanhua Song, Xinzhen Zhang. 2023. Optimal Sizing and Pricing of Grid-Connected Renewable Power to Ammonia Systems Considering the Limited Flexibility of Ammonia Synthesis. *IEEE Transactions on Power Systems*, 1–18.

Thirunavukkarasu M., Yashwant Sawle, Himadri Lala. 2023. A Comprehensive Review on Optimization of Hybrid Renewable Energy Systems Using Various Optimization Techniques. *Renewable and Sustainable Energy Reviews* 176: 113192.

Noël Timothy, Yiran Cao, Gabriele Laudadio. 2019. The Fundamentals Behind the Use of Flow Reactors in Electrochemistry. *Accounts of Chemical Research* 52 (10): 2858–2869.

Baruah Abhinandan, Mousumi Basu, Deeshank Amuley. 2021. Modeling of an Autonomous Hybrid Renewable Energy System for Electrification of a Township: A Case Study for Sikkim, India. *Renewable and Sustainable Energy Reviews* 135: 110158.

Maleki Akbar, Fathollah Pourfayaz. 2015. Optimal Sizing of Autonomous Hybrid Photovoltaic/Wind/Battery Power System with LPSP Technology by Using Evolutionary Algorithms. *Solar Energy* 115: 471–483.

Zheng, Siyuan, and Kai Wang. 2022. Electrosynthesis of Tetrabenzylthiuram Disulfide via Flow Reactors. *Chemical Engineering Science* 257: 117717.