Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Review

Multi-scale energy systems engineering for optimal natural gas utilization

William W. Tso[a,b], C. Doga Demirhan[a,b], Christodoulos A. Floudas[a,b], Efstratios N. Pistikopoulos[a,b,*]

[a] Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, USA
[b] Texas A&M Energy Institute, Frederick E. Giesecke Engineering Research Building, Texas A&M University, College Station, TX 77845, USA

ARTICLE INFO

Keywords:
Natural gas
Multi-scale energy systems engineering
Optimization
Modeling
Synthesis
Supply chain

ABSTRACT

Due to advances in hydraulic fracturing and horizontal drilling, the abundance of inexpensive natural gas has revolutionized the energy industry. As the world population increases, natural gas will play a prominent role in satisfying new energy demands and transitioning society toward cleaner and more sustainable energy. Natural gas is a flexible energy resource that can be utilized for electric power generation, heating, transportation fuel, and synthesizing commodity chemicals. Given the numerous alternatives, a methodology for analyzing and optimizing natural gas utilization is necessary to construct efficient, reliable, affordable, and environmentally conscious natural gas systems. Multi-scale energy systems engineering is a holistic approach that considers the impact different spatial and temporal scales have toward the design and optimization of an overall energy system. Accurately capturing atomic, molecular, unit, process, and supply chain characteristics and their interactions are all important toward the optimal energy system design. We showcase the applicability of the multi-scale energy systems engineering for optimizing natural gas systems such as novel conversion technologies, integrated processing plants, and supply chain networks. Without considering the effects of different scales in a systematic integrated way, we risk converging on suboptimal energy systems.

1. Introduction

As the world population continues to grow (projected to eclipse 10 billion by 2055 [1]) and emerging economies in Asia and Africa accelerate forward, global energy demand is expected to expand 30% by 2040 [2]. Even with falling costs of renewable energy technologies and their increasing penetration, governmental entities and corporate companies (such as the U.S. EIA [3], IEA [2], ExxonMobil [4], BP [5], and Shell [6]) all expect natural gas to play a key role in the energy transition. Within the United States, natural gas has been displacing petroleum in the industrial sector and coal in the electric power sector [7], highlighting the versatility of natural gas as an energy feedstock for both synthesizing chemical products and generating power. Fig. 1 highlights a sampling of the alternatives for natural gas utilization. In fact, energy demands in the industrial and electric power sectors are estimated to be the fastest growing [4], and natural gas is well-positioned to alleviate the increased burden. In the developing world, while coal remains the primary feedstock, natural gas is gaining momentum since it is a cost-competitive and much cleaner alternative.

Globally, natural gas accounts for approximately a quarter of the energy mix [8], and its demand is expected to grow by 40% through 2040 [4]. Fig. 2 gives a snapshot of the historical production and price of natural gas in the United States. Although there is an abundance of proven and inexpensive natural gas resources (in 2017, 6831.7 trillion cubic feet [8] and $2.96/million BTU in the United States [9]), it is paramount that we judiciously allocate its end usages, especially if we are to meet energy demands in the most affordable and least carbon intensive manner. Global CO_2 emissions reached a record peak of 32.5 gigatons [10] in 2017. Switching from petroleum and coal to a cleaner fossil fuel such as natural gas would help to reduce these emissions. Moreover, challenges in optimally utilizing natural gas span across many different scales including atomistic studies, material development, reactor design, process synthesis, and supply chain analysis. Each challenge at every scale constitutes a subsystem of the overall larger natural gas system. In determining the optimal utilization of natural gas, it is imperative that we consider the integration of all scales.

We begin by summarizing the two main routes for utilizing natural gas: upgrading to valuable products through catalysis or burning as a fuel source for heat and power. Then, we discuss the multi-scale systems engineering framework, a methodology for investigating energy systems through considering interactions across spatial and temporal

* Corresponding author.
E-mail address: stratos@tamu.edu (E.N. Pistikopoulos).

https://doi.org/10.1016/j.cattod.2019.09.009
Received 6 November 2018; Received in revised form 13 July 2019; Accepted 9 September 2019
0920-5861/

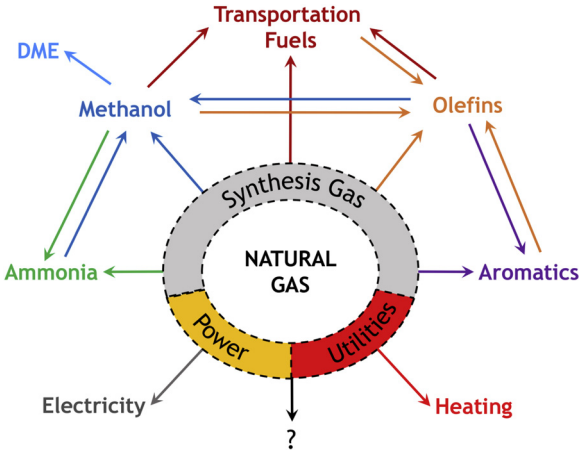

Fig. 1. Several natural gas utilization routes.

