2023

Modular Supply Network Optimization of Renewable Ammonia and Methanol Co-production

Benjamin Akoh
ba00041@mix.wvu.edu

Modular Supply Network Optimization of Renewable Ammonia and Methanol Co-production

Benjamin Akoh

Problem Report submitted to

the Statler College of Engineering and Mineral Resources

at West Virginia University

In partial fulfillment of the requirements for the degree of

Master of Science

In

Chemical Engineering

Yuhe Tian, Ph.D., Committer Chair

Srinivas Palanki, Ph.D.

Fernando Lima, Ph.D.

Department of Chemical and Biomedical Engineering

Morgantown, West Virginia

2023

Keywords: Ammonia; Methanol; Hydrogen; Solar; Wind; Optimization; Supply Chain

Abstract

Modular Supply Network Optimization of Renewable Ammonia and Methanol Co-production

Benjamin Akoh

To reduce the use of fossil fuels and other carbonaceous fuels, renewable energy sources such as solar, wind, geothermal energy have been suggested to be promising alternative energy that guarantee sustainable and clean environment. However, the availability of renewable energy has been limited due to its dependence on weather and geographical location. This challenge is intended to be solved by the utilization of the renewable energy in the production of chemical energy carriers. Hydrogen has been proposed as a potential renewable energy carrier, however, its chemical instability and high liquefaction energy makes researchers seek for other alternative energy carriers. Ammonia and methanol can serve as promising alternative energy carriers due to their chemical stability at room temperature, low liquefaction energy, high energy value. The co-production of these high energy dense energy carriers offers economic and environmental advantages since their synthesis involve the direct utilization of CO_2 and common unit operations. This problem report aims to review the optimization of the co-production of methanol and ammonia from renewable energy. Form this review, research challenges and opportunities are identified in the following areas: (i) optimization of methanol and ammonia co-production under renewable and demand uncertainty, (ii) impacts of the modular exponent on the feasibility of co-production of ammonia and methanol, and (iii) development of modern computational tools for systems-based analysis.

Acknowledgements

Over the past two years of my studies toward this MSc, I have been inspired and encouraged by different peoples.

I would like to first express my sincere appreciation to my advisor, Dr. Yuhe Tian, for her mentorship, patience and encouragement during the course of this work. Thank you for been a great mentor.

I also want to appreciate my committee members, Dr. Srinivas Palanki and Dr. Fernando Lima for their time and contributions towards the success of the work.

I am also grateful to Dr. Cerasela Zoica Dinu, Dr. Nagasree Garapati, and Dr. Ogunade Ibukun for their mentorship and encouragement during the MSc program.

I would also like to appreciate all the graduate students in the department of Chemical Engineering, especially my Lab members, Ayooluwa Akintola and Md Abdullah Al Masud for their supports and kindness.

Finally, I am sincerely grateful to my family members for their unconditional love and care in my life journey

Table of Contents

CHAPTER 1. Introduction

The global population has been observed to be growing astronomically with time. The United Nations (UN) estimated the world population to be 8 billion at the end of 2022 fiscal year which is a 1 billion increase from 2010 [1]. The population is expected to rise to 9.7 billion in 2050 and could reach 10.4 billion around the 2080s. As the global population is increasing, there will be an exponential increase in the consumption of the social amenities of the society such as energy. Energy demand has been shown to be increasing with the global population. The higher the population, the higher the consumption of energy. The US Energy Information Administration (EIA) estimated the global energy consumption in 2021 to be 603.321 quad BTU which is almost double the consumption rate of 292.94 quad BTU in 1980 [2]. They further projected a 50% increase in energy consumption by 2050. This exponential energy demand is largely driven by population and economic growth. To meet this growing energy demand, there is a need to look towards renewable energy sources (wind, geothermal and solar) to supplement the conventional energy sources such as coal and fossil fuels. Renewable fuels are primarily energy derived from solar, wind and geothermal. They are proven to be environmentally safe such that their usage can lead to drastic reduction in CO_2 emissions. The adoption of these fuels has begun in many countries such as China, USA, Germany and among others. For instance, in 2021, 18% of the energy consumed in the USA was renewable energy which is 12.2 Quad BTU [3]. Although renewable energy consumption is projected to be 20 quad BTU, [3,4], the production capacity of renewable energy is largely limited by its dependence on season of times and geographical location. To solve this problem, chemical storages have been studied to store these energies for later use. Hydrogen is suggested to be a promising energy carrier for renewable energy [5]. However, the chemical instability and high liquefaction energy of hydrogen gas makes researchers find other stable energy carriers.

Among other promising energy carriers, methanol (MeOH) is found to be a good supplement to hydrogen due to its high energy-density (22.7 MJ/kg, 18 MJ/L HHV) and wide applicability to be used as fuel [6], solvent, and intermediate feedstocks for synthesizing hundreds of chemical and products, including dimethyl ether (DME), gasoline, kerosene, olefin, and among others [7]. MeOH is one of the top produced chemical substances with the global production of about 92 metric million tons/year in 2016 [8]. It can be used as a transportation fuel, hydrogen carrier for fuel cells and for electricity generation. At present, commercial MeOH is mainly produced in a two-step process, wherein steam methane reforming (SMR) reaction converts CH_4 into syngas (i.e., a mixture of H_2, CO and CO_2). The syngas formed is further converted into MeOH, at elevated temperature (~523.15 K) and pressure (50–100 bar) [9]. This conventional method of producing MeOH is used to satisfy 90% of the global demand but it largely contributes to the global emission of CO_2 (670–790 g CO_2e/kg MeOH [10,11]). This motivates the production of methanol with renewable energy, for instance, using power from solar and/or wind turbines to produce the precursors needed for its synthesis. Consequently, the development of Power-to-MeOH synthesis with renewable energy has received considerable attention over the years. One of the forerunners in Power-to-MeOH synthesis is via CO_2 hydrogenation with renewable hydrogen in a two-step process [12]. Decades of R&D efforts on catalytic CO_2 hydrogenation made this process economically competitive as compared to the conventional MeOH synthesis route [13].

Ammonia is equally considered a good candidate for storing energy due to its high chemical and thermal stability. Ammonia can easily be liquified and transported because of its low boiling point and pressure, hence, requires low energy for liquefaction. Although the synthesis of ammonia from its elemental precursors is environmentally friendly, the conventional large production of ammonia contributes to 1% global carbon emission. This is primarily due to the utilization of fossil fuels such as coal, natural gas to produce hydrogen molecules, a needed reactant for ammonia synthesis [14,15]. This then necessitates the need for the usage of renewable sources of energy to power ammonia production. Ammonia is an essential chemical that is quite responsible for the easy accessibility of food to the world since it is generally used as a precursor or directly as a fertilizer [16], hence, its well-established supply chain. These facts ultimately made ammonia an attractive energy carrier. This research is essentially highlighting the benefits of integrating renewable power plants in the production of ammonia and methanol, and also to reduce unit operations by co-producing ammonia and methanol in the same plant since their synthesis involves a common molecule, i.e., hydrogen.

The conventional ammonia and methanol production results in the release into the atmosphere about 0.5 Gt and 0.3 Gt of carbon per annum respectively [17,18]. This emission is solely due to the utilization of fossil fuels in running the production of the energy carriers. This environmental problem associated with the conventional production could be solved by integrating renewable energy into the process plant. Wind and solar energy sources have been found to be clean and sustainable. Compared to the conventional method of production, integration of renewable energy into ammonia and methanol production can potentially reduce carbon footprint by 65 to 90% [19]. Hence, the need to study the renewable production of ammonia and methanol.

In order to accomplish this task, the review study of the energy carriers would be carried out across their production scale, network scale, and energy conversion level to cover the supply chain of the energy carriers. This study on the co-production of ammonia and methanol is motivated by the following advantages over standalone production: (i) Reduction in unit operations such as steam methane reforming, water electrolysis for the production of hydrogen, which is a common reactant in methanol and ammonia synthesis, (ii) Multi-functional use of shared utilities, (iii) Reduction in unit cost of production and emissions, and (v) Flexible operations and control of ammonia and methanol unit independently. These advantages of integrated methanol and ammonia production would ultimately lead to lower Capital expenditure (CAPEX) and operating expenditure resulting in higher return on investment and reduction in environmental damages.

This study is aimed at achieving the following objectives:

1. Process synthesis of energy-chemical co-production plants to determine optimal and sustainable process routes
2. Integrated energy systems operation under renewable energy intermittency
3. Dynamic supply chain optimization with considerations of modular plants

CHAPTER 2. Towards Energy Transition

2.1 Ammonia in Energy Transition

2.1.1 Ammonia as Energy Carrier

Ammonia is found to be a suitable alternative energy carrier because its lack of carbon in its molecular structure. Ammonia allows hydrogen to be stored in liquid form without needing a cryogenic storage [20]. Furthermore, Ammonia can be synthesized from renewable hydrogen and nitrogen from air, and hence, does not directly involve carbon/CO species. This makes ammonia an attractive energy carrier since its production is environmentally friendly. Energy, nitrogen and water are the only reactants and feedstock required from the production of ammonia.

Table 1: Properties of Various forms of Energy Carriers [21]

Fuel	Energy Density LHV (Mj/Kg)	Volumetric Energy Density (Gj/m^3)	Storage Pressure (Bar)	Liquified Storage Temperature(°C)	Hydrogen Content %H
Compressed Hydrogen	120	4.7	700	20	100
Liquid Hydrogen	120	8.5	1	-253	100
Ethanol	26.7	21.1	1	20	13.04
Methanol	19.9	15.8	1	20	12.5
Liquid Methane	50	23.4	1	-162	25
Liquid Ammonia	18.6	12.7	1	-34	17.64

As shown in table 1, storing ammonia is less energy intensive compared to other energy carriers such as hydrogen and methanol. For instance, through gaseous has low energy density of 4.7 GJ/m^3 compared to liquified hydrogen (8.5 GJ/m^3), liquefying hydrogen is an energy intensive process requiring a compressed pressure of 700 bar [22]. These properties of ammonia make ammonia an attractive sustainable and cheap energy carrier.

2.1.2 Synthesis of Ammonia

Ammonia is mainly synthesized through a chemical reaction termed Harber-Bosch Process, it is a reaction which is commonly used and studied in the laboratory and industry for over centuries. The Harber-Bosch process is used to produce about 85% of the world's ammonia [23]. For effective yield of ammonia, the reaction must be catalytically performed at the temperature and pressure of 400-500ºC and 10-30 MPa respectively which required 30 MJ/kg-NH_3 of energy [24]. The feedstocks for the synthesis of ammonia are Hydrogen from coal, oil, natural gas (mostly methane) and nitrogen obtained from air [25]. Ammonia is directly synthesized by reacting Hydrogen gas with Nitrogen gas in the presence of iron filling as catalyst. The stoichiometry of the reaction is represented in Equation (1).

$$3H_2 + N_2 \rightleftharpoons 2NH_3 \qquad \Delta H_{27^oC} = -46.35\ kJ/mol \qquad (1).$$

Regardless of the exothermic nature of the Harber-Bosch process, the energy of ammonia, 28.4 Gjt^{1} is greatly higher than the energy loss, 1.5 Gjt^{-1} during the reaction [26]. The energy consumption of the Harber-Bosch process largely depends on the plant size, and source of the hydrogen. The energy consumption values with NG, Coal, and fuel oils are 7.8, 10.6 and 11.7 MWh per ton of ammonia respectively with the corresponding CO_2 emission of 1.6, 3.0, and 3.8 tons per ton of ammonia [27]. Due to high emission associated with conventional ammonia production, researches are ongoing on the viability of the use of renewable energy such as wind, solar, geothermal, biomass for ammonia production. Furthermore, Figure 1 shows the blueprint of ammonia as hydrogen carrier. Renewables energy such as wind, solar, hydro and geothermal are used to power the electrolysis of water to give hydrogen (feedstock), this process is largely responsible for the environmental friendliness of ammonia synthesis.

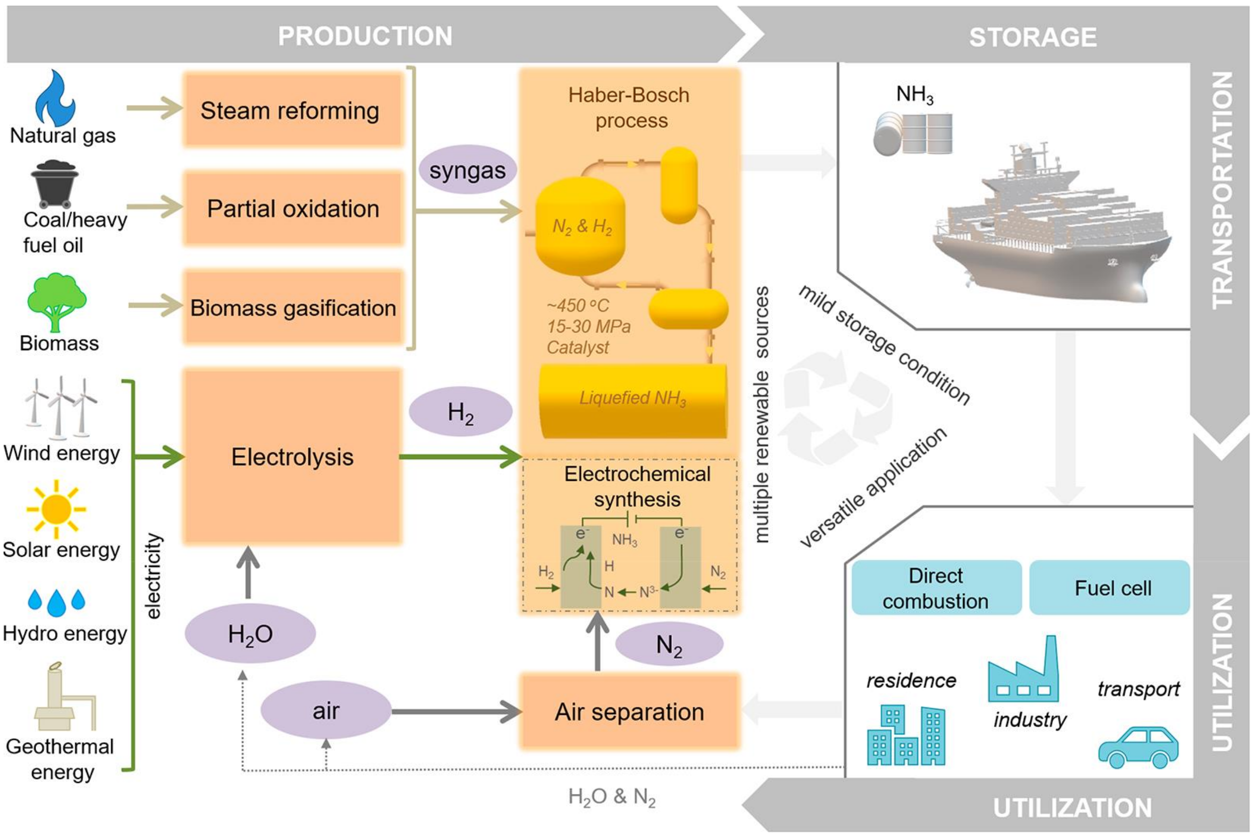

Figure 1. The schematic of Ammonia as Energy carrier [28]

2.1.3 Ammonia Energy Conversion Technology

The carbon-free molecule structure of ammonia and its high hydrogen content of 17.6 wt% makes it a promising energy carrier for energy and electricity generation. Ammonia can be liquefied at low temperature, dissolved in water for high energy storage and transported to end-users [29]. Among other conversion technology for ammonia, fuel cells and gas turbines are receiving attractions from industries and researchers due to their relatively high conversion efficiencies. Some of the advantages associated to ammonia fuel cells includes high conversion efficiency, low emission of oxides of Sulphur, nitrogen and other contaminants, easy operation and among others. Table 2 summarizes the fuel cells that utilizes ammonia as direct fuel.