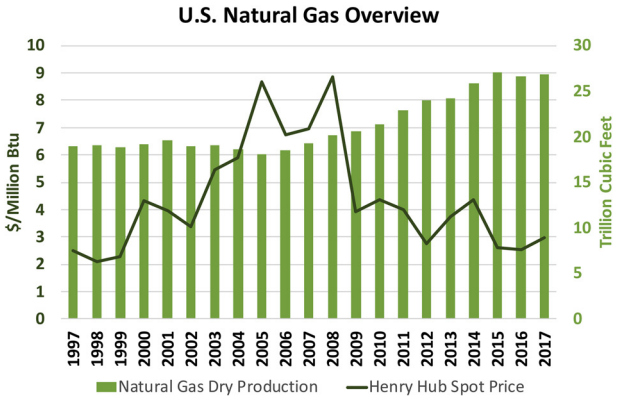

Fig. 2. Historical dry production and price of natural gas in the United States.

scales. Next, we describe applications of this approach on natural gas systems with examples from our research. Finally, we conclude with the outstanding challenges for multi-scale systems engineering and some remarks on natural gas.

2. Natural gas utilization

2.1. Heat and power generation

The simplest and oldest application for natural gas is producing heat from burning it. For power usage, hot exhaust gas from the combustion is used to drive steam production and turbines through a Rankine cycle. In 2018, nearly 74% of all natural gas utilization in the United States was for heat and power purposes [7]. Likewise, significant progress has been made in combined cycle power plants that add in the Brayton cycle to produce power through a gas turbine and heat recovery to create steam, driving the Rankine cycle. In 2016, GE achieved a world record 62.22% efficiency for combined cycle power plants [11]. Co-generation plants producing heat, power (CHP), and sometimes cooling are also under heavy deployment [12]. While the focus of this work is on the product synthesis from natural gas through chemical catalysis, the described multi-scale energy systems engineering concept in Section 3 are applicable to heat and power systems as well. For example, Diangelakis and Pistikopoulos [13] describe a multi-scale model for the optimal design, control, and operation of residential CHP units that have improved economic performance.

2.2. Feedstock for catalysis

About 23% of natural gas is used for industrial applications other than heat and power generation [7]. While how much of this amount is directly used for chemical synthesis is not clear, natural gas traditionally has been the main source of synthesis gas (syngas), an important precursor to useful products such as ammonia, methanol, and their derivatives. Catalysis studies on natural gas focus on improving conversion to either syngas as an indirect intermediate to the final product or the direct conversion to the interested compound [14]. A direct conversion example is the oxidative coupling of methane to produce ethane or ethylene [15,16]. Syngas production from natural gas has been commercially very successful and is a mature technology due to its much higher conversion rate (~90%) compared to direct routes (~20%). Development on direct routes for converting natural gas remains a great challenge in catalysis [17–19]. Nickel oxide is the most well-known catalyst for facilitating the steam reforming of natural gas to syngas [20]. A catalyst's performance heavily influences the economic performance of an overall production process. Tso et al. [21] describe the decision between iron oxide and nickel oxide for the chemical looping reforming of natural gas and highlights how the former is economically advantageous.

3. Multi-scale energy systems engineering

Energy systems arise with different length and time characteristics. Fig. 3 depicts the modeling considerations for varying sizes of energy systems. At the atomic and molecular scale, catalysts excite compound transformations through chemical bond reformation while obeying energy constraints due to quantum mechanics and thermodynamics. Models based on density functional theory and Monte Carlo simulations aim to capture the physicochemical phenomena of the transformation. At the unit scale, reactors convert reactants into products through heat, mass, and momentum transfer. Models such as computational fluid dynamics (CFD) attempt to represent the transport phenomena and

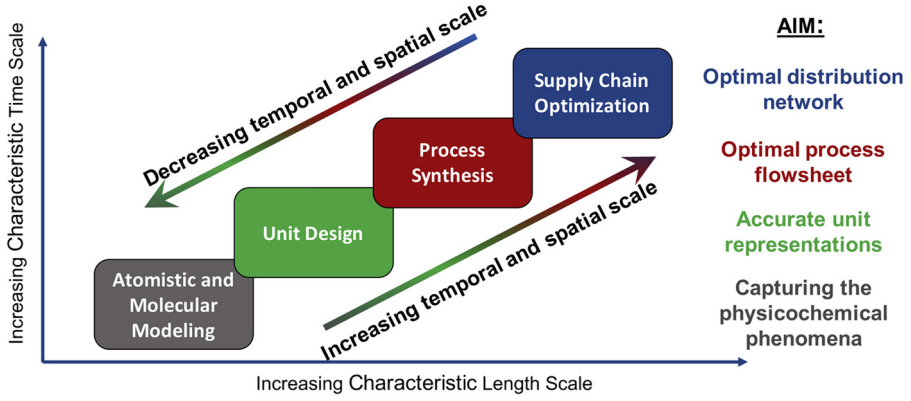

Fig. 3. Multi-scale models spanning across characteristic length and time scales.

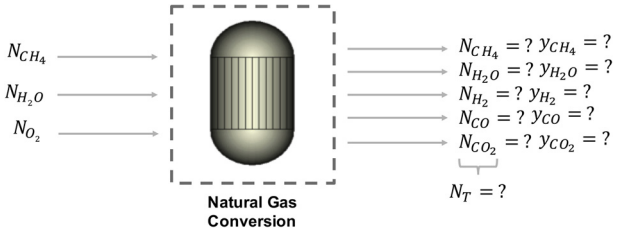

Fig. 4. Overview of natural gas conversion.

reaction kinetics inside the unit. At the process level, pipes, pumps, and valves coordinate the movement of material and energy streams across different units in the plant to produce the desired final product. Process synthesis approaches seek to model the operational logistics of the plant. At the network level, supply chains organize the transportation of goods from source to destination in shipping the product to the end consumer. Supply chain optimization models determine the orchestration of all raw inputs, intermediates, and outputs.

At each scale, we observe a separate energy system represented with a model that is appropriate for its individual length and time features. For example, macroscale models such as process synthesis would be ill-equipped to describe the dynamics occurring during chemical catalysis. The structuring of a larger system into smaller subsystems facilitates the understanding of finer details that otherwise likely would be absent from a higher level analysis [22]. This benefits the in-depth study and refinement of each subsystem, but does not express a complete picture of the entire energy system. There are interactions between the different subsystems that are not incorporated into the aforementioned structure. For example, catalyst design not only affects performance of the reaction it promotes and the reactor itself, but also impacts the operational success of other units in the plant, especially those immediately downstream like a distillation unit which depends heavily on the composition of its inlet stream coming from the reactor. Because decisions made on smaller systems can have significant ramifications on larger ones, it important to adopt a holistic approach toward understanding the behavior of an entire system so that both minute details are correctly represented and macro relationships are also accounted for. We risk losing key information from segmenting the entire system [23].

Toward a unified methodology, multi-scale energy systems engineering is the use of fundamental engineering tools (synthesis, design, modeling, simulation, and optimization) across varying length and time scales to bridge the gap between systems through analyzing phenomena that have inter-spatial and inter-temporal behavior and consequences [24]. The methodology can be carried out either sequentially or simultaneously. In a sequential manner, this is the inclusion of results from smaller scaled studies as informational input into a larger scaled investigation. An example would be creating simplified input-output models from detailed CFD simulations of each process unit to be used in a process synthesis model to find optimal process flowsheets. A simultaneous approach would be the development of an integrated framework that coordinates two or more scales in length and time. An example would be the optimization of a reactor with embedded information about the kinetics of several catalysts, and the goal is to simultaneously find the optimal reactor design and catalyst choice.

Appropriately assessing spatial and temporal variance is vital for the implementation and success of new natural gas applications, particularly because its composition varies by location, price fluctuates throughout the year, and demand is not uniform. Although natural gas is abundantly and cheaply available, we should undertake a multi-scale strategy to optimally utilize our resources, especially since such favorable conditions are not guaranteed to persist. For upgrading natural gas to valuable products, there are outstanding questions regarding: (1) optimal conversion technologies, (2) optimal integrated processes, and (3) optimal supply chain networks. It is essential to address these issues in a coordinated fashion to develop robust, affordable, environmentally-conscious, and efficient natural gas systems.

In the following sections, we showcase the applicability of the multi-scale energy systems engineering methodology toward examining and developing these natural gas systems with examples from our research. We highlight the need for accurate modeling and optimization at every stage. Chemical looping and microchannel reactors are discussed as new natural gas conversion options, ammonia, methanol, olefins, and aromatics productions are explored as integrated processes, and a nationwide supply chain of liquid transportation fuels is investigated as an example of a possible network for exploiting natural gas.