Furthermore, ammonia have been used as a direct fuel in turbine engines and internal combustion engines. A combustion efficiency of 40-60% have been reported by Reiter and Kong [30] when ammonia is blended with diesel in a four-cylinder turbocharged diesel engine. They further reported a reduction in the emissions of soot. Researches and implementation of the direct use of ammonia as fuel in turbine engines is ongoing. For instance, a research group at Fukushima Renewable Energy Institute, Japan, has successively used ammonia to run a micro gas turbine of 50 kW capacity with 89-96 % combustion efficiency [31]. Ammonia due to its carbon neutrality and low liquefaction energy, would replace conventional fuels in the future.

Table 2: Ammonia Fuel Cell Technologies.

Fuel Cells	Type	Operating Temperature (°C)	Power Density (mW/cm^2)	Efficiency (%)	References
Alkaline Fuel Cells	Molten hydroxide NaOH/KOH	220	16	-	[32]
	KOH	80	8.86	-	[33]
Alkaline Membrane Fuel Cells	KOH	50	-	-	[34]
Solid Oxide Fuell Cells	Sm_2O_3-CeO_2	650	1190	-	[35]
Microbial Fuel Cells	-	-	132	-	[36]

2.2 Methanol in Energy Transition

2.2.1 Methanol as an energy carrier

Methanol have been identified as a promising alternative hydrogen carrier because of its thermodynamic stability. Compared to other energy carriers, methanol is a liquid room temperature and hence, allows easy transportation and storage. The energy storage of methanol was reported to be within the range of 13.8 % and 17.6 % [37]. Several works have been done on the viable of methanol as an energy carrier [38, 39, 40]. The properties of methanol compared to other energy carriers are summarized in table 1.

2.2.2 Conventional and Renewable Synthesis of Methanol

Commercially, methanol was produced in 1923 at BASF's Leuna site [41]. Extensive review works have been done on the history of methanol production [41, 42]. the production capacity of methanol on a large scale have risen to more than 5000 metric tons per days [41]. In recent times, methanol production comprises of three stages; synthesis gas production, methanol synthesis and methanol purification as shown in Figure 2.

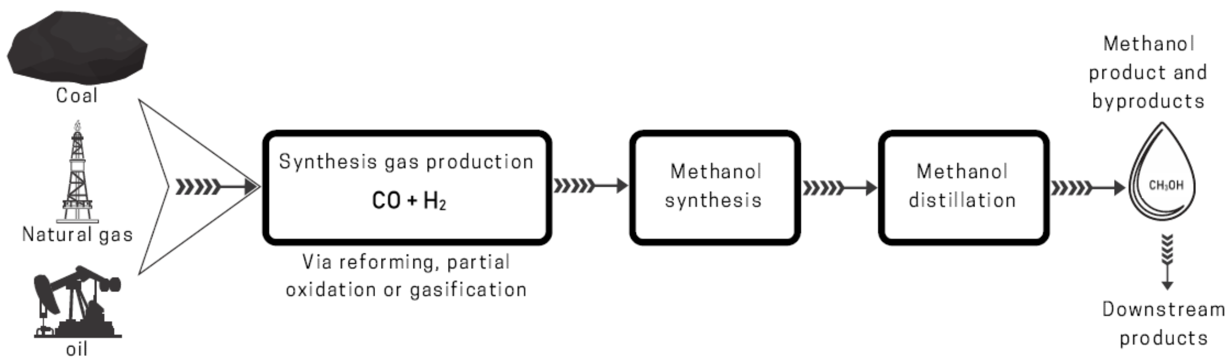

Figure 2. Schematic diagram of conventional methanol production process [42]

Conventionally, the synthetic gas is predominantly produced from non-renewable sources such as coal, Natural gas, liquified petroleum gas and biomass [43]. The syngas primarily contains CO, CO_2, H_2 and H_2O. On the commercial scale, methanol is produced at 200-300 ^oC and 50-100 bars over copper-based catalyst [44,45]. The synthesis of methanol basically involves the reverse water-gas shift and hydrogenations of the oxides of carbon.

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H_{298K} = -91\,\frac{kJ}{mol} \qquad (2)$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H_{298K} = -49\,\frac{kJ}{mol} \qquad (3)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H_{298K} = +41\,\frac{kJ}{mol} \qquad (4)$$

The synthetic gas production stage has received numerous attentions due to its importance in the technoeconomic and environmental sustainability of methanol production plant. To curb the problem of emission associated with methanol production, methanol is been from renewable feedstocks such as hydrogen from water electrolysis powered by renewable energy (solar, wind and geothermal) and carbon dioxide from biogas or air capture [46,47].

Furthermore, the integration of renewable energy in methanol production from captured CO_2 allows it to be used as a carbon source for the industry [48,49,50].

2.2.3 Methanol Energy Conversion Technologies

Methanol containing 12.5 wt% of hydrogen have been utilized as alternative energy fuel for decades. In 2012, about 85% of methanol produced was used in the chemical industry for the manufacturing other derivatives [51]. However, there is a paradigm shift that leads to the energy sector is consuming 40% of methanol production [52]. Methanol usage as fuels in internal combustion engines is due to its high latent heat, no carbon-carbon bond, fast-burning velocity and high-octane rating, hence, knock resistance [53,54]. In recent times, methanol is used as a precursor to produce other alcohols, Methyl Tertiary Butyl Ether (MTBE) which are utilized as blends in gasolines [55]. Furthermore, for effective energy conversion, methanol is used in fuel cells such as direct methanol fuel cells (DMFCs), High Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFCs) to generate electricity. HT-PEMFCs have been reported to have 50% electricity conversion efficiency [56].

2.3. Renewable Energy Sources

2.3.1. Wind Energy

Wind energy has been a fast-growing renewable energy in global energy systems. Wind been a clean and sustainable form of energy can be converted to power via wind turbine generator which is under development. There is a gradual increase in the power output of a wind turbine. According to figure 3, the yearly wind energy contribution to the total U.S. electricity is currently at about 380 billion kWh in 2021 which is 98% increase from 2000 [57].

Texas has the largest market for wind energy in the U.S. because of its enormous wind resources. The state consumed about 10 % of the generated electricity from wind energy, accounting for the 16% of the total generation capacity in 2018. Despite the abundance of the wind energy resources, there is a problem of connecting the supply and the demand which leads to grid inefficiency to transmit within long-distance.

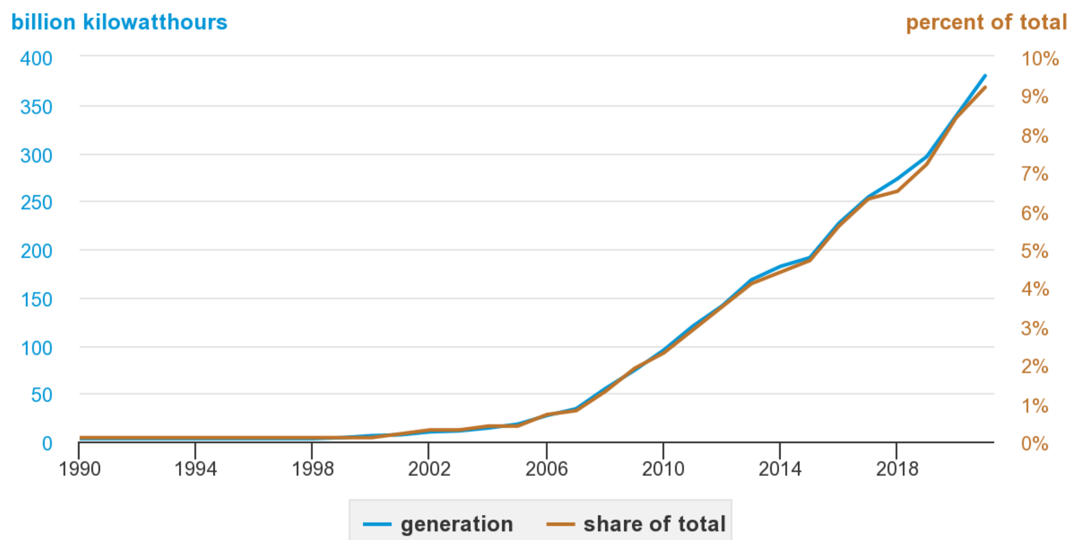

Figure 3. Wind energy generated and the percentage of the electricity shared [58]

2.3.2. Solar Energy

The use of solar energy as an alternative energy source is rapidly growing because its carbon neutrality. This growth is largely encouraged by the financial incentives for the solar energy usage. The solar energy consumption in the U.S increased from about 600 billion BTU in 1984 to almost 1,501 trillion BTU in 2021 with 4% of the solar energy been used for heating. In 2021, the annual electricity contribution by solar energy was about 164 billion kWh which is an increase of about 99.99% from 1984. There is a mismatch between the location of supply and demand which creates inefficiency in grid transmission.

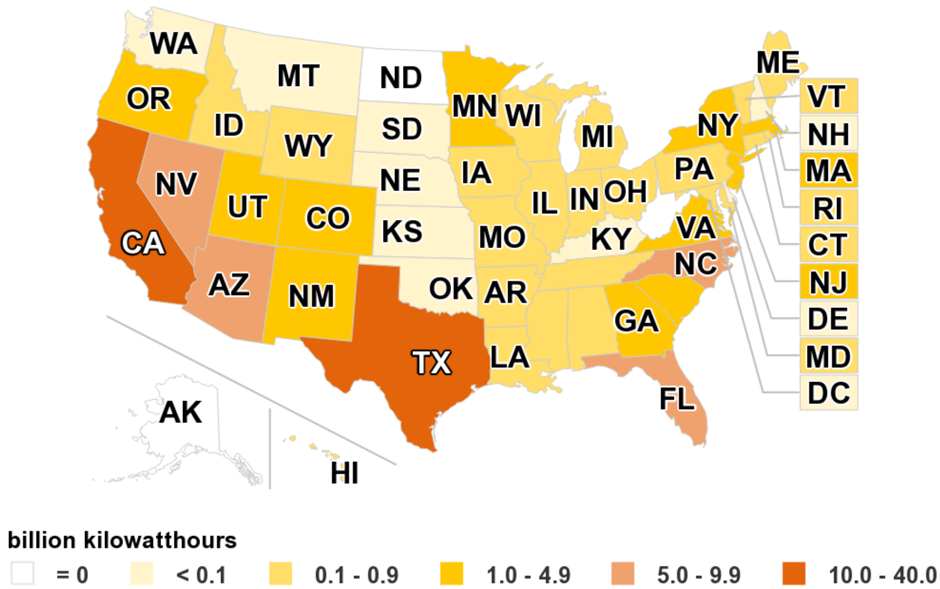

Figure 4. Solar Electricity generated by U.S. states [58]

CHAPTER 3. Process Synthesis of Energy-Chemical Co-Production Plants to Determine Optimal and Optimal Sustainable Process Routes.

3.1 Process Design and Optimization

Process design optimization is the selection of the optimal process flow or routes to produce a desired product. The performance of the proposed design is evaluated through economic analysis, environmental sustainability, and or a combination of the two above.

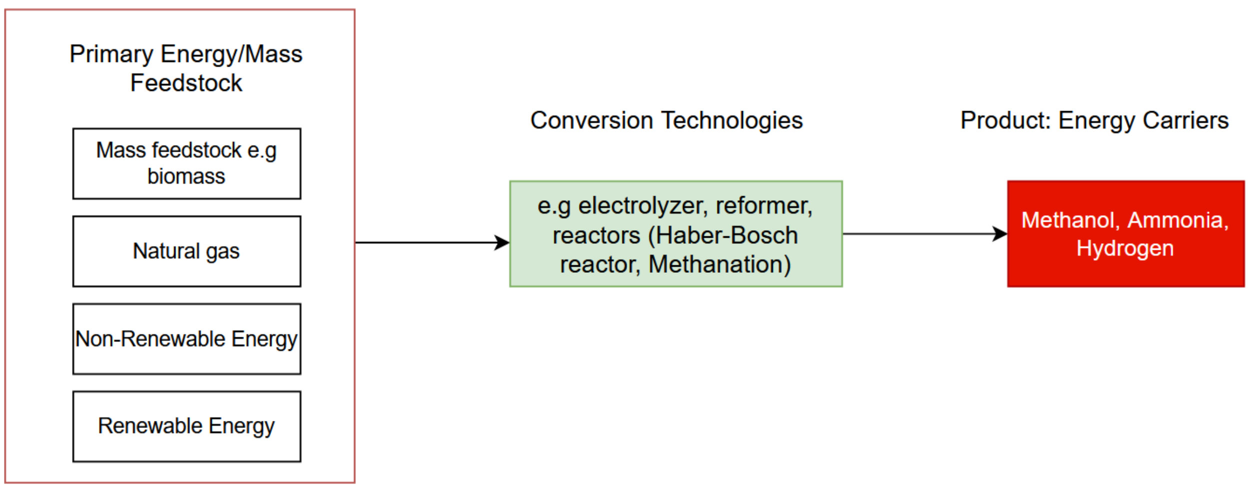

Figure 5: Process Superstructure for a typical process design and optimization routes.

3.1.1 Methanol Production

The optimal design of methanol synthesis is one of the research relevant to studying methanol as an energy carrier. Liu *et al.,*2020 [59] investigated the operability of a proposed design for producing methanol from sour natural gas. They incorporated a steam reforming technology with hydrogenation of CO_2/CO unit operation. They determine the maximum profit from running their design by solving a multi-variant optimization model in Aspen Plus using a built-in SQP optimizer. Their results showed an operating profit of \$8.69 MM/yr.

Borisut and Nuchitprasittichai, 2019 [60] formulated a non-linear response surface methodology to optimize the methanol production from CO_2 hydrogenation by minimizing the operation cost of the process. The model was solved in Microsoft Excel using an NLP solver. They reported a minimum production cost of $565.54 per ton at some optimal reaction conditions.

Zang *et al.,* 2021 [61] performed a techno-analysis on methanol synthesis from the hydrogenation of industrial byproduct CO_2. They reduced methanol price from $0.56-0.59/kg when a CO_2 credit of $35/MT is applied. The optimal design of methanol production has been investigated using multi-objective models.

Taghdisan *et al*., 2015 [62] formulated a multi-objective model to minimize CO_2 emission and maximum methanol production using a genetic algorithm. They reported an optimal methanol production and CO_2 efficiency of 196 ton/hr and 345 KgCO_2/ton MeOH.

Arora *et al*., 2018 [63] used a grey-box optimization algorithm to obtain the optimal design of a proposed sorption-enhanced methanol synthesis process. They formulated a multi-objective model to optimize syn gas consumption and methanol yield.

Li *et al.,* 2020 [64] developed a multi-objective model to minimize the production cost of methanol from shale and simultaneously minimize the emissions from the plants. Their results displayed a minimum operation cost of 58.13 $/ton methanol with the lowest emission of CO_2, SO_2, NOx and soot to be 124.7 kg/ton, 0.181 kg/ton, 0.226 kg/ton and 0.054 kg/ton, respectively.

Zhang and Desideri *et al*., 2020 [65] formulated an MINLP multi-objective problem to maximize energy efficiency and minimize methanol production cost. They used this model to determine the optimal design of a proposed heat-integrated model for methanol production based on co-electrolysis. The minimum production cost and maximum LHV energy efficiency of $530/ton methanol and 72%, respectively, through a Pareto-optimal multi-objective solution.

3.1.2 Ammonia Synthesis

Many researchers are developing complex nonlinear models to describe the optimal design and synthesis of ammonia production either in steady or dynamic conditions or both [66].