While we focus on the unit, process, and supply chain levels because this is our area of expertise, we emphasize that the atomistic and molecular level where catalysis resides is an integral part of the methodology. Rigorous and thorough catalysis work is important for properly assessing outcomes on these subsequent levels. Ultimately, our aim is to expose the broader aspects of an energy system's development to catalysis focused researchers who may be unfamiliar. To accelerate development, it is necessary for researchers to communicate with others from outside disciplines and to evolve a more holistic mindset. We hope this work serves as an illustrative introduction to multi-scale energy systems engineering, in particular for advancing natural gas systems and the important synergistic benefits of doing so in a multi-scale approach.

4. Natural gas conversion units

Traditionally for synthesizing chemical products, natural gas has proceeded through a syngas intermediate (a mixture of mostly CO and H_2) before further downstream upgrading. The two major industrial methods for natural gas conversion to syngas are steam reforming and autothermal reforming. Fig. 4 presents a bird eye's view of natural gas conversion. In these processes, O_2 and/or H_2O are fed with natural gas to produce syngas from oxidizing methane, and the overall reaction is highly endothermic. Heat is supplied to steam reforming from an external fuel source, while oxygen partially oxidizes some of the inlet natural gas to provide heat in autothermal reforming. While largely successful, reforming has its limitations. Excess oxygen and steam help improve natural gas conversion, prevent coking, and sustain catalyst, but also lead to increased amounts of CO_2 and H_2 in the effluent. This reduces the syngas purity, end product yield, and process efficiency; furthermore, extra conditioning units are needed to adjust the syngas composition before the upgrading. Autothermal reforming also requires pure oxygen, which is acquired from costly air separation. Economically, reforming processes do not scale down well [25].

Chemical looping and microchannel reactors attempt to resolve the disadvantages associated with reforming. Chemical looping separates the overall reaction into two reactors (one oxidation and one reduction) with circulating metal oxides connecting them and serving as oxygen carriers (Fig. 5). Heat is internally supplied from the air reactor to the fuel reactor, and there is inherent oxygen separation from air. Chemical looping produces a higher concentration of syngas, without needing excess oxygen or steam, and has greater per-pass conversions of natural gas due to Le Châtelier's principle from operating at lower pressures than reforming [26]. These advantages lead to cost savings associated with upgrading units, and chemical looping systems themselves also have lower capital costs than reforming reactors. Microchannel reactors are miniature (< 1 mm) devices in which chemical reactions occur in confined channel (Fig. 6). They offer advantages over conventionally sized equipment in terms of energy consumption, transport dynamics, reaction kinetics, modularity, and finer control. For reforming, a highly endothermic process, the enhanced heat transfer that microchannel reactors provide enables greater energy efficiency, smaller equipment sizes, and higher conversion of natural gas [27]. These advantages materialize into potential economic benefits, especially for smaller scaled processes.

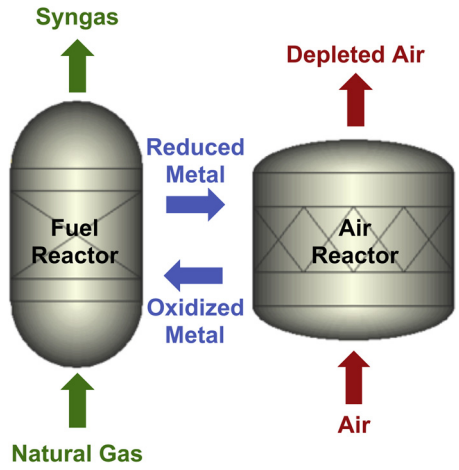

Fig. 5. Process scheme of chemical looping for natural gas conversion.

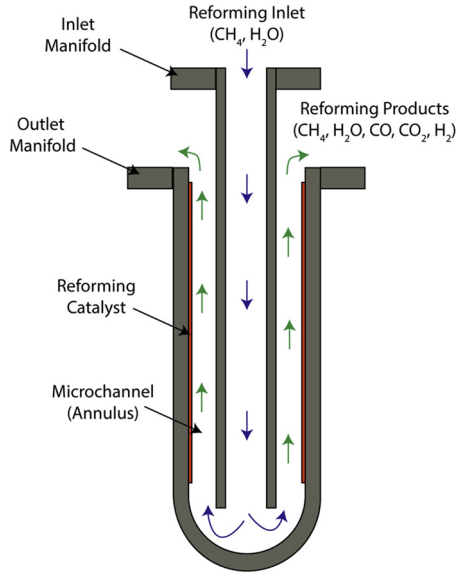

Fig. 6. An example microchannel reactor for natural gas conversion.

Computational simulation approaches have been employed to study both chemical looping and microchannel reactors for natural gas conversion to syngas. Various studies have showcased the ability to predict their performance to a very detailed degree [28–31], and experiment validation has been important in generating continuous feedback for model development [32,33]. At the unit level, these models are important to accurately depict the interplay between local heat, mass, and momentum transport dynamics and chemical reaction kinetics. Moreover, they represent the first stage in our multi-scale strategy and provide a basis for further refinement and optimization investigation. However, simulations like computational fluid dynamics (CFD) may require several hours to converge to a solution due to a large number of variables and nonlinear equations. While this leads to rigorous and accurate results, it is impractical to simultaneously incorporate such simulations as part of a larger model.

To facilitate the information provided by simulations as input into a larger scaled study, such as the process synthesis of a natural gas based plant, a bridging method is needed to close the spatial and temporal gap between the unit level and process level. These surrogate models should be simple enough so that they are computationally inexpensive, but also accurate enough in capturing the essence of the original model. One way to develop a surrogate model is fit a grey-box optimization/parameter estimation on the data generated from the simulations for different scenarios [34]. Onel et al. [35] fitted a surrogate model with only four parameters to describe the CFD simulations of a microchannel reactor for varying space velocities and steam-to-methane ratios with an average error of 0.43%. From 8-fold cross validation, the average testing error was between 0.5% and 0.6%, again reiterating that the surrogate model was able to accurately replicate the CFD simulations with simplified representations. Another way to create a surrogate is to approximate the simulation with a coarse first-principles model. Tso et al. [21] fitted a disjunctive programming model based on thermodynamic equilibrium to perfectly describe the AspenPlus simulations of an iron oxide chemical looping process with varying temperature, pressure, and oxygen-to-carbon ratios. Other surrogate model types include regression, interpolation, and neural network based methods [36]. Depending on the application, the type of surrogate model should be chosen accordingly.

Detailed models of process units are useful for simulating and optimizing the individual performance of the unit. But without scale bridging models, it is difficult to study the optimal unit operation within the context of the rest of the process. Accurate surrogate models allowed both studies [21,35] to pass the information appropriately from the unit level to the process level in order to evaluate novel natural gas conversion routes against conventional reforming in a liquid transportation fuels production refinery. By bridging the spatial and temporal gaps, we can now optimize the operation of chemical looping and microchannel reactors within the rest of the natural gas to liquid fuels (GTL) plant. Compared to conventional reforming, Onel et al. [35] noted that microchannel reactors can lead to cost savings of about $10/bbl for 500–5000 barrels per day GTL plants and utilizing microchannel reactors in tandem with reforming is even more cost effective. The discovery of this beneficial interaction arises from the multi-scale strategy; if we had analyzed microchannel reactors separately at the unit level instead of the process level, we would not have come across this result. Similarly, Tso et al. [21] observed that chemical looping reactors can lead to cost savings of 25–40% compared to reforming due to a significant increase in electricity coproduction and decreased investment costs. In the GTL process synthesis, chemical looping reactors are selected to operate at higher pressures, which was not the case when they were optimized separately on the unit level. Another highlight of using unit models in the process synthesis is that it allows us to directly assess the economic implications of using different catalysts for chemical looping. Even though iron oxide has a lower natural gas conversion to syngas than nickel oxide, using the former over the latter leads to 5–9% savings in GTL plant cost because iron oxide holds more oxygen molecules per volume than nickel oxide does. Reactor economics are calculated by volume, and using iron oxide leads to a smaller unit size than nickel oxide. We emphasize that these pressure and metal oxide results would be unforeseeable without a multi-scale methodology. In a myopic single scale view, lower pressure and nickel oxide would have been selected instead without considering synergies with other scales.

5. Natural gas process synthesis

Natural gas is prized as the primary source of industrial hydrogen and a favorable feedstock for synthesizing chemical products. Two important chemicals produced from natural gas are ammonia and methanol. Ammonia is predominantly used for fertilizer production, while methanol is a precursor to other chemicals like olefins, aromatics, formaldehyde, acetic acid, and dimethyl ether. Ammonia is crucial to the agricultural industry and for providing the means to large-scale food production to sustain the world population. Methanol derivatives are utilized in many of the commodity chemicals such as plastics, textiles, and pharmaceuticals that we enjoy in our daily lives and help us maintain our modern lifestyle. Particularly, methanol usage for the on-purpose production of olefins and aromatics is expected to increase significantly [37]. In the coming decade, demands for both ammonia

and methanol are expected to skyrocket from growth primarily in Asia, as more people's socioeconomic status and living standards rise [38,39].