Palys *et al.,* 2018 [67] developed a dynamic model for absorbent-enhanced methanol production. This model was used to formulate an MINLP to evaluate the optimal process design and minimize the net present cost of the process. They found that the proposed process with a 0.77 capacity exponent and production scale below 6075 kg/h is less expensive than the conventional Haber-Bosch process.

Sanchez *et al.,* 2018 [68] formulated multiple NLPs to determine the optimal design of ammonia-to-power technology. In their proposed process, they incorporated a catalytic membrane reactor for ammonia decomposition and further performed selective catalytic reduction to remove oxides of nitrogen emissions during the decomposition process. At the end of their work, they obtained the levelized power cost of $0.23/kWh at a 100 MW scale and the range of 30 to 45% as ammonia-to-power efficiencies.

Demirhan *et al*., 2019 [69] developed a process flowsheet of integrated biomass-based ammonia production powered by wind and solar energy. The model was formulated as MINLP and solved using a deterministic global optimization-based branch-and-bound- algorithm. They found that a 75% GHG restriction is placed, biomass-ammonia route is comparable to the conventional routes.

Xu *et al.,* 2020 [70] proposed a 24-hour scheduling model to represent ammonia storage in a CHP microgrid. To reduce computational complexity, the MINLP model was decomposed into NLP and MIQP. They found that using ammonia as energy storage in CHP is less efficient in scenarios such as charge/discharge and on/off.

3.2 Operational Optimization: Planning and Scheduling

Planning and Scheduling deals with the management of plant resources so as to produce a product that meets the demand requirement [71. The planning and scheduling activities are commonly performed over a time period. The metrics for determining the effectiveness of a proposed scheduling method includes minimizing cost, reducing carbon emission, reducing utilities consumption, maximizing profit. These metrics are mostly achieved using PSE methods. Many researchers have utilized PSE techniques to study the scheduling and planning of methanol and ammonia production process.

3.2.1 Methanol

Xi *et al.*, 2021 [72] proposed an AI based energy scheduling for a steel mill gas utilization system (SMGUS) integrated with a renewable energy and carbon capture and storage (CCUS) technologies. They applied the AI technologies of GBRT (Gradient boosted regression trees) and PSO (Particle swarm operation) to the scheduling to control the interactions between the unit operations to obtain a safe, low-carbon and economical SMGUS operation. To capture and utilize the CO_2 from the SMGUS, methanol production plant was incorporated into their proposed design. First principal models were formulated to model the key unit operations involve in the process. They used the GBRT machine learning algorithm to develop surrogate models using the input-output data from the first principal models. In their study, they minimized the cost of producing methanol over a scheduling period of 24 hours. Their objective function accounts for the cost of emission, profit of selling crude methanol, cost of grid electricity. The optimization equation was solved using Particle swarm optimization algorithm (PSO) an AI based algorithm. Three scenarios were considered; Conventional SMGUS with Renewable power, SMGUS without considering CO_2 utilization and proposed low-carbon SMGUS. Their results show that optimal scheduling could be used to manage the integration of renewable energy to process, leading to 62% reduction in carbon emission and 126 ton of methanol production in 24 hrs.

Zheng *et al.*, 2022 [73] performed a data-driven robust optimization for optimal scheduling of power to methanol. They built optimization model for the conventional on-grid power-to-methanol system such as electrolyzer model, methanol converter model, material and energy flow model. The scheduling was done for a 24 hours operation. They fixed the daily methanol production to minimize the daily operational cost of methanol production. They account for the uncertainity in the price uncertaining by introducing a forcast error parameter into the cost function. The MILP formulation was solved using Guropi and CPLEX. The hourly electricity prices parameter was obtained by using a multi-layer perception neural network (MLPNN) to predict the electricity price parameter. The input and output parameter into the network were the previous seven-day price and the next day hourly price. They concluded that the proposed scheduling, the operational cost could be reduced by 4.5% and the levelized cost of methanol was within 584 to 1146 €/t.

Svitnic and Sundmacher, 2022 [74] optimized the scheduling of a renewable production process with a waste-heat integration using FluxMax technique. They used the FluxMax technique to formulate the heat integration model for the utility section of the process. Models was formulated for the different sections of the proposed design. Notably, the renewable energy (solar and wind) time generation series of 8760 hrs were model aggregated into a daily profile of 24 hrs using *tsam-time series aggregation module*, this allows for proper representation of the seasonal variation of the renewable energy. The scheduling for methanol storage was performed for time stamp of days. The resulting linear model was implemented in GAMS and solved using CPLEX. The obtained that optimal design gave a levelized cost of 1392 \$/t and 799 \$/t for the reference year (2019) and 2030 respectively.

Chen *et al.,* 2021 [75] optimized the scheduling of renewable methanol production process to understand the interaction between renewable mix, storage sizing and dispatchable energy price. The renewable energy mix considered are solar and wind, they study their daily generation over a year period which is cumulatively 8760 hrs. The intermittency of the renewable energy was accounted for using extent of surplus generation factor (over-provision factor). The full storage operation is measure from time 1 hr to time 8760. The scheduling design was achieved by minimizing the levelized cost of MeOH for an assumed plant life of 30 years. In parallel to the minimization, the levelized energy cost was minimized. The optimization is done using data from two locations; Kramer Junction and Norderney. The NLP optimization problem was solved using FMINCON solver in MATLAB. They found that the minimized levelized cost of MeOH was 106 \$/MWh and 103 \$/MWh for operations in Kramer Junction and Norderney respectively using a dispatchable energy price of 230 \$/MWh.

Chen and Yang (2021) [76] studied the effects of renewable methanol production flexibility by optimizing the system operation. They formulated a planning and scheduling model to explained the operations of electrolysis, methanol synthesis, and distillation. To deal with the challenge of varying ramping capacities and dynamic ranges, they suggested the installation of storage for hydrogen and raw methanol produced. The LP was formulated for a year period and a hourly horizon for scheduling process. The LP was implemented in GAMS and solved using CPLEX solver. They obtained that the methanol production cost was reduced by 35% by combining the over-sized and dynamically operated electrolysis and methanol processes.

3.2.2 Ammonia

Palys and Daoutidis, 2020 [77] compared the economic viability of ammonia as renewable energy storage to conventional hydrogen energy. They formulated a MILP combined capacity planning and scheduling model to minimize the levelized cost of energy by determining the optimal production rates, unit selection and size, and storage inventories for each period of operation. They aggregated the hourly resolution input data into 672 optimal scheduling periods. The developed model was tested on the data from 15 U.S cities to comprehensively study the geographical sparsity of renewable energy. The model was formulated in GAMS and solved using CPLEX. They found that the use of hydrogen in the locations with high solar potential slightly lowers the LCOE, whereas a 30% reduction in LCOE is provided with the usage of Ammonia in the location with high wind potential and greater seasonal storage demands.

Allman *et al.*, 2018 [78] applied a time-variant operation to study the optimal scheduling of a proposed wind-powered ammonia production process. They proposed an approach for determining the optimal design of time variant system. Of the novelties of this work is the removement of the time variant, or operational constraints from CDS (combined design and scheduling) and placing them into a newly optimal scheduling problem. A scheduling informed design model was formulated for a 48-hour scheduling horizon. The wind speed forecasts were generated using normal distribution centered around a historical load value. The operating cost of the process was minimized and the model was applied to a wind-powered ammonia production. The problems were modeled in GAMS and solved using CPLEX. They concluded that the proposed design improves the computational tractability of the design problems and high prediction accuracy of the operating cost.

Palys *et al.*, 2019 [79] proposed design for renewable ammonia production process which is suitable for food-energy-water sustainability, the ammonia was synthesis from an agricultural waste using renewable energy from wind. They formulated a hourly scheduling optimization model over a year, to account for the seasonal variation in the wind energy generation, demands for ammonia, water and power. The demand for power, ammonia and hydrogen were accounted for in the formulation. Notably, a discretization was performed for hourly battery charge and chemical storage. To demonstrate the effectiveness of the proposed design, they minimized the net present cost of the process. They reported a converging time of the MILP formulated to be 1 hour

25 minutes and 44 seconds. They found that the optimal net present cost for the system was $56, 500 with a corresponding reduction in emission cost of $12.90/ton of CO_2. Furthermore, their system was able to prevent the importation of 477m of water and water loss of 558, 000 m of cooling water.

Osman *et al.,* 2020 [80] proposed a design for the continuous production of renewable ammonia. They formulated an MILP to optimize the selection, sizing, scheduling of the upstream electrical and thermal energy, nitrogen and hydrogen production and storage. To study the scheduling of the production of the ammonia, a full year hourly resolution was considered. They found the present-day levelized cost of ammonia (LCOA) of $718/ton NH_3 and further reduction of the LCOA to $450/ton NH_3 due reduction in projected technology cost.

Armijo and Philibert, 2020 [81] used a simulation-based optimization technique to calculate ammonia production costs over a range of synthesis-to-electrolysis and solar-wind rations. They determined the optimal sizing of the PV arrays and wind turbines energy production while scheduling the purchase of "firming" power from the local utility. They further computed the size of hydrogen buffer storage from its oversizing and the configuration that demonstrate lowest cost of production is labeled optimal. At the end of their optimization, they found that a reduced ammonia production cost of below $500/t of ammonia and further concluded that their proposed configuration can be cost competitive.

Kelley *et al.*, 2022 [82] developed a Hammerstein-Weiner process flowsheet model based on the first principles and linear dynamic blocks to describe the dynamics of ammonia synthesis loop. They utilized this model to formulate a time-variant demand response (DR) scheduling problem. They solved the formulated problem using gPROMs, and found a 50% reduction of the peak-time power consumption in each of the considered cases.

Nayak-Luke *et al*., 2018 [83] expanded on their previous work to include a rule-based scheduling to find the optimal cost of producing renewable ammonia for 534 locations. The availability of the wind and solar energy was scheduled using hourly resolution, and then optimized the power generation fractions and the system design. Their formulation was modeled and solved in MATLAB. They found that the future production cost of ammonia to be $310/ton in 2030, a decrease from $473/ton today.

3.2.3 Hydrogen Production

El-Taweel *et al.*, 2019 [84] proposed a model for hydrogen production through electrolysis and the optimal scheduling of hydrogen fueling stations to be used in transportation and other electricity needs. Their major contributions are; (i) the evaluation of the profitability of the hydrogen stations under capacity-based demand response (CBDR) (ii) the incorporation of the CBDR management system to achieve profit at lower hydrogen sale price (iii) the demonstration of the responses of the hydrogen fueling stations under variable demand. Their proposed model is aimed at maintaining the expected profit using stacked profit and also to procure lowest values for hydrogen sale prices. The optimization horizon is taken to be 3 hours with 1-hour interval and the hydrogen storage is prepared for the next available hour. The non-linear problem was solved in MATLAB in a convergence time of about 10 seconds. They found that the annual rate of return of the plant was $1.475 M at a 13% of the CAPEX value of the plant.

Palys and Daoutidis, 2020 [85] performed a comprehensive techno-economic analysis of a combined renewable hydrogen and ammonia for energy storage. They utilized a consecutive temporal clustering algorithm to model the varaible-length operation periods which are then used as input into the optimization model. A full year hourly time series data was used as input into the algorithm. the objective of the model developed was to minimize the levelized cost of energy (LCOE) supply, consisting of the total capital investment of all the units, total operating cost in each weighted period. The annualized net present cost of the capital investment was calculated using a discount rate of 10% for 20 years. The formulated MILP was solved using CPLEX in GAMS. They found that hydrogen and ammonia storage is more suited in cities with high solar intensity and wind capacity respectively. The LCOE for the combined system was obtained to be within $0.17 /kWh and $ 0.28 / kWh.

Marocco *et al*., 2021 [86] formulated a MILP problem to evaluate the optimal design of renewable hydrogen battery energy system for off-grid insular environments. In their work, they utilized a means of times of use to evaluate the effect of demand response program, and worked on the single-layer MILP approaches with a 1-year horizon. The ambient air temperature and solar irradiance were modeled using an hourly data as input. To evaluate the effect of the demand response program, they used a time-of-use method over a daily time horizon by switching between loads at expensive periods to cheaper periods. The reliability of the hydrogen battery system was determined by minimizing the localized cost of energy of the system. They MILP was modeled in MATLAB and solved using IBM CPLEX. Their results suggests that LCOE changes from 0.455 €/kWh to about 0.402 €/kWh without and with demand response program respectively. They suggested that the reduction in cost is probably due to the decrease in the battery storage capacity.

Arora *et al*., 2022 [87] demonstrated the optimization of a proposed renewable hydrogen production for refueling stations. They used a process intensification concept to propose a small-scale and modular hydrogen production technology powered by a renewable energy. Sorption enhanced reaction process was used as the intensified process for the hydrogen production, this sorption process simultaneously performs chemical reaction and the removal of the byproduct. During the formulation, artificial neural network regression model was developed to explain the nonlinear dynamics of the sorption enhanced-steam methane reforming process, which takes process design and operation commands as input. The MILP model was formulated to minimize the hydrogen production cost at a time horizon of one representative day for 4320 discrete time periods. The formulated model was applied to Oakland, CA and then the nation for the investigation of the effect of hydrogen demand, renewable energy on the cost of hydrogen produced. Their results showed that for nationwide hydrogen production of 2 ton/day, hydrogen can be produced 50% less than the conventional method.

Mallapragada *et al*., 2020 [88] conducted a survey to determine the optimal PV-based hydrogen production costs with the aim of determining the schedules and sizes of PV arrays, batteries and electrolysis to satisfy continuous hydrogen production set point. They realized that $2.5 /kg of hydrogen or less can be achieved through an over-sized electrolysis which is powered with solar energy, thereby minimizing the local battery capacity. Therefore, their designs were conclusively suggested to be favorable considering the reduction in the cost of electrolysis and hydrogen storage.

Zhang *et al*., 2018 [89] Performed the optimization of a hybrid system of renewable hydrogen storage and battery using a simulated annealing algorithm. In their approach, they proposed a hybrid heuristic method which include the chaotic search, harmony search, and simulated annealing algorithms. The model developed was to optimize the supply of residential electricity load through a stand-alone hybrid energy system, with the aim of minimizing the cost of the hybrid energy system. Notably, the optimal sizing of the components of the energy systems including the hydrogen storage, solar and wind energy were evaluated. Their model was formulated and solved in MATLAB. They found that the life cycle cost of wind turbine, batteries and converter are 67%, 5%, and 28% respectively. Hence, from the low value of the relative mean index of the algorithm, they conclude that the proposed algorithm is more robust than the other algorithms.

3.2.3 Combined Chemical Energy Storage

Due to the potentials of the stand-alone chemical energy carriers such as hydrogen, ammonia, and methanol, many researchers are making efforts in studying the operability of the combined production of two of the common chemical storage or the combination of the three carriers.

Yuksel *et al.*, 2021 [90] developed a novel a combined energy plant for the co-production of hydrogen and ammonia. In their proposed plant, a treated freshwater was sent to a PEM electrolyzer powered by the electricity from the methane gas turbine. The water-splitting reaction took place at the PEM unit. They further combined the generated hydrogen for the synthesis of ammonia gas. The energetic and exergetic efficiency of the proposed plant was evaluated using a parametric analysis. Each unit of the process plant was modeled using mass, energy, exergy and entropy balance and these equations were solved in Engineering Equation Solver pocket software. They found out that the hydrogen and ammonia production rates decrease from 0.0665 kg/s and 0.2582 kg/s to 0.0587 kg/s and 0.2310 kg/s respectively with increase in the pinch point temperature of the superheater. On the other hand, the increasing mass flow rate of the methane fuel contributes positively to the performance of the plant.