Moreover, ammonia and methanol are seen as alternatives to the hydrogen economy [40,41]. While the hydrogen's gravimetric energy density is excellent, its volume energy density is abysmal. This is a challenge because more space for a tank will be needed on any apparatus, such as a hydrogen car, that is powered by hydrogen. Hydrogen also suffers from poor storage properties. To effectively transport hydrogen, cryogenic (−253 °C) or highly pressurized conditions (350-700 bar) are required. Ammonia and methanol are liquids under mild to ambient conditions, making their storage and transportation much easier. Likewise, the volume energy density of ammonia and methanol are an order of magnitude better than that of hydrogen. For applications, such as chemical storing intermittent energy such as solar and wind (e.g., using renewable energy to power natural gas conversion), ammonia and methanol also have a decent H_2 weight density of 17.8% and 12.6%, respectively.

At the same time, the industrial productions of ammonia and methanol are very energy consuming and carbon intensive processes. Clever process design and synthesis are necessary to construct new plants and retrofit existing ones to meet the additional chemical requirements in a energy and carbon efficient way. Even though ammonia and methanol are both produced from natural gas, typically their productions have been kept as separated processes, though methanol has been used as hedge against ammonia production when market prices lowered [42]. In the previous section, we saw multi-scale energy systems engineering being used to bridge the unit and process levels. Multi-scale energy systems engineering, particularly flowsheet optimization through process synthesis, can also be used to investigate energy systems at the same level and their optimal integration. This is especially important for natural gas based processes because there are a plethora of utilization alternatives and chemicals that could be produced, including ammonia and methanol. The outstanding problems are what is optimal to produce and how much of it. For chemical synthesis from natural gas, all routes to end products proceed through a syngas intermediate. Because of this, there are opportunities to integrate different natural gas process together to exploit the usage of common units, decrease costs of production, and improve process efficiency.

No greater example would be the integration of ammonia and methanol production, especially given their projected growth in demand. Mixed-integer nonlinear programming (MINLP) is a technique often used for process synthesis by mathematically modeling the mass and energy balances as constraints and having binary variables that are associated with the existence of a unit or not [43]. For example, ammonia and methanol production can be connected by a common set of upstream units, but which of these units are the optimal to connect the two productions is not clear (Fig. 7). Economic and technological feasibility constraints are also included in the process synthesis model. Moreover, material and energy flows, like the final product ratio or how much heat to supply to the reformer, are treated as variables to be solved for. All together the process synthesis considers a superstructure of all possible alternatives for the plant and an optimization algorithm solves for the optimal plant. For ammonia and methanol production, this means we can derive their optimal integration, how much of each chemical to produce and the units to do so. This is the power of process synthesis and optimization for plant design and retrofit.

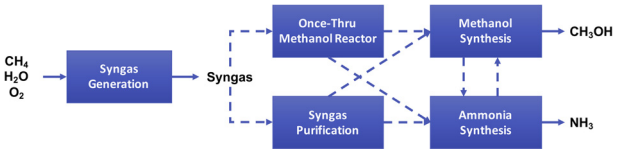

Fig. 7. Overview of the possible ways to integrate ammonia and methanol production.

Tso et al. [44] describes a process synthesis for coproducing ammonia and methanol from natural gas and biomass with 50% reduction in greenhouse gas emissions. Fig. 8 shows the process superstructure of all alternatives in ammonia and methanol coproduction. For a 500 metric tons (MT) of H_2 equivalent per day production, the authors concluded that the optimal product mix is storing 64% of the H_2 in methanol and 36% in ammonia, corresponding to 2560 MT/day of methanol and 1020 MT/day of ammonia. There is a total cost savings of 4–7% for the combined production compared to the single productions. When biomass is dropped as a feedstock, the product ratio of ammonia to methanol is fixed to 50:50, and greenhouse gases are constrained to be no more than existing ammonia and methanol plants, there is a 2–3% investment cost savings. In each case, an once-through methanol reactor was selected to connect the ammonia and methanol production sections. The once-through reactor acts produces methanol from syngas, while also doubling as an oxide purification step leading to the ammonia synthesis reactor. Light byproduct gases from the methanol synthesis and ammonia synthesis reactors that are recycled to each other also connect the two processes. From these two examples, we observe the potential of producing ammonia and methanol simultaneously together. The optimal integration of ammonia and methanol production under different scenarios will be the subject of a subsequent publication.