Palys and Daoutidis, 2020 [91] performed a comprehensive techno-economic analysis of a combined renewable hydrogen and ammonia for energy storage. They utilized a consecutive temporal clustering algorithm to model the variable-length operation periods which are then used as input into the optimization model. A full year hourly time series data was used as input into the algorithm. the objective of the model developed was to minimize the levelized cost of energy (LCOE) supply, consisting of the total capital investment of all the units, total operating cost in each weighted period. The annualized net present cost of the capital investment was calculated using a discount rate of 10% for 20 years. The formulated MILP was solved using CPLEX in GAMS. They found that hydrogen and ammonia storage is more suited in cities with high solar intensity and wind capacity respectively. The LCOE for the combined system was obtained to be within \$0.17 /kWh and \$ 0.28 / kWh.

Ganzer and Dowell, 2020 [92] compared optimal production of methanol and ammonia from solar renewable energy. Their formulation includes the optimal scheduling and its effect on the renewable process design. In their modeling, a sequence of days was considered to represent year to account for the seasonal intermittency of the renewable energy, a hourly resolution which is represented by six sequences of twelve days. Accounting for the heat utilized in their process, heat integration in the process was evaluated using a minimum temperature approach for the streams exchanging heat. Their formulation was aimed at minimizing the operating cost of the production process including the contribution of the operational and capital expenditure of the proposed superstructure. The MILP model was implemented in GAMS and solved using CPLEX, which was applied to two locations; London and Dubai. They found that the cost of producing ammonia and methanol in London are both 6000 \$/t and in Dubai are 2600 \$/t and 1700 \$/t respectively. Furthermore, they concluded that the use of renewable energy makes the entire process to be driven by the Capital expenditure as against the conventional operational expenditure driven.

Palys *et al*., 2021 [93] formulated a combined optimal design and scheduling model for the production of renewable hydrogen and ammonia for combined heat and power use. Their model is to minimize the annual net present cost of supplying power and heat at different period of scheduling. The scheduling horizon of the model was chosen to be a full year with hourly resolution. To capture the seasonal variability of the renewable energy, temporal aggregation by consecutive clustering with full year hourly resolution time series data of 8760 was utilized. The formulated MILP was implemented in GAMS and solved suing CPLEX, with a computational time of 8 hours and 40 minutes. Their model was applied to 12 different cities in the USA. They found that at least 85% of the power demands and 75% heat demands were met using the renewable energy.

CHAPTER 4. Integrated Energy Systems Optimization under Renewable Energy Uncertainties

The availability of renewable energy sources significantly depends on weather and geographical location. This temporal fluctuation introduced uncertainties into every energy system powered by renewable energy, which could be have impact on the operation and effectiveness of the energy system. This section tends to highlight the literatures that optimize the renewable energy powered systems under the impact of the renewable energy uncertainties.

4.1 Methanol-integrated energy system

Martin, 2016 [94] optimized the production of renewable methanol under uncertainty. They developed a surrogate model for the operation of the process and cost estimation. This was to include uncertainty into the multiperiod optimization problem and the surrogate model was formulated under steady condition. The uncertain parameters such as the solar and wind energy availability was accounted for using two-stage stochastic programming. The probability distribution of the uncertain parameters was approximately discretized. This was done using three different levels of solar irradiation, low, medium, and another three levels representing wind velocity over monthly basis. They finally determined the third uncertain variable to be the electricity cost. The MILP formulated is to minimize the methanol production cost, and the problem was implemented in GAMS. They applied their problem to two cases, Spain and UK. They concluded that the usage of wind turbines is favorable in UK and the excess electricity would be produced in winter, while in Spain, electricity could be produced from solar panels ad sold without restriction.

Martin and Grossmann, 2018 [95] developed a two-stage stochastic programming problem to minimize the cost of producing bioethanol from biomass and renewable energy. In their formulations, they considered the power demand, biomass, wind and solar availability to be uncertain. Three scenarios were considered for each of the parameters, probability of low, medium and high. The optimal integration of renewable technologies into the proposed design was to be determined over 12 months. The formulated MILP was solved in GAMS using CPLEX. They found that the system demonstrated a slight reduction in CO_2 emission of 0.23 t/s and there is a larger investment of 4 billion € due to the production of additional hydrogen and hydropower as well as methane as a form of excess power.

Li *et al.*, 2023 [96] designed and optimized a proposed flexible poly-generation process for methanol and formic acid under uncertain product price. They developed a surrogate model of the production of methanol and formic acid using Aspen Plus to determine the optimum process parameters, and performed a sensitivity analysis on the impact of the vent gas on energy consumption and capacity of the equipment. Assuming the methanol and formic acid prices as uncertain parameter, they performed a two-stage optimization on the integrated system. After their work, they achieved an increase in the annual net profit of 8.97% and decrease of return on investment by 4.67%.

Lee *et al.*, 2022 [97] formulated a two-stage stochastic optimization problem to optimize the design and emulation of renewable electrochemical CO_2 reduction to methanol. In their design, methanol is synthesized when CO_2 is reduced by reacting it with hydrogen from water in a proton exchange membrane powered by wind and solar energy. In their the two-stage stochastic optimization is performed to account for the uncertainty in the availability of the wind and solar energy. To account for the seasonal variation in the wind and solar intensity, 30 weather scenarios were generated for a year. The objective function of the optimization problem is to minimize the overall cost of the proposed system. Their formulated MILP was modeled in Pyomo and solved using Gurobi. Their results show that at a methanol price of 550 $/ton, the optimized design of the system is economically viable. Also, the two-stage stochastic optimization demonstrated to be the best way of addressing the uncertain availability of the renewable energy sources.

Chen *et al.*, 2021 [98] evaluated the impact of process flexibility on the production of methanol from different renewable energy sources. In their work, they tried to understand the mechanism of the influence of flexibility on the economic and environmental metrics of a renewable methanol production process. Their proposed superstructure involves the reaction of CO_2 with the generated hydrogen from water electrolyzer. Each of the unit operations is explained using a simple equilibrium and kinetic model. Notable, the renewable energy fluctuation in availability was modeled using the hourly dispatchable energy and the today capacity factor of the wind and solar sources. Their formulation is aimed at the minimization of levelized cost of methanol. They found that the levelized cost of methanol reduced by 21 and 34% in the two locations considered when the production was 100% renewable.

Gu *et al.*, 2022 [99] performed the techno-economic analysis on the green methanol process plant. They proposed a renewable methanol plant comprising a hydrogen generation unit and the CO_2 hydrogenation unit. The economy of the system was evaluated by minimizing the levelized cost of methanol to ascertain the performance of the proposed plant, and with the combination of the effect of wind turbines, Photovoltaics arrays fluctuations, electrolyzer capacity on the levelized cost of methanol of the renewable plant. furthermore, they performed the sensitivity of the economic analysis on the fluctuation of the prices of the renewable energy (wind turbines, solar energy). The one-way sensitivity analysis performed showed that when the price pf the Photovoltaics array reduced by 50%, the levelized cost of methanol of the solar powered H_2-Methanol system decreased by 28% (4618 RMB/ton). Whereas, the levelized cost of methanol of hybrid-H_2-Methanol system and wind-H_2-Methanol system reduces by 32% and 37% respectively when the price of wind turbines decreases by 50%.

Huang *et al.,* 2022[100] combined the study of the modular design of renewable methanol production process. They evaluated the impact of uncertainty in renewable energy and the modular designs on the operation of the methanol synthesis lines by considering the continuity and stable operation targets. In their proposed methanol production superstructure, hydrogen is generated from a solar and wind energy driven electrolysis and combined with a captured CO_2. In addition to the material balances of the unit operations in ASPEN HYSYS, heat integration was performed and included among the constraints in their formulation. The MILP formulated was implemented in GAMS and solved using CPLEX. They found that the energy storage capacity needed in the modular methanol unit are significantly reduced to 85.33% and 87.36% for battery and hydrogen respectively, which was attributed to the ability of the modular methanol production system to account for the fluctuations in the renewable energy through the adjusting of the number of the modular production lines. Furthermore, they explained that it could be means that the methanol synthesis is capable of maximizing the production capacity when the renewable energy is abundant and minimize the energy consumption when the renewable energy is insufficient.

4.2 Ammonia Production under uncertainty

Verleysen *et al*., 2020 [101] performed the optimization of wind powered ammonia synthesis under operational uncertainties. They modeled the main unit operations (Pressure Swind Adsorption, Haber-Bosch Reactor) in Aspen Hysys and the wind speed was converted to wind power in Python. The models of the unit operations were optimized using a Multi-Objective Genetic Algorithm (MOGA) to determine a set of optimized designs and further used Polynomial Chaos Expansion Algorithm (PCE) to quantify the uncertainties parameters for each subunit. They further formulated a Robust Optimization programming problem (a combination of the MOGA and PCE) to maximize the wind energy storage through a metric, load factor. Their preliminary results suggests that an effective design produces 3.2 times more Ammonia with 2.6 times less robustness. On further global sensitivity analysis, average ammonia production is more by 99.7% with a reactor with a controllable temperature.

Verleysen *et al*., 2021 [102] studied the sensitivity of a dynamic synthesis process for flexible seasonal energy storage. They created a dynamic Haber-Bosch loop in ASPEN Plus dynamics which includes operational and parametric uncertainties. The operational uncertainties considered in their study include variant temperature at the; reactor inlet, condenser's cooling and variant H_2/N_2 ratio at the Haber-Bosch synthesis inlet feed. The temperature fluctuation at the reactor inlet and condenser's cooling was modeled using gaussian distribution. To quantify the combined effect of all the uncertain parameters on the performance of the systems, global sensitivity analysis was done. Sobol's decomposition was performed to quantify these contributions. They further extended their model to include a polynomial chaos expansion. The problem was model in Aspen Plus Dynamics. They found that the uncertainty on the inlet temperature controls the overall standard deviation of the ammonia synthesis by 87.8%.

Laṡṡåk *et al*., 2010 [103] formulated models to determine the effect of parameter uncertainty on the modeling of industrial reactor considering safety and operability. The influence of temperature fluctuation was evaluated using the enthalpy of the reaction. Gaussian normal distribution probability function was used to describe the uncertain temperature parameter. This model was solved using Monte Carlo approach. They found that a small change in the uncertain parameter or combination of the key parameters can lead to a greater change in the steady states results of the operating quantities.

Dechany Antoine, 2021 [104] formulated multi-objective model to perform optimization and quantification of uncertainty of renewable Ammonia-to-power approach. They proposed a design for the conversion of renewable ammonia into power using a proton exchange membrane fuel cell. The operability of their proposed design was evaluated through the voltage and current output from the fuel cell. In their optimization, their objective functions were grouped into four to reduce computational cost, they include the minimization of the power overshoot, minimization of the voltage response transient time, minimize the average difference between the power demand and the power produced by the system in a unit time step. To quantify the uncertainty, a Polynomial Chaos Expansion (PCE) algorithm was used and the characterization of the uncertain parameters were evaluated using probability density function which follows a Gaussian normal distribution. They found that extreme high uncertainties (between 64.1% and 92.1%) are caused from the variation in power demand throughout the year.

Ghappani and Karimi, 2023 [105] determined the optimal operation of an energy hub with combined heat, hydrogen and power system powered by renewable ammonia. In their proposed energy hub, wind, solar energy sources, hydrogen and ammonia are integrated as a flexible energy hub with combined heat, power and hydrogen system. In the modeling, the power capacity of each of the systems in the energy hub was model including the ammonia energy carrier system. The objective function of the optimization is the minimization of operational cost of the hub with the cost contribution of each of the systems. Notably, the uncertainty associated with the availability of solar and wind power, was modeled by generating stochastic scenarios using Monte Carlo approach. The MILP formulated was modeled in GAMS and solved using CPLEX solver. They found that there was a 16.8% cost reduction when ammonia energy carrier is used as fuel in the energy hub.

Verleysen *et al*., 2022 [106] performed the optimization of remote and local production of renewable ammonia under uncertainty. They proposed a standalone power-to-Ammonia system which was divided into five parts starting from the part where sun irradiation is converted to energy and to the part where the produced ammonia is transported to the demand site. Each part of the system was modeled individually using energy and material balances. The operability of the proposed design was evaluated using multi-objective functions; minimizing the levelized cost of ammonia, maximizing the total energy efficiency of ammonia in the system while accounting for the influence of uncertainty. In characterizing the uncertain parameters, solar irradiance and temperature were considered as Gaussian distributions while other uncertain parameters are represented as uniform distribution. They formulated the robust design optimization model using Polynomial Chaos Expansion approach and applied their problem two countries namely; Belgium and Morrocco. After comparing the flexible and robust design optimization, they found that there is a 48.2% reduction in the ammonia production with 20.9% increase in flexibility.

Cesaro *et al*., 2021 [107] forecasted the levelized cost of electricity generated from a renewable ammonia production plant. In their work, they hope to (i) predict the levelized cost of ammonia (LCOA) produced from a solar energy and its sensitivity on the LCOA (ii) predict the levelized cost of electricity (LCOE) from a plant that convert ammonia to power to meet energy demand. Their contribution is in the production of ammonia using a solar energy and batteries and the conversion of ammonia to power using combine cycle gas turbines. They formulated two separate models for minimize the LCOA of green ammonia synthesis and the localized cost of electricity of ammonia-to-power technology. When performing the sensitivity analysis on the renewable intermittency on the LCOA and LCOE, they found that the average of the lowest and the highest sensitivity are approximately 294 $/t and 450 $/t.

Qi *et al*., 2022 [108] proposed a surrogate based optimal design for a green ammonia and electricity co-production system through the use of liquid air energy storage. They hypothesized that the liquid air energy storage (LAES) has a large storage capacity with no geographical restrictions. To deal with the situation of renewable energy intermittency, the concept of co-production system was introduced which can absorb the dispatchable electricity produced from the grid while meeting the electricity demand at a peak hour and therefore leading to a reduction in cost. Furthermore, a scheduling model was integrated with the renewable power generating profile at an hourly resolution to study the influence of the power allocation and storage sizing on renewable generation and the cost of producing the green ammonia. The peak hours for the electricity generation were assumed to be 8 hours every day from 12 am to 8 pm. The formulated model was to minimize the levelized cost of ammonia which was gotten to be 360.74 €/t at a renewable penetration of 77% suggesting that the renewable ammonia is cost-effective compared to the conventional ammonia production process.

4.3 Hydrogen Production under Renewable Uncertainties

Serrano-Arevalo *et al*., 2023 [109] formulated a MILP problem for the optimization of renewable hydrogen production under renewable energy and storage uncertainty. Their model was aimed at minimizing the energy production cost and the emission taking into account the intermittency of the renewable energy. They presented a disjunctive optimization model to guide in the selection of the different energy generation processes and their corresponding storage units. To account for the variability of the solar and wind energy, the renewable technologies were divided into variable technologies and non-variable technologies. Their formulated MILP was applied to a case study in Mexico, particularly the peninsular region. Their model was implemented in GAMS and solved using CPLEX. They found that an increase of 300 $/t hydrogen in the selling price decreases the total cost by 1.80 %, and triples the profits and increase the hydrogen production. furthermore, about 913.92 t of CO_2 was saved when the renewable technologies are compared to the conventional technologies.