The following are the examples of process synthesis extended to olefins and aromatics. For producing olefins from natural gas via methanol, Onel et al. [45] observed profit margins between $8/GJ to $18/GJ for total production amounts from 100 MT/day to 5000 MT/day. The optimal product mix of olefins is 34% ethylene, 50% propylene, 14% 1-butene, and 2% 2-butene with methanol-to-olefins (MTO) and butene distillation as two key technological choices. Similarly, for natural gas to aromatics via methanol, Niziolek et al. [46] discovered profit margins between $0.40/GJ to $6/GJ for total production amounts from 500 MT/day to 5000 MT/day. The 100 MT/day natural gas to aromatics plant was unprofitable, requiring a cost of about $9/GJ. The optimal product mix of aromatics is 10% benzene, 46% *para*-xylene, and 44% *ortho*-xylene with methanol-to-aromatics (MTA), *ortho*-xylene distllation, UOP Tatoray, UOP TAC9, and UOP Cyclar as key technological choices. Again, this reiterates the powerful utilization of process synthesis and optimization as fundamental multi-scale energy systems engineering tools for identifying the optimal integration of processes toward manufacturing products from natural gas.

6. Natural gas supply chain networks

Even with advances in vehicle electrification and fuel economy, the US EIA expects the demand for gasoline, diesel, and jet fuel to remain fairly steady through 2050 [3]. Concurrently, net imports of crude oil are expected to go down, increasing the pressure on domestic oil production to keep up with the demand. Producing synthetic fuels from other domestic feedstocks like biomass, coal, or natural gas might relieve some of this demand and lessen our reliance on foreign crude oil, enhancing national energy independence and security. Increased domestic production will also provide some insurances against fluctuating crude oil prices from negatively impacting our economy. Natural gas is a more favorable feedstock for synthetic fuels production because of its high carbon to hydrogen ratio, lowering CO_2 emissions compared to coal, and smaller capital investment costs associated with GTL plants compared to biomass ones. In fact, there are several commercial GTL plants in operation. Examples include Sasol's Oryx plant in South Africa and Shell's Pearl and Bintulu plants in Malaysia and Qatar, respectively.

However, these GTL plants by in large are single entity operations. For liquid transportation fuels production from natural gas to displace crude oil on a national level, a large-scale network of GTL plants needs to be constructed. Supply chain networks coordinate the transport of feedstocks to the plant and distribution of fuel products to the market (Fig. 9). There are logistical limitations such as natural gas availability

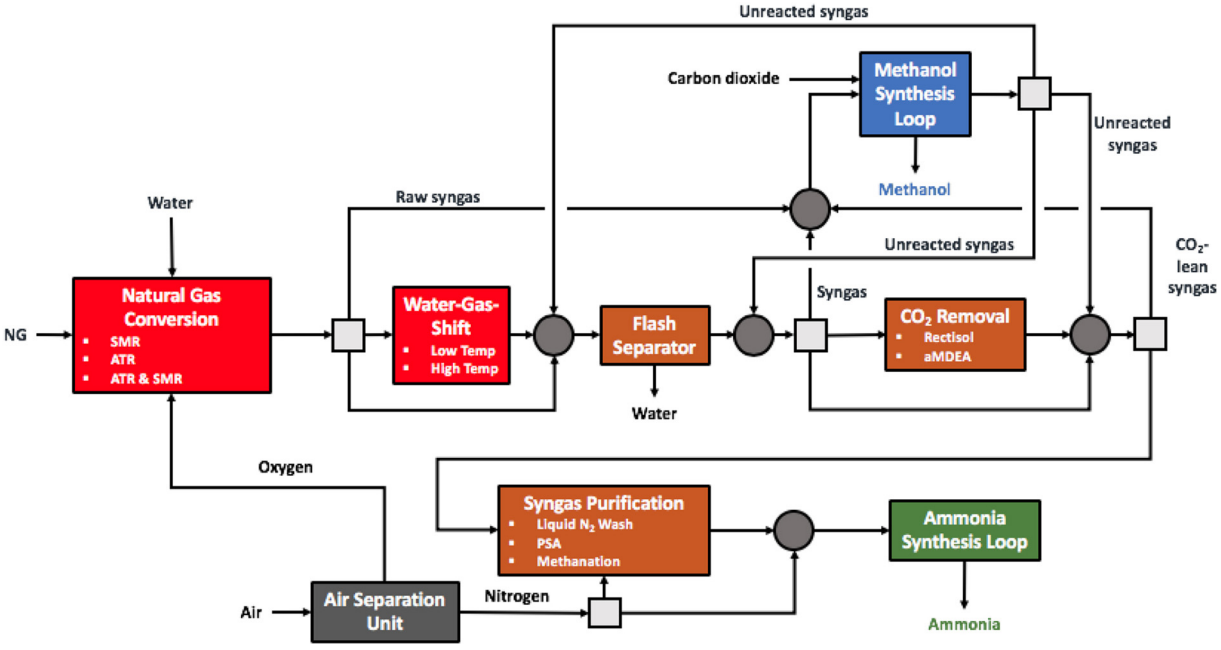

Fig. 8. Process superstructure of technological unit alternatives for ammonia and methanol production.