Tatar *et al*., 2022 [110] formulated a novel MILP model for the optimal design and operation of a microgrid integrated with green hydrogen under renewable uncertainties and demand scenarios. They utilized a probabilistic scenario generation approach to handle the uncertainty associated with the wind speed, air temperature, solar irradiance. The solar irradiance is modeled using its dependence on air temperature, alternatively, the variation in the wind speed is modeled according the Weibull distribution equation. Finally, to accurately model the uncertainty of the renewable energy, they formulated the time variant renewable energy using probability density distribution with generated scenarios covering next twenty years. Their formulation is to minimize the net present cost of the microgrid over twenty years, which was implemented in GAMS and solved using CPLEX. They found that the electricity demand is mostly met through the solar energy for the likely and mid-likely scenarios and the bio gasifiers for the unlikely scenarios. Furthermore, at

12% inflation rate, the initial investment, operational and maintenance cost is 9.6, 8.01 and 7.36 billion TRY for the likely, mid-likely and unlikely scenarios respectively.

Cooper *et al*., 2022 [111] formulated a framework for the design and operation of a large-scale stand-alone wind powered water electrolyzer. They intend to minimize the levelized cost of hydrogen and the emission from the proposed design. In their formulation, the time-variant power consumed by the electrolyzer was calculated using a block specific fractional ramping rate approach. To model the behavior of the system to the changes in the renewable inputs, three electricity profiles were considered to be the starting point. Notably, the second profile represents the wind power profile with an hourly data for every quarter year. The profiles equally provide the energy as a framework with a full 3983 hrs. The MILP formulated was modeled in GAMS and solved using CPLEX. They found that the levelized cost of hydrogen for regular wind profile, wind quarter load, are 1.9% and 8.9% respectively at a hydrogen production rate of 6%. They stated that this difference is due to the difference between the electrolyzer used.

Mehrjerdi *et al*., 2020 [112] integrated a hydrogen system with a solar energy unit. They considered the off-grid system for three different buildings operated through peer-to-peer home energy management, and each building energy demand is met via solar panels and hydrogen storage. To handle the uncertainty associated with the renewable energy, they formulated a stochastic MILP model using 10 scenarios of the solar energy capacity factor and power demand, with four season representative days and hourly resolution for the operation decisions. Their MILP was modeled in GAMS and solved using CPLEX. They found that the fuel cell and the elctrolyzer overcomes the uncertainty by adapting to the changes in the different scenarios, and hence, cause a balance between the power generation and consumption. In addition, at hour 20 and 18, the system is fuel cell and electrolyzer driven respectively, and the cost remains unchanged after 7 scenarios of operation.

Kotzur *et al*., 2018 [113] evaluated the influence of time variant aggregation approach on a wind and solar-based stand-alone hydrogen energy storage systems. They formulated a MILP to determine the optimal sizing of the renewable generation for hydrogen production, storage and fuel cell technologies. They found that the cost of the energy system is mainly driven by the renewable energy investment, and also, the optimal hydrogen storage has a higher capacity for longer storage duration than the batteries storage technologies.

Heras and Martin, 2021 [114] proposed a time-invariant a low-cost magnesium hydrogen energy hub for the storage of wind and solar energy. They hypothesized that magnesium hydrogen is low-cost storage chemical for solar and wind energy, and hence developed a non-linear programming model for the storage and the discharging of the chemical storage. Their formulated model was to found the optimal location, and the scaling of the proposed storage technologies along with the hydrogen production through electrolysis and the wind and solar generation in Spain. The formulated model was implemented in GAMS and solved using CONOPT solver. They found that if the heat and O_2 byproduct are sold, the cost of electricity is as low as \$0.1 /kWh.

Qi *et al*., 2021 [115] formulated a two-stage stochastic programming for the optimization of the capacity of a high temperature electrolysis system for dynamic operation. In their proposed system, hydrogen is generated from a renewable powered water electrolyzer. Their model is to address the impact of wind-solar intermittency on the optimal capacities and operation of the proposed systems. To account for the seasonal and daily temporal characteristics of the renewable energies, a probability distance approach was used to reduce the number of generated scenarios. The reduction method was used to reduce the time periods to 96 from 8760 for four representative days. The formulated stochastic model was used to minimize the capital expenditure of the high-temperature electrolysis system. To solve the developed nonconvex MINLP, an integrated interior-point and branch and bound algorithm was employed. They found that the at above hydrogen price of about 4.2 \$/kg, the optimal device capacities increased with the power source fluctuation, while at a price below 4.2 \$/kg, the optimal capacities decreased with the fluctuation. They stated that this was due to the renewable energy spillage.

Giannakoudis *et al*., 2010 [116] used a stochastic annealing algorithm to handle the renewable uncertainty in the optimal design and operation of hydrogen production and storage systems. In their systems they considered the production of hydrogen using wind and solar energy sources. The weather uncertainty associated with the renewable energy was determine through the metrological and historical data of the solar and wind energy, hence, the uncertain parameters considered in their formulations are solar radiation, wind speed, and the efficiencies of the electrolyzer and the fuel cell. The net present value of the investment for operating period of ten year was to be minimized. The formulation was applied to two cases; with uncertainty and without uncertainty of solar radiation and wind speed. They observed a robust performance under an achievable system design, in response to uncertain operating conditions.

4.4 Combined Chemical Storage production

Hernandez-Perez *et al.,*2022 [117] formulated a multi-objective model for optimizing ammonia and methanol production processes under shale/natural gas ratio uncertainties. Their multi-stage optimization was carried out by first simulating the co-production process in ASPEN HYSYS to evaluate the performance of the process through their economic objective function and the sensitivity of the design parameters on the feed stream. To perform the optimization of the processes, they applied an improved multi-objective differential evolution (I-MODE) algorithm based on a metaheuristic-deterministic optimization strategy. This algorithm is based on a simulated stochastic optimization method and hence used to address the uncertain introduced into the system through natural gas composition fluctuation. They found that the net profit of the process is 388 MM$/yr and total emission of 3.3 MM TonCO_2/yr at an optimized shale/natural gas feed and division fraction of 130170 lb/hr and 0.31 respectively.

Zhang *et al.*, 2019 [118] formulated a MILP model for the integration of design and operation of renewable energy fuels and power networks. In their superstructure, they considered the wind, solar, biomass, hydro and waste as the renewable energy input. These energy sources were used to power different unit operations for the production of multi-energy storages such as bioethanol, hydrogen, methanol, thermal energy and others. To address the uncertain with the renewable energy, they divided the planning horizon (a year) into seasons through a representative set of time periods. Their multi-scale model was formulated to minimize the total cost of the energy production, this model was implemented in Julia and solved using CPEX. Applying the model to Spain, particularly in Almeria, they found that 10% of gasoline, 5% of diesel and 60% of electricity demanded can be met using the renewable process network.

Kenkel *et al*., 2022 [119] performed the optimization of a superstructure for the production of fuels from renewable energy sources. Among the fuels produced is the jet fuel which production involves different routes including methanol production, Fischer-Tropsch, biomass-to-X process. Their modeling is carried out using a novel approach, Open Superstructure modeling and Optimization Framework (OUTDOOR). This method is to basically account for the advance mass balances of each of the processes and the uncertain data associated with the superstructure. The OUTDOOR model was formulated as MILP which aimed to minimize the net production cost of the entire process. The model was implemented in PyOMO and solved using guropi solver. They found that the cost of production using the integrated biomass-methanol-to-jet fuel plant is 211 Eur/MWh which is a reduction from 21% to 11.5% as compared to the electricity or biomass-based plant.

Demirhan *et al*., 2020 [120] demonstrated the reliance of a novel multiscale energy systems approach for the optimization of renewable power generation and storage systems. Their proposed design consists of renewable energy sources from wind and solar energy, hydrogen synthesis from water hydrolyzer, which was then sent to the methanol synthesis for the hydrogenation of captured CO_2 for the production of methanol, also, part of the hydrogen produced from water electrolysis was further combined with N_2 from air to produce ammonia. In their MILP formulation, the intermittency in the availability of wind and solar energy is handled using a Time representation and data clustering approach, which involves the distribution of the characteristic time into season, which was taken as a 24-hr. process, and used k-means clustering approach to reduce the data set into small clusters. The formulated MILP was used to minimize the total annualized cost of meeting the power demand, which was applied to data from Texas and New York. They found that the dense energy carriers are capable of reducing the total power generation and the battery storage by 30-50% when renewable energy is used.

Tso *et al*., 2018 [121] performed a deterministic global optimization of a renewable ammonia and methanol co-production processes. They formulated a MINLP model with the objective for the minimization of the cost of hydrogen production, with a set hydrogen production output of 500 MT/day. The computational studies were carried out on three processes, methanol production only, ammonia only, and ammonia-methanol co-production. From their mass conversion analysis, the 500 MT/day of hydrogen was used for the production of 2830 MT/day ammonia and 4000

MT/day methanol. Emission was restricted to less than 50%. They found that the co-production of ammonia and methanol reduces the breakeven price of methanol and ammonia individual production to about 4-7%.

Li *et al*., 2023 [122] designed and optimized the poly-generation process for the production of renewable methanol and formic acid from the hydrogenation of CO_2. In addition to the uncertainty associated with renewable energy source, they included the price related uncertainty. They applied a two-staged scenario approach to model the uncertainty section of the process. This approach involves the representation of the uncertain parameters using Gaussian probability distribution. To evaluate the flexibility of the process, they minimized the return on investment of the production from the gas feed, CO_2 and H_2 of 200 and 572.73 kmol/h, respectively. They found that under uncertain condition, the flexibility indices of the methanol and formic acid production processes are 1.088 and 1.194 respectively, leading to an increase of fixed investment cost to $ 39190000. Conclusively, the flexible process can lead to a higher profit and reduces market risk.

CHAPTER 5. Supply Chain Optimization

Considering the promising potential of hydrogen, methanol, and ammonia in storing the fluctuating renewable energy, the study of the supply chain of the energy carriers have attracted the attention of many researchers. This section highlights the works done the optimization of the supply chain of the energy carriers to inform decision makers of the optimal location, optimal facility sizing, optimal production capacity and optimal transportation/distribution routes for meeting the demand.

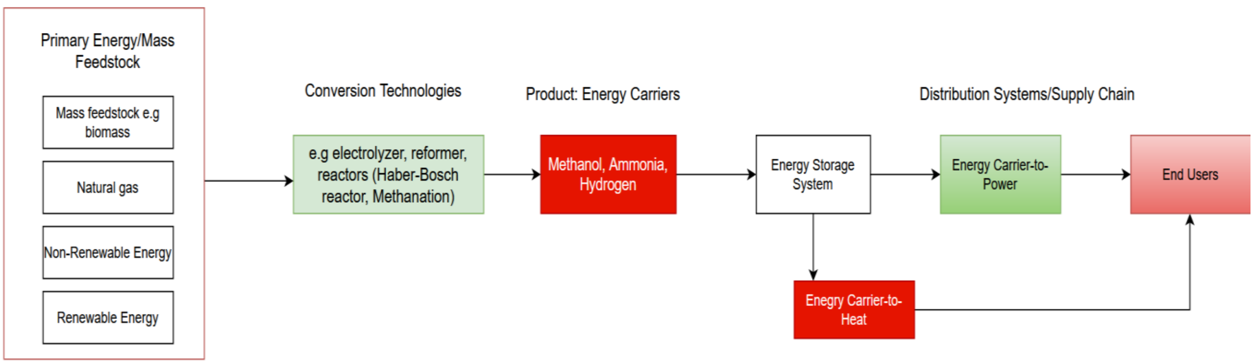

Figure 6: Superstructure for a supply chain network of multiproduct systems

5.1 Methanol Supply Chain Optimization

Methanol is a promising energy carrier which has caught the attention of several researchers. Hence, there is a need for the optimization of its supply chain.

Villicaña-García *et al*., 2020 [123] performed the optimization of supply chain of methanol produced from conventional and unconventional resources using economic incentives. In their work, unconventional sources of natural gas considered are shale gas and offshore extraction, with uncertainties associated with the demand of the natural gas and methanol. Their formulation contains the constraints on the total natural gas distributed to the markets: Both extracted and imported natural gas, the amount of natural gas distributed to the cities and methanol production facilities, the cost of transporting the natural gas to the markets (Cities and methanol facilities), the Natural gas sale, expected Methanol production, Cost of Methanol production in the new plants, Operating cost of producing Methanol in existing facilities, Cost of importing Methanol, Amount of methanol distributed to the markets (imported, produced in new and existing plants), Methanol transportation cost, and among others. The MILP was modeled to maximize the profit and minimize fresh water usage and CO_2 emitted. To introduce the economic incentive term, three scenarios were considered. Methanol production greater than the expected production leading to greater incentives, Methanol production lower than expected production leading to penalization of the incentives, and methanol production equal to the expected production leading to the basis incentives. Disjunction was utilized to allow for the selection of one scenario at a time for the new and existing plant. The total incentive is the sum of the incentives in the new and existing plant. The MILP was applied to a case study in Mexico with two scenarios; methanol is produced without considering uncertainty and economic incentive Ton, and methanol production with uncertainty and economic incentive. They found that production of new methanol plants, the incentive generated are about 113% better than the importation and production from existing plants.

Leduc *et al*.,2008 [124] formulated a facility location model to optimize the location of a wood gasification process plants for the production of methanol. Their model was aimed to determine the optimal sizes and locations of plants and gas stations. In their formulation, considered the parameters to be number of biomass supply locations, gas stations, demand sites. Notably, the heat recovery system was integrated into their plant and total cost of the plants were minimized to determine the optimal sites for the plants. Among their parameters are the methanol conversion of 60%, heat conversion of 10%, load hours of 7200 hrs and the economic life of the plants to be 25 years. To ascertain the feasibility of their formulation, they tested the model on different plants located at designated locations in Austria, they marked three production sites with M5, M10 and M20 representing the location for the production of different blends of methanol-5ton gasoline, Methanol-10tons gasoline and Methanol-20 tons gasoline respectively. They found that there is sufficient arable land (8%) for the production of M5, M10 and M20 in Austria, and cost of methanol could be lowered by 12% when heat is recovered.

Jeong *et al*., 2018 [125] incorporated Geographical information system (GIS) with MILP model to study the supply chain optimization of biodiesel. In their study, they simulated the minimum cost routes between origins-destinations (oilseed supply-biodiesel plants, biodiesel plants-biodiesel demand, and biodiesel plants-demand site) using origin-destination cost matrix approach, a network analysis function. Their MILP was to minimize the supply chain cost by optimizing the oilseed, biodiesel and the meal flows through the transportation routes. The model was computed to meet 100% and 20% of the biodiesel demand and fossil diesel demand respectively, for a specific region. The formulated MILP was applied to regions in Montana, South Dakota and North Dakota. They found that the plant construction, biodiesel production and transportation contributed 5.2, 76.1 and 18.6 % respectively to the optimized cost of $67.3 million/year. Considering the transportation network, they found that cost of supply chain significantly depends on the transportation cost, and hence, the transportation cost would decrease when new transportation routes and infrastructures are developed.

Moretti *et al*., 2021 [126] provided a detailed MILP for the optimization of bio-methanol supply chains from wood chip biomass. The optimization problem was defined for one year operation and the models account for the multi-feedstock biomass supply, seasonal biomass availability, inter-model and multi-model transportation, and the sizing of the pre-processing facilities. Their formulated model was to minimize the fuel production cost which comprises the annual operating cost, annualized investment cost. Their model was applied to a case study in Italy, and solved for five different scenarios; S1: rejects the selection of optimal conversion plant site, S2 and S3: limited the feedstock availability to woodchips and secondary residues, S4: do not allow transportation by train and S5: prevent train transportation and used a less accurate conversion plant cost function. They found that the cost of producing methanol in S1, S2, S3, S4 and S5 are 431.5 €/ton, 505.8 €/ton, 433.4 €/ton, 442.2 €/ton and 432.5 €/ton respectively. They concluded that the methanol production form multiple feedstocks was advantageous compared to a single feed process.

Nugroho *et al*., 2022 [127] optimized the supply chain of methanol produced from a biomass. Their supply chain formulation includes the cost of biogas, syngas generation, methanol synthesis, methanol retailing and methanol transportation. These functions contributed to the objective function for maximizing the supply chain profits. In addition, they integrated a stochastic optimization into the stimulation which optimizes the methanol prices at $670 and $500 at methanol factories and distributions, and as well minimizes the carbon emissions. They found that in the biogas and methanol plants, the biogas farmers, methanol retailers and the transporters received 52%, 19%, 25%, and 4% of the profits respectively.

Liu *et al*., 2014 [128] performed a supply chain multi-objective optimization of biofuel production via different process routes. In their study, they integrated a life cycle assessment with the supply chain model to perform the trade-offs between the economic, emission, energy objectives and the choice between the distributed and centralized process routes. Their centralized routes involve the transportation of the raw materials via different routes to the production factories while the distribution pathways involve the transportation of raw materials to the pre-treatment location and then converted to the intermediate products. The life cycle assessment of the biofuel was divided into biomass production, fuel production, fuel consumption and transportation. The multi-objective MILP formulated was divided into three parts; (i) maximization of revenue (ii) minimization of energy usage (iii) minimization of emission, and was solved using ϵ-constraint approach. After applying the developed model to 24 provinces in China, they found that the scale effect of factories in the centralized system was promising compared to the effect of the lower transportation cost in the distribution pathways.

5.2 Ammonia Supply Chain

Allman and Daoutidis, 2016 [129] developed a new framework for renewable ammonia supply chain in Minnesota, optimizing their capacity and location. In their formulation, the problem was constraint through ammonia balances at the different nodes in the supply chain, maximum capacity, and the nonnegativity of the production and distribution variables. The nonlinear programming problem was formulated to determine the optimal location of a new ammonia production plants and the capacity of the plant, this was done through the minimization of the annualized cost of the supply chain. The model was solved using BARON solver and applied to data from Minnesota in the USA. They found that in the base case, the optimal location at Dexter in Minnesota with a capacity of 140029 t/y. In addition, the cost of purchasing ammonia, building and operating new plant, and the transportation contributed 63%, 26% and 11% of the annual supply chain cost. Evaluating the uncertainty associated with the ammonia supply, wind energy availability using Monte Carlo analysis suggested that the 48% of the time, building new renewable facilities is optimal. Finally, they found that a carbon tax of $35/t decreases the supply chain emissions by 65%.

Allman *et al*., 2017 [130] developed a framework for the optimization of renewable and conventional ammonia supply chain. In their optimization, they tried to compare the environmental and economic cost of conventional and renewable ammonia. The conventional ammonia supply chain involves the production of ammonia in a large quantity, transported, transported via rail or pipeline to distribution sites and then to the local demand. The renewable route of ammonia production was incorporated into the centralized production supply chain. The MILP objective function consist the minimizing the annualized cost of ammonia supply chain and the CO_2 emission from the processing plant for 20-year operation. The formulated framework was applied to data from Minnesota and Iowa, and solved using BARON solver. They found that the base case results favor ammonia purchase from conventional plant and their further analysis showed that a carbon tax of more than $25/t will decrease the optimal supply chain by building large renewable plants.

Li *et al*., 2020 [131] formulated a framework for the optimization of the supply chain of renewable ammonia and electricity co-production. Their optimization consists the minimization of ammonia production cost by optimizing the facility location, capacities and the supply among the different regions in inner Mongolia. The wind energy capacity was predetermined to be approximately 60 GW with a full load hour of 4000 hrs. The formulation constraints include the limit on the planning capacities of the electrolyzer, hydrogen buffer tank, hydrogen storage tank. They found that the average localized cost of ammonia in inner Mongolia from wind and conventional energy are 0.57 €/kg and 0.41 €/kg respectively, which is a reduction of 30% in the capacity cost of the plants.

Zhao *et al*., 2021 [132] evaluated a proposed optimal supply chain and expansion of renewable ammonia producing in China. Their supply chain consists the hydrogen production, transportation, hydrogen storage, and the ammonia production using the produced hydrogen. The MILP optimization model involves the decision variables; number of electrolyzer, hydrogen distribution rate, hydrogen storage at the power plant and ammonia plant, oxygen storage inventory in the power plant. Their objective function is to minimize the total cost of expanded supply system which is make-up of the cost of hydrogen production, cost of hydrogen storage, hydrogen transportation cost, oxygen storage cost and the revenue from oxygen sales. In their case study, they considered ammonia production capacity of 300000 t/y, wind and solar utilization hour of 2780 and 1520 h/y respectively. Their results show that the cost of renewable ammonia will double the conventional production route due to the higher hydrogen production cost. Furthermore, their revenue from oxygen by-product sale could reduce the total cost of renewable hydrogen production.

Salmon *et al*., 2021 [133] formulated a model for the optimization of the intercontinental energy transport of green ammonia production. Their proposed ammonia production superstructure involves the use of renewable energy to power water electrolysis, followed by the synthesis of ammonia in electrical Haber-Bosch reactor, which is projected to be likely available in 2050. The formulated MILP minimizes the net present value of delivering ammonia to the different demand sites at the specified global locations. This objective function consists the sum of capital expenditure and the operational expenditure of the distribution cost, and a discount of 7% was applied for an operational time of 20 years. They found that the economies of scales of the renewable ammonia generated a production rate of about 10 million tonnes per annum from less than 1 million tonnes per annum.

5.3 Hydrogen Supply Chain

Woo *et al*., 2016 [134] optimized the supply chain of hydrogen from biomass. Their aim is to formulate an optimization model that incorporate the biomass supply chain into the biomass-to-hydrogen supply chain, and can equally accounts for the logistic operation under biomass yield and demand uncertainties. Their design includes hydrogen production from four different biomass due to their availability and high energy content, these includes the forest, agricultural, industrial residues. The developed MILP consists of constraints on quantity of land used for the biomass, mass balance constraints, facility capacity, with an objective of minimizing the total annualized cost of the hydrogen supply chain. The formulated model was applied to six regions in Jeju, South Korea and solved using CPLEX solver in GAMS. They found that the hydrogen demand was met by developing new gasification plant when the importation dependence rate is 15%, until the hydrogen demand gets to 12, 400 ton/year.

Yang *et al*., 2020 [135] formulated a model for the planning and operation of wind-powered hydrogen supply chain network in some regions in China. Their proposed supply chain network involves the production of hydrogen from the electrolysis of water using wind, storing the hydrogen, and the distribution of the hydrogen to a fueling station and industrial demand site. They handle the uncertainty associated to the wind energy using probability density function, while the hydrogen demand uncertainty was modeled using scenarios represented on probability density function. Their model includes, the hydrogen production constraints, hydrogen transportation constraints, hydrogen storage constraints, wind-batteries constraints, hydrogen demand constraints, and the constraints on the design of the unit operations. The two-staged MILP was formulated to minimize the capital and operating cost the process. The formulated model was applied to a case study in Fujian province in China, and solved using CPLEX. They found that increase in the hydrogen demand increases the total cost of the hydrogen supply chain network, while the levelized cost of hydrogen reduces with increase in hydrogen demand. The levelized cost of hydrogen ranges from 3.073 $/kg to 3.155 $/kg for different hydrogen demand and changes by 9.5% when the unit cost of the wind turbine was changed by 20%.

Almansoori and Shah, 2012 [136] developed a three-stage optimization framework for hydrogen supply chain under demand uncertainty. They utilize a scenario planning method for handling the fluctuation in hydrogen demand over a long-term planning horizon, and the variations in the demand were represented using a moderate number of scenarios represented by probability function. At the end, they aim to help the decision makers on 'Here-and-now and 'wait-and-see' decisions which are determined from the prediction of the structure of the network, for instance, optimal location, sizing, and the capacity of the hydrogen production plants. A three-stage stochastic optimization model are broken into; first stage assumed that the hydrogen demand is deterministic, the second stage assumes the demand is uncertain. They considered nine different demand scenarios for the three time periods which each is represented using 6-year intervals. The model consists of the demand constraints, primary energy sources constraints, and others. The MILP developed minimized the total daily cost of hydrogen network. They found that the mode of transportation affects the total cost of hydrogen, and the variation in the demand has a significant impact on the cost.

Won *et al.*, 2017 [137] optimized the supply of renewable hydrogen. They presented a superstructure that consists, different primary energy sources, electricity generation technologies, various hydrogen production technologies, and the distribution of the hydrogen. They used Weibull's probability distribution for developing the behavior of wind using mean wind speed. Their formulated MILP was aimed to minimize the total annual cost of hydrogen supply systems, and this model was applied to Jeju Island in Korea. Their optimal configuration and operation results showed that hydrogen demand is primarily met using alkaline electrolyzer powered by wind turbines and direct gasification representing 89.8% and 10.2% of the hydrogen demand.

5.4 Combined Energy Carriers

Ogumerem *et al.*, 2019 [138] formulated MILP optimization model for the optimization of the supply of renewable hydrogen, ammonia and methanol. They applied their model to two case; (i) short-term case for hydrogen supply chain in California (ii) long-term case for methanol and ammonia supply chains in Texas. In the hydrogen supply chain, they considered the distribution of produced hydrogen for the plant to meet the demand of a set costumers over a given time-period, the use of different hydrogen production technologies and the transportation modes. In modeling the transportation constraints, they assumed that the vehicles are traveling at 12,000 miles per year. Their multi-objective optimization is to minimize the net present value and the emission from the plants. The minimum net present value found was about 5.565 billion dollars at zero emission. Considering ammonia and methanol supply chain in Texas, they found that levelized cost of energy for ammonia and methanol are \$0.664/kWh and \$0.636/kWh respectively, and concluded that decrease in the cost of renewable energy production favors the entire processes.

Demirhan *et al.*, 2021 [139] developed a multi-stage energy system approach for the optimization of multi-product network. They demonstrated an optimization approach for the optimal design and operation of poly-generation systems that is capable of utilizing renewable energy to produce power, synthetic fuels, chemical energy fuels (ammonia, methanol, hydrogen). They account for the fluctuation in the availability of renewable energy using hourly resolution, which was modeled for an entire year (8760 steps/periods). To reduce the computational burden associated with the generation of large scenerios, agglomerative hierarchical clustering approach was used. Meaning the wind speed, solar irradiation, electricity prices and power load data were clustered together. The multi-objective MILP was formulated for the minimization of the total emission form the system and the total cost of the operating the network. They also determine the optimal levelized cost for zero-emission in hydrogen, methanol and ammonia production. They found that the power and hydrogen generation significantly play a role in the integration of the multi-product network since the both serve as precursors for the production of other products.

5.5 Modular Energy Systems

Palys *et al*., 2018 [16] investigated the optimization of the supply chain of modular wind-powered ammonia production under the influence of production exponent. In their research Minnesota and Iowa states were used as case study. The model developed using a mixed integer non-linear program model and solved in GAMS and BARON respectively. At the end of the experiment, a reduction in the Haber-Bosch conventional cost from $830/t and $745/t to $610/t and $575/t in Minnesota and Iowa respectively at a convenient production exponent of 0.9. This was attributed to the increase in the savings as a result of economies of mass production caused by increasing demand and the availability of large amount of wind in Iowa state to serve the increasing demand which allows for higher reduction in transportation costs with the modular approach.

Huang *et al.,* 2022[100] combined the study of the modular design of renewable methanol production process. They evaluated the impact of uncertainty in renewable energy and the modular designs on the operation of the methanol synthesis lines by considering the continuity and stable operation targets. In their proposed methanol production superstructure, hydrogen is generated from a solar and wind energy driven electrolysis and combined with a captured CO_2. In addition to the material balances of the unit operations in ASPEN HYSYS, heat integration was performed and included among the constraints in their formulation. The MILP formulated was implemented in GAMS and solved using CPLEX. They found that the energy storage capacity needed in the modular methanol unit are significantly reduced to 85.33% and 87.36% for battery and hydrogen respectively, which was attributed to the ability of the modular methanol production system to account for the fluctuations in the renewable energy through the adjusting of the number of the modular production lines. Furthermore, they explained that it could be means that the methanol synthesis is capable of maximizing the production capacity when the renewable energy is abundant and minimize the energy consumption when the renewable energy is insufficient.

Allman *et al*., 2021 [140] performed the supply chain optimization of a modular biomass waste-to-energy system. They proposed both deterministic and two-stage stochastic optimization frameworks for waste-to-energy systems, considering the minimum cost of the modular and conventional units. The stochastic optimization is to account for the uncertainty in the modular units, which was introduced from the biomass supply. Their formulation is to minimize the supply chain cost of the energy system. A value of the module mobility (VMM) function was used to quantify the economic benefits of the modular units. They found that a saving of 1-4% per year were realized when modular production units were used.

Allen *et al.,* 2020 [141] formulated a MILP model for the supply chain optimization for modular units. Their formulation was for the determination of the optimal real-time scheduling of supply chain network of a mobile modular units. The objective of the formulation was to minimize the operational cost of the supply chain network. The MILP formulated was applied to a wastewater effluents treatment modular unit. They found that it is more economical to operate a modular unit than conventional unit.

Chen and Grossmann *et al*., 2019 [142] formulated a generalized disjunctive programming model for the optimization of modular process synthesis. Their problem was formulated as a multiperiod allocation, facility location, and design model which compared the effect of the selection of conventional and modular units on the economics of the supply chain. The optimization framework comprises of the main decision variables includes the locations of the potential units, production capacity, shipment of raw materials from the suppliers to the facilities sites, and the Boolean decision parameters for the selection of the modular and conventional units. Their objective is to maximize the net present value of the network. The framework was applied for the bioethanol production process. In the case study, the cost of the process network and production allocation were minimized. The modular and conventional cases were solved using Gurobi and Pyomo-GAMS, respectively. They reported a reduction in the transportation cost by $372 million when modular unit is used.

Baldea *et al*., 2019 [143] used a scaling function to demonstrate the modularization of a processing plant and the cost implication of running a modular unit. In their cost function, they related the cost of operating a plant and the processing capacity of the plants. A modular exponent was used to make the decision of scaling down/up. This proposed formulation was applied to a modular ammonia production plant. They compared the cost implication of scaling down/up of the processing plant, and consequently evaluated the effect of reactor and compressor unit operations. They found that if there scaled down the production from the large conventional plant to the modular plant, the capacity and the reactor would reduce by a factor of 2514 and 976 respectively.

Conclusion

There has been substantial amount of work done on the optimization of the production of the single energy carriers such as hydrogen, methanol, and ammonia using renewable energy. The optimal operation, optimal scheduling, the influence of various uncertainties and the supply chain of this single product networks have been well understood and researched. The continuous investigation in the optimization of co-production of ammonia and methanol is important due to; (i) the reduction in operating cost (ii) reduction in unit operation since their production shared common units and (iii) the reduction in carbon emission. However, limited works [138,139] have been identified to have been conducted on the optimization of methanol and ammonia Co-production unit. Therefore, there are still problems relating to the optimization of methanol and ammonia co-production, these include;

1. The consideration of the modular methanol and ammonia co-production plant
2. The investigation into the flexibility of the modular units
3. The formulation of robust optimization model to handle the uncertainties (demand, renewable energy, associated with the co-production plant
4. The integration of modern Artificial Intelligence Algorithms such as machine learning algorithms (supervised, unsupervised learning algorithms) in Process Systems Engineering.

References

[1] United Nations Department of Economic and Social Affairs, Population Division (2022). World Population Prospects 2022: Summary of Results. UN DESA/POP/2022/TR/NO. 3.

[2] US. EIA, 2022. What is the United States' share of world energy consumption? https://www.eia.gov/tools/faqs/faq.php?id=87&t=1

[3] US. Energy Information Administration (EIA), 2022 monthly Energy Review, Aprill 2022.

[4] U.S. EIA (2022) Annual Energy Outlook 2022.

[5] Kojima, Y. (2019). Hydrogen storage materials for hydrogen and energy carriers. International Journal of Hydrogen Energy, 44(33), 18179-18192.

[6] Yaashikaa PR, Senthil Kumar P, Varjani SJ, Saravanan A. A review on photochemical, biochemical and electrochemical transformation of CO2 into value-added products. J CO2 Util 2019;33:131–47.

[7] Zhang H, Wang L, Van J, Mar´echal F, Desideri U. Techno-economic optimization of CO_2-to-methanol with solid-oxide electrolyzer. Energies 2019;12:3742.

[8] Dalena F, Senatore A, Marino A, Gordano A, Basile M, Basile A. Methanol production and applications: an overview. In: Basile A, Dalena F, editors. Methanol: Elsevier; 2018. p. 3–28 [chapter 1].

[9] Lange J-P. Methanol synthesis: a short review of technology improvements. Catal Today 2001; 64:3–8.

[10] Kourkoumpas DS, Papadimou E, Atsonios K, Karellas S, Grammelis P, Kakaras E. Implementation of the Power to Methanol concept by using CO2 from lignite power plants: Techno-economic investigation. Int J Hydrogen Energy 2016;41:16674–87.

[11] Borisut P, Nuchitprasittichai A. Methanol production via CO2 hydrogenation:

[12] Kourkoumpas DS, Papadimou E, Atsonios K, Karellas S, Grammelis P, Kakaras E. Implementation of the Power to Methanol concept by using CO2 from lignite power plants: Techno-economic investigation. Int J Hydrogen Energy 2016;41:16674–87.

[13] Borisut P, Nuchitprasittichai A. Methanol production via CO2 hydrogenation:

[14] Smil, V. Enriching the earth: Fritz Haber, Carl Bosch, and the transformation of world food production; MIT Press: 2004.

[15] Swaminathan, B.; Sukalac, K. Technology transfer and mitigation of climate change: The fertilizer industry perspective. IPCC Expert Meeting on Industrial Technology Development, Transfer and Diffusion, Tokyo, Japan. 2004.

[16] Palys, M. J., Allman, A., & Daoutidis, P. (2018). Exploring the benefits of modular renewable-powered ammonia production: A supply chain optimization study. Industrial & Engineering Chemistry Research, 58(15), 5898-5908.

[17] Institute for Industrial Productivity. Industrial Efficiency Technology Database – Ammonia.

[18] IRENA (2021), Innovation outlook: Renewable Methanol'

[19] Charlie Hodson (2018). Renewable Methanol Report.

[20] ITF. Decarbonising Maritime Transport. Pathways to Zero-Carbon Shipping by 2035; International Transport Forum: Paris, France, 2018.

[21] Cheliotis, M.; Boulougouris, E.; Trivyza, N.; Theotokatos, G.; Livanos, G.; Mantalos, G.; Stubos, A.; Stamatakis, E.; Venetsanos, A.Review on the Safe Use of Ammonia Fuel Cells in the Maritime Industry. Energies **2021**, 14, 3023.

[22] Bourne, C.; Nietsch, T.; Griffiths, D.; Morley, J. Application of Fuel Cells in Surface Ships; Rolls-Royce Strategic Systems Engineering:Derby, UK, 2001.

[23] Rafiqul, I.; Weber, C.; Lehmann, B.; Voss, A. Energy e_ciency improvements in ammonia production-perspectives and uncertainties. Energy **2005**, 30, 2487–2504.

[24] Wang, L.; Xia, M.;Wang, H.; Huang, K.; Qian, C.; Maravelias, C.T.; Ozin, G.A. Greening ammonia toward the solar ammonia refinery. Joule **2018**, 2, 1055–1074.

[25] D.K. Minet Rg, Cost-Effective Methods for Hydrogen Production, Int J Hydrogen Energy, (1983)

[26] B. M., Potential Importance of Hydrogen as a Future Solution To Environmental And Transportation Problems, Int J Hydrogen Energy, 33 (2008).

[27] Feeding the Earth, Energy Efficiency and CO2 emissions in ammonia production. Dec 2009.http://www.fertilizer.org/imis20/images/Library_Downloads/2009_IFA_energy_efficiency.pdf?WebsiteKey=411e9724-4bda-422f-abfc-8152ed74f306&= 0 4 % 3 b h t t p % 3 a % 2 f % 2 f www.f e r t i l i z e rorg%3a80%2fen%2fimages%2fLibrary_Downloads%2f2009_IFA_energy_efficiency.pdf

[28] Xue, M., Wang, Q., Lin, B. L., & Tsunemi, K. (2019). Assessment of ammonia as an energy carrier from the perspective of carbon and nitrogen footprints. ACS Sustainable Chemistry & Engineering, 7(14), 12494-12500.

[29] Pan, Z., Liu, Y., Tahir, A., Esan, O. C., Zhu, J., Chen, R., & An, L. (2022). A discrete regenerative fuel cell mediated by ammonia for renewable energy conversion and storage. Applied Energy, 322, 119463.

[30] J. Yang, H. Muroyama, T. Matsui and K. Eguchi, J. Power Sources, 2014, 245, 277–282.

[31] Pan, Z., Liu, Y., Tahir, A., Esan, O. C., Zhu, J., Chen, R., & An, L. (2022). A discrete regenerative fuel cell mediated by ammonia for renewable energy conversion and storage. Applied Energy, 322, 119463.

[32] Suzuki, S.; Muroyama, H.; Matsui, T.; Eguchi, K. Fundamental studies on direct ammonia fuel cell employing anion exchange membrane. J. Power Sour. **2012**, 208, 257–262.

[33] Meng, G.; Jiang, C.; Ma, J.; Ma, Q.; Liu, X. Comparative study on the performance of a SDC-based SOFC fueled by ammonia and hydrogen. J. Power Sources 2007, 173, 189−193.

[34] Rossi, R., Yang, W., Zikmund, E., Pant, D., & Logan, B. E. (2018). In situ biofilm removal from air cathodes in microbial fuel cells treating domestic wastewater. Bioresource technology, 265, 200-206.

[35] Reiter, A.J.; Kong, S.C. Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel. Fuel **2011**, 90, 87–97.

[36] B. Stoeckl, V. Suboti´c, M. Preininger, M. Schwaiger, N. Evic, H. Schroettner and C. Hochenauer, Electrochim. Acta, 2019, 298, 874–883.

[37] Rihko-Struckmann LK, Peschel A, Hanke-Rauschenbach R, Sundmacher K. Assessment of Methanol Synthesis Utilizing Exhaust CO2 for Chemical Storage of Electrical Energy. Industrial & Engineering Chemistry Research 2010;49:11073–8

[38] M. Bertau, H. Offermanns, L. Plass, F. Schmidt and H.-J. Wernicke, eds., Methanol: The Basic Chemical and Energy Feedstock of the Future, Springer Berlin Heidelberg, Berlin, Heidelberg, 2014.

[39] G. A. Olah, A. Goeppert and G. K. S. Prakash, The Journal of organic chemistry, 2009, **74**(2), 487.

[40] C. Hank, S. Gelpke, A. Schnabl, R. J. White, J. Full, N. Wiebe, T. Smolinka, A. Schaadt, H.-M. Henning and C. Hebling, Sustainable Energy Fuels, 2018, **2**(6), 1244.

[41] Sheldon, D. Methanol Production - A Technical History. Johns. Matthey Technol. Rev. **2017**, 61, 172–182, doi:10.1595/205651317X695622.

[42] Bertau, M.; Offermanns, H.; Plass, L.; Schmidt, F.; Wernicke, H.J.; Methanol: The Basic Chemical and Energy Feedstock of the Future: Asinger's Vision Today; Springer: Berlin/Heidelberg, Germany, 2014, doi:10.1007/978-3-642-39709-7.

[43] Simon Araya, S., Liso, V., Cui, X., Li, N., Zhu, J., Sahlin, S. L., ... & Kær, S. K. (2020). A review of the methanol economy: the fuel cell route. Energies, 13(3), 596.

[44] Bozzano, G.; Manenti, F. Efficient methanol synthesis: Perspectives, technologies and optimization strategies.Prog. Energy Combust. Sci. **2016**, 56, 71–105, doi:10.1016/J.PECS.2016.06.001.

[45] Barbieri, G.; Marigliano, G.; Golemme, G.; Drioli, E. Simulation of CO_2 hydrogenation with CH_3OH removal in a zeolite membrane reactor. Chem. Eng. J. **2002**, 85, 53–59, doi:10.1016/S1385-8947(01)00143-7.

[46] Wernicke, H.J.; Plass, L.; Schmidt, F. Methanol Generation. In Methanol: The Basic Chemical and Energy Feedstock of the Future: Asinger's Vision Today; Bertau, M., Offermanns, H., Plass, L., Schmidt, F.,Wernicke, H.J., Eds.; Springer: Berlin/Heidelberg, Germany, 2014; pp. 51–301, doi:10.1007/978-3-642-39709-7_4.

[47] Gahleitner, G. Hydrogen from renewable electricity: An international review of power-to-gas pilot plants for stationary applications. Int. J. Hydrog. Energy **2013**, 38, 2039–2061, doi:10.1016/J.IJHYDENE.2012.12.010.

[48] Bui, M.; Adjiman, C.S.; Bardow, A.; Anthony, E.J.; Boston, A.; Brown, S.; Fennell, P.S.; Fuss, S.; Galindo, A.; Hackett, L.A.; et al. Carbon capture and storage (CCS): The way forward. Energy Environ. Sci. **2018**, 11, 1062–1176, doi:10.1039/c7ee02342a.

[49] Räuchle K, Plass L, Wernicke H-J, Bertau M. Methanol for renewable energy storage and utilization. Energy Technol 2016;4(1):193–200. https://doi.org/10.1002/ente. 201500322.

[50] Olah GA, Prakash GKS, Goeppert A. Anthropogenic chemical carbon cycle for a sustainable future. J Am Chem Soc 2011;133(33):12881–98. https://doi.org/10. 1021/ja202642y.

[51] Olah GA. Towards oil independence through renewable methanol chemistry. Angewandte Chemie - Int Ed 2013;52(1):104–7. https://doi.org/10.1002/anie.201204995.

[52] Ott, J.; Gronemann, V.; Pontzen, F.; Fiedler, E.; Grossmann, G.; Kersebohm, D.B.;Weiss, G.;Witte, C. Methanol. In Ullmann's Encyclopedia of Industrial Chemistry;Wiley-VCH Verlag GmbH & Co. KGaA:Weinheim, Germany, 2012; doi:10.1002/14356007.a16_465.pub3.

[53] Methanol Institute. Methanol|Methanol Institute. Available online: https://www.methanol.org (accessed on 10 December 2019).

[54] Zhen, X.; Wang, Y. An overview of methanol as an internal combustion engine fuel. Renew. Sustain. Energy Rev. **2015**, 52, 477–493, doi:10.1016/J.RSER.2015.07.083

[55] Verhelst, S.; Turner, J.W.; Sileghem, L.; Vancoillie, J. Methanol as a fuel for internal combustion engines. Prog. Energy Combust. Sci. **2019**, 70, 43–88, doi:10.1016/J.PECS.2018.10.001

[56] Fuel freedom foundation. When California had 15,000 methanol cars—Fuel Freedom

Foundation. Available online: https://www.fuelfreedom.org/when-california-had-15000-methanol-cars/ (accessed on 10 December 2019).

[57] SerEnergy A/S. The Benefits of Methanol Fuel Cells. Available online: https://serenergy.com/ (accessed on 10 December 2019).

[58] U.S. Energy Information Administration, Electric Power Monthly, February 2022, preliminary data for 2021.

[59] Liu, H., Qu, J., Pan, M., Zhang, B., Chen, Q., & He, C. (2020). Design and optimization of small-scale methanol production from sour natural gas by integrating reforming with hydrogenation. *International Journal of Hydrogen Energy*, *45*(59), 34483-34493.

[60] Borisut, P., & Nuchitprasittichai, A. (2019). Methanol production via CO_2 hydrogenation: sensitivity analysis and simulation—based optimization. *Frontiers in Energy Research*, *7*, 81.

[61] Zang, G., Sun, P., Elgowainy, A., & Wang, M. (2021). Technoeconomic and life cycle analysis of synthetic methanol production from hydrogen and industrial byproduct CO_2. *Environmental Science & Technology*, *55*(8), 5248-5257.

[62] Taghdisian, H., Pishvaie, M. R., & Farhadi, F. (2015). Multi-objective optimization approach for green design of methanol plant based on CO_2-efficeincy indicator. *Journal of cleaner production*, *103*, 640-650.

[63] Arora, A., Iyer, S. S., Bajaj, I., & Hasan, M. F. (2018). Optimal methanol production via sorption-enhanced reaction process. *Industrial & Engineering Chemistry Research*, *57*(42), 14143-14161.

[64] Li, W., Zhuang, Y., Liu, L., Zhang, L., & Du, J. (2020). Process evaluation and optimization of methanol production from shale gas based on kinetics modeling. *Journal of Cleaner Production*, *274*, 123153.

[65] Zhang, H., & Desideri, U. (2020). Techno-economic optimization of power-to-methanol with co-electrolysis of CO_2 and H_2O in solid-oxide electrolyzers. *Energy*, *199*, 117498.

[66] Palys, M. J., & Daoutidis, P. (2022). Power-to-X: A review and perspective. *Computers & Chemical Engineering*, 107948.

[67] Palys, M. J., McCormick, A., Cussler, E. L., & Daoutidis, P. (2018). Modeling and optimal design of absorbent enhanced ammonia synthesis. *Processes*, *6*(7), 91.

[68] Sánchez, A., & Martín, M. (2018). Optimal renewable production of ammonia from water and air. *Journal of Cleaner Production*, *178*, 325-342.

[69] Demirhan, C. D., Tso, W. W., Powell, J. B., & Pistikopoulos, E. N. (2019). Sustainable

ammonia production through process synthesis and global optimization. *AIChE Journal*, *65*(7), e16498.

[70] Xu, D., Zhou, B., Wu, Q., Chung, C. Y., Li, C., Huang, S., & Chen, S. (2020). Integrated modelling and enhanced utilization of power-to-ammonia for high renewable penetrated multi-energy systems. *IEEE Transactions on Power Systems*, *35*(6), 4769-4780.

[71] Pistikopoulos, E. N., Barbosa-Povoa, A., Lee, J. H., Misener, R., Mitsos, A., Reklaitis, G. V., ... & Gani, R. (2021). Process systems engineering–the generation next?. *Computers & Chemical Engineering*, *147*, 107252.

[72] Xi, H., Wu, X., Chen, X., & Sha, P. (2021). Artificial intelligent based energy scheduling of steel mill gas utilization system towards carbon neutrality. *Applied Energy*, *295*, 117069.

[73] Zheng, Y., You, S., Li, X., Bindner, H. W., & Münster, M. (2022). Data-driven robust optimization for optimal scheduling of power to methanol. *Energy Conversion and Management*, *256*, 115338.

[74] Svitnič, T., & Sundmacher, K. (2022). Renewable methanol production: Optimization-based design, scheduling and waste-heat utilization with the FluxMax approach. *Applied Energy*, *326*, 120017.

[75] Chen, C., Yang, A., & Bañares-Alcántara, R. (2021). Renewable methanol production: Understanding the interplay between storage sizing, renewable mix and dispatchable energy price. *Advances in Applied Energy*, *2*, 100021.

[76] Chen, C., & Yang, A. (2021). Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production. *Energy Conversion and Management*, *228*, 113673.

[77] Palys, M. J., & Daoutidis, P. (2020). Using hydrogen and ammonia for renewable energy storage: A geographically comprehensive techno-economic study. *Computers & Chemical Engineering*, *136*, 106785.

[78] Allman, A., Palys, M. J., & Daoutidis, P. (2019). Scheduling-informed optimal design of systems with time-varying operation: A wind-powered ammonia case study. *AIChE Journal*, *65*(7), e16434.

[79] Palys, M. J., Allman, A., Kuznetsov, A., & Daoutidis, P. (2019). Concept and Design Optimization of a Novel Ammonia-Based System for Food-Energy-Water Sustainability. In *Computer Aided Chemical Engineering* (Vol. 47, pp. 65-70). Elsevier.

[80] Osman, O., Sgouridis, S., & Sleptchenko, A. (2020). Scaling the production of renewable ammonia: A techno-economic optimization applied in regions with high insolation. *Journal of cleaner production*, *271*, 121627.

[81] Armijo, J., & Philibert, C. (2020). Flexible production of green hydrogen and ammonia from variable solar and wind energy: Case study of Chile and Argentina. *International Journal of Hydrogen Energy*, *45*(3), 1541-1558.

[82] Kelley, M. T., Do, T. T., & Baldea, M. (2022). Evaluating the demand response potential of ammonia plants. *AIChE Journal*, *68*(3), e17552.

[83] Nayak-Luke, R., Bañares-Alcántara, R., & Wilkinson, I. (2018). "Green" ammonia: impact of renewable energy intermittency on plant sizing and levelized cost of ammonia. *Industrial & Engineering Chemistry Research*, *57*(43), 14607-14616.

[84] El-Taweel, N. A., Khani, H., & Farag, H. E. (2018). Hydrogen storage optimal scheduling for fuel supply and capacity-based demand response program under dynamic hydrogen pricing. *IEEE transactions on smart grid*, *10*(4), 4531-4542.

[85] Palys, M. J., & Daoutidis, P. (2020). Using hydrogen and ammonia for renewable energy storage: A geographically comprehensive techno-economic study. *Computers & Chemical Engineering*, *136*, 106785.

[86] Marocco, P., Ferrero, D., Martelli, E., Santarelli, M., & Lanzini, A. (2021). An MILP approach for the optimal design of renewable battery-hydrogen energy systems for off-grid insular communities. *Energy Conversion and Management*, *245*, 114564.

[87] Arora, A., Zantye, M. S., & Hasan, M. F. (2022). Sustainable hydrogen manufacturing via renewable-integrated intensified process for refueling stations. *Applied Energy*, *311*, 118667.

[88] Mallapragada, D. S., Gençer, E., Insinger, P., Keith, D. W., & O'Sullivan, F. M. (2020). Can industrial-scale solar hydrogen supplied from commodity technologies be cost competitive by 2030?. *Cell Reports Physical Science*, *1*(9), 100174.

[89] Zhang, W., Maleki, A., Rosen, M. A., & Liu, J. (2018). Optimization with a simulated annealing algorithm of a hybrid system for renewable energy including battery and hydrogen storage. *Energy*, *163*, 191-207.

[90] Yuksel, Y. E., Ozturk, M., & Dincer, I. (2021). Development of a novel combined energy plant for multigeneration with hydrogen and ammonia production. *International Journal of Hydrogen Energy*, *46*(57), 28980-28994.

[91] Ganzer, C., & Mac Dowell, N. (2020). A comparative assessment framework for sustainable production of fuels and chemicals explicitly accounting for intermittency. *Sustainable Energy & Fuels*, *4*(8), 3888-3903.

[92] Palys, M. J., Mitrai, I., & Daoutidis, P. (2023). Renewable hydrogen and ammonia for combined heat and power systems in remote locations: Optimal design and scheduling. *Optimal Control Applications and Methods*, *44*(2), 719-738.

[93] Martín, M. (2016). Methodology for solar and wind energy chemical storage facilities design under uncertainty: Methanol production from CO2 and hydrogen. *Computers & Chemical Engineering*, *92*, 43-54.

[94] Martín, M., & Grossmann, I. E. (2018). Optimal integration of renewable based processes for fuels and power production: Spain case study. *Applied Energy*, *213*, 595-610.

[95] Li, Q., Machida, H., Ren, X., Feng, Z., & Norinaga, K. (2023). Design and optimization of the flexible poly-generation process for methanol and formic acid from CO2 hydrogenation under uncertain product prices. *International Journal of Hydrogen Energy*.

[96] Lee, J., Ryu, K. H., & Lee, J. H. (2022). Optimal design and evaluation of electrochemical CO2 reduction system with renewable energy generation using two-stage stochastic programming. *Journal of CO2 Utilization*, *61*, 102026.

[97] Chen, C., & Yang, A. (2021). Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production. *Energy Conversion and Management*, *228*, 113673.

[98] Gu, Y., Wang, D., Chen, Q., & Tang, Z. (2022). Techno-economic analysis of green Methanol plant with optimal design of renewable hydrogen production: A case study in China. *International Journal of Hydrogen Energy*, *47*(8), 5085-5100.

[99] Huang, R., Kang, L., & Liu, Y. (2022). Renewable synthetic methanol system design based on modular production lines. *Renewable and Sustainable Energy Reviews*, *161*, 112379.

[100] Verleysen, K., Coppitters, D., Parente, A., De Paepe, W., & Contino, F. (2020). How can power-to-ammonia be robust? Optimization of an ammonia synthesis plant powered by a wind turbine considering operational uncertainties. *Fuel*, *266*, 117049.

[101] Verleysen, K., Parente, A., & Contino, F. (2021). How sensitive is a dynamic ammonia synthesis process? Global sensitivity analysis of a dynamic Haber-Bosch process (for flexible seasonal energy storage). *Energy*, *232*, 121016.

[102] Laššák, P., Labovský, J., & Jelemenský, Ľ. (2010). Influence of parameter uncertainty on modeling of industrial ammonia reactor for safety and operability analysis. *Journal of Loss Prevention in the Process Industries*, *23*(2), 280-288.

[103] Dechany, Antoine. Unleash the renewable power within ammonia: optimization and uncertainty quantification of the Ammonia-to-Power pathway. Ecole polytechnique de Louvain, Université catholique de Louvain, 2021. Prom. : Contino, Francesco ; Verleysen, Kevin. http://hdl.handle.net/2078.1/thesis:30714

[104] Ghappani, S. A., & Karimi, A. (2023). Optimal operation framework of an energy hub with combined heat, hydrogen, and power (CHHP) system based on ammonia. *Energy*, *266*, 126407.

[105] Verleysen, K., Parente, A., & Contino, F. (2022). How does a resilient, flexible ammonia process look? Robust design optimization of a Haber-Bosch process with optimal dynamic control powered by wind. *Proceedings of the Combustion Institute*.

[106] Cesaro, Z., Ives, M., Nayak-Luke, R., Mason, M., & Bañares-Alcántara, R. (2021). Ammonia to power: Forecasting the levelized cost of electricity from green ammonia in large-scale power plants. *Applied Energy*, *282*, 116009.

[107] Qi, M., Kim, M., Vo, N. D., Yin, L., Liu, Y., Park, J., & Moon, I. (2022). Proposal and surrogate-based cost-optimal design of an innovative green ammonia and electricity co-production system via liquid air energy storage. *Applied Energy*, *314*, 118965.

[108] Serrano-Arévalo, T. I., Tovar-Facio, J., & Ponce-Ortega, J. M. (2023). Optimal Incorporation of Intermittent Renewable Energy Storage Units and Green Hydrogen Production in the Electrical Sector. *Energies*, *16*(6), 2609.

[109] Tatar, S. M., Akulker, H., Sildir, H., & Aydin, E. (2022). Optimal design and operation of integrated microgrids under intermittent renewable energy sources coupled with green hydrogen and demand scenarios. *International Journal of Hydrogen Energy*, *47*(65), 27848-27865

[110] Cooper, N., Horend, C., Röben, F., Bardow, A., & Shah, N. (2022). A framework for the design & operation of a large-scale wind-powered hydrogen electrolyzer hub. *International Journal of Hydrogen Energy*, *47*(14), 8671-8686.

[111] Mehrjerdi, H. (2020). Peer-to-peer home energy management incorporating hydrogen storage system and solar generating units. *Renewable Energy*, *156*, 183-192.

[112] Kotzur, L., Markewitz, P., Robinius, M., & Stolten, D. (2018). Impact of different time series aggregation methods on optimal energy system design. *Renewable energy*, *117*, 474-487.

[113] Heras, J., & Martín, M. (2021). Multiscale analysis for power-to-gas-to-power facilities based on energy storage. *Computers & Chemical Engineering*, *144*, 107147.

[114] Qi, R., Qiu, Y., Lin, J., Song, Y., Li, W., Xing, X., & Hu, Q. (2021). Two-stage stochastic programming-based capacity optimization for a high-temperature electrolysis system considering dynamic operation strategies. *Journal of Energy Storage*, *40*, 102733.

[115] Giannakoudis, G., Papadopoulos, A. I., Seferlis, P., & Voutetakis, S. (2010). Optimum design and operation under uncertainty of power systems using renewable energy sources and hydrogen storage. *International journal of hydrogen energy*, *35*(3), 872-891.

[116] Hernández-Pérez, L. G., Alsuhaibani, A. S., Ponce-Ortega, J. M., & El-Halwagi, M. M. (2022). Multi-objective optimization of ammonia and methanol production processes considering uncertain feedstock compositions of shale/natural gas. *Chemical Engineering Research and Design*, *187*, 27-40.

[117] Zhang, Q., Martín, M., & Grossmann, I. E. (2019). Integrated design and operation of renewables-based fuels and power production networks. *Computers & Chemical Engineering*, *122*, 80-92.

[118] Kenkel, P., Wassermann, T., & Zondervan, E. (2022). Renewable Fuels from Integrated Power-and Biomass-to-X Processes: A Superstructure Optimization Study. *Processes*, *10*(7), 1298.

[119] Demirhan, C. D., Tso, W. W., Powell, J. B., Heuberger, C. F., & Pistikopoulos, E. N. (2020). A multiscale energy systems engineering approach for renewable power generation and storage optimization. *Industrial & Engineering Chemistry Research*, *59*(16), 7706-7721.

[120] Tso, W. W., Demirhan, C. D., Powell, J. B., & Pistikopoulos, E. N. (2018). Toward optimal synthesis of renewable ammonia and methanol processes (RAMP). In *Computer Aided Chemical Engineering* (Vol. 44, pp. 1705-1710). Elsevier.

[121] Li, Q., Machida, H., Ren, X., Feng, Z., & Norinaga, K. (2023). Design and optimization of the flexible poly-generation process for methanol and formic acid from CO2 hydrogenation under uncertain product prices. *International Journal of Hydrogen Energy*.

[122] Villicaña-García, E., El-Halwagi, M. M., & Ponce-Ortega, J. M. (2020). Involving economic incentives in optimizing the methanol supply chain considering conventional and unconventional resources. Applied Thermal Engineering, 166, 114622.

[123] Leduc, S., Schwab, D., Dotzauer, E., Schmid, E., & Obersteiner, M. (2008). Optimal location of wood gasification plants for methanol production with heat recovery. *International Journal of Energy Research*, *32*(12), 1080-1091.

[124] Jeong, H., Sieverding, H. L., & Stone, J. J. (2019). Biodiesel supply chain optimization modeled with geographical information system (GIS) and Mixed-Integer Linear Programming (MILP) for the northern great plains region. BioEnergy research, 12(1), 229-240.

[125] Moretti, L., Milani, M., Lozza, G. G., & Manzolini, G. (2021). A detailed MILP formulation for the optimal design of advanced biofuel supply chains. *Renewable Energy*, *171*, 159-175.

[126] Nugroho, Y. K., Zhu, L., & Heavey, C. (2022). Building an agent-based techno-economic assessment coupled with life cycle assessment of biomass to methanol supply chains. *Applied Energy*, *309*, 118449.

[127] Liu, Z., Qiu, T., & Chen, B. (2014). A study of the LCA based biofuel supply chain multi-objective optimization model with multi-conversion paths in China. *Applied Energy*, *126*, 221-234.

[128] Allman, W. A., & Daoutidis, P. (2016). Ammonia supply chains: A new framework for

renewable generation with a case study for Minnesota. In *Computer Aided Chemical Engineering* (Vol. 38, pp. 1395-1400). Elsevier.

[129] Allman, A.; Daoutidis, P.; Tiffany, D.; Kelley, S. A framework for ammonia supply chain optimization incorporating conventional and renewable generation. AIChE J. 2017, 63, 4390−4402

[130] Li, J., Lin, J., Heuser, P. M., Heinrichs, H. U., Xiao, J., Liu, F., ... & Stolten, D. (2020). Optimal Configuration of Wind-to-Ammonia with the Electric Network and Hydrogen Supply Chain: A Case Study of Inner Mongolia. *arXiv preprint arXiv:2006.14778*.

[131] Zhao, H., Kamp, L. M., & Lukszo, Z. (2021). Exploring supply chain design and expansion planning of China's green ammonia production with an optimization-based simulation approach. *international journal of hydrogen energy*, *46*(64), 32331-32349.

[132] Salmon, N., Bañares-Alcántara, R., & Nayak-Luke, R. (2021). Optimization of green ammonia distribution systems for intercontinental energy transport. *Iscience*, *24*(8), 102903.

[133] Woo, Y. B., Cho, S., Kim, J., & Kim, B. S. (2016). Optimization-based approach for strategic design and operation of a biomass-to-hydrogen supply chain. *International Journal of Hydrogen Energy*, *41*(12), 5405-5418.

[134] Yang, G., Jiang, Y., & You, S. (2020). Planning and operation of a hydrogen supply chain network based on the off-grid wind-hydrogen coupling system. *International Journal of Hydrogen Energy*, *45*(41), 20721-20739.

[135] Almansoori, A., & Shah, N. (2012). Design and operation of a stochastic hydrogen supply chain network under demand uncertainty. *International journal of hydrogen energy*, *37*(5), 3965-3977.

[136] Won, W., Kwon, H., Han, J. H., & Kim, J. (2017). Design and operation of renewable energy sources based hydrogen supply system: Technology integration and optimization. *Renewable Energy*, *103*, 226-238.

[137] Ogumerem, G. S., Tso, W. W., Demirhan, C. D., Lee, S. Y., Song, H. E., & Pistikopoulos, E. N. (2019). Toward the optimization of hydrogen, ammonia, and methanol supply chains. *IFAC-PapersOnLine*, *52*(1), 844-849.

[138] Demirhan, C. D., Tso, W. W., Powell, J. B., & Pistikopoulos, E. N. (2021). A multi-scale energy systems engineering approach towards integrated multi-product network optimization. *Applied Energy*, *281*, 116020.

[139] Brook, A., Kendrick, D., & Meeraus, A. (1988). GAMS, a user's guide. *ACM Signum Newsletter*, *23*(3-4), 10-11.

[140] Allman, A., Lee, C., Martín, M., & Zhang, Q. (2021). Biomass waste-to-energy supply chain optimization with mobile production modules. *Computers & Chemical Engineering*, *150*, 107326.

[141] Allen, R. C., Avraamidou, S., & Pistikopoulos, E. N. (2020). Production scheduling of supply chains comprised of modular production units. *IFAC-PapersOnLine*, *53*(2), 11452-11457.

[142] Chen, Q., & Grossmann, I. E. (2019). Effective generalized disjunctive programming models for modular process synthesis. *Industrial & Engineering Chemistry Research*, *58*(15), 5873-5886.

[143] Baldea, M., Snowden, B. A., & Do, T. T. (2019). Scaling Relations in Modular Process Design. In *Computer Aided Chemical Engineering* (Vol. 47, pp. 481-485). Elsevier.