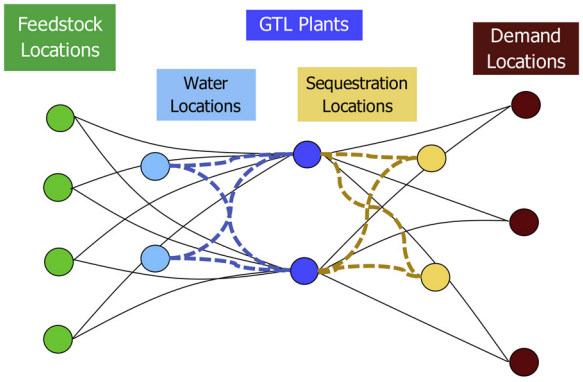

Fig. 9. Supply chain network of GTL plants connecting supply to demand.

and CO_2 sequestration capacity in different geographical locations that must be obeyed. Other local obligations with electricity, water sources, plant construction costs, market demand, and transportation modes should also be respected. Effective management of the entire network will determine the feasibility of the GTL supply chain in replacing crude oil and its overall profitability. An optimization framework that models the network flows and incorporates these logistical considerations to determine the strategic placements of GTL plants is a an important tool that can maximize the profitability of the entire GTL supply chain [47,48].

Supply chain optimization is a macro-scale problem, and it is the compilation of all the energy systems that are directly before it (Fig. 10). This means that information from the lower level problems must be appropriately transferred to the macro level. For example, strategically placing GTL plants on the network level involves utilizing information about the optimal plant performance from the process level. By considering a location to construct a GTL plant, it makes sense that the plant one decides to build would be the optimal one. Moreover, due to economies of scale, GTL plants outputting different product amounts will have varying economic and technical performances, and the strategic placement of GTL plants should also consider this. However, it is impractical to solve an inner process synthesis model within an outer supply chain optimization. To work around this, optimization results from the process synthesis of individual GTL plants can be included as parameter values into the supply chain problem, effectively bridging the gap between the two. This demonstrates another example of the multi-scale energy systems engineering approach. First, the process synthesis is solved and optimal GTL plants are determined. Next, information from the optimal plants are included into the supply chain model.

Supply chain models are also mixed-integer optimization problems that treat network flows as variables to solve for and the existence of a site to be determined by a binary variable [49]. Logistical limitations are included as constraints. Elia et al. [50] constructed an optimization model for studying nationwide, regional, and state-wide supply chain of GTL systems. The authors concluded that breakeven oil prices (BEOPs) for a nationwide GTL system is between $65/bbl and $80/bbl. Most regional (i.e. Northeast, Southeast, Midwest, Southwest, and Central) GTL systems have BEOPs that range from $65/bbl to $91/bbl, while the Western region is more expensive with BEOPs between $106/bbl and $123/bbl. Finally, Texas has BEOPs between $55/bbl and $65/bbl. Most of these BEOPs are competitive with crude oil prices, especially if they spike like they did in 2008. It is particularly interesting to note that areas with ample natural gas supply are sometimes selected to have a small GTL plant or no plant at all. Without a multi-scale strategy, one would likely built a large GTL plant at a site with lots of natural gas. Only by considering interactions between other GTL plants in the network, resource constraints, environmental restrictions, and market demands, do we observe that sometimes the best decision for natural gas utilization is none at all. This is not an intuitive result and comes directly from the multi-scale approach. Elia et al. [51] also extended the supply chain model to consider temporal factors since implementing a GTL network will likely occur over time and is not likely an once here and now decision.

Without earlier results from the process synthesis, the supply chain optimization could have returned worse BEOPs and given a wrong impression about the viability of a GTL network. Moreover, it is also important that accurate information is passed from the unit level to the process level for the supply chain optimization. For example, if imprecise surrogate models were used for a natural gas conversion technology, then the process synthesis may lead to a different solution, which in turn may cause the supply chain model to give a different result as well. Due to the multi-scale nature of energy systems like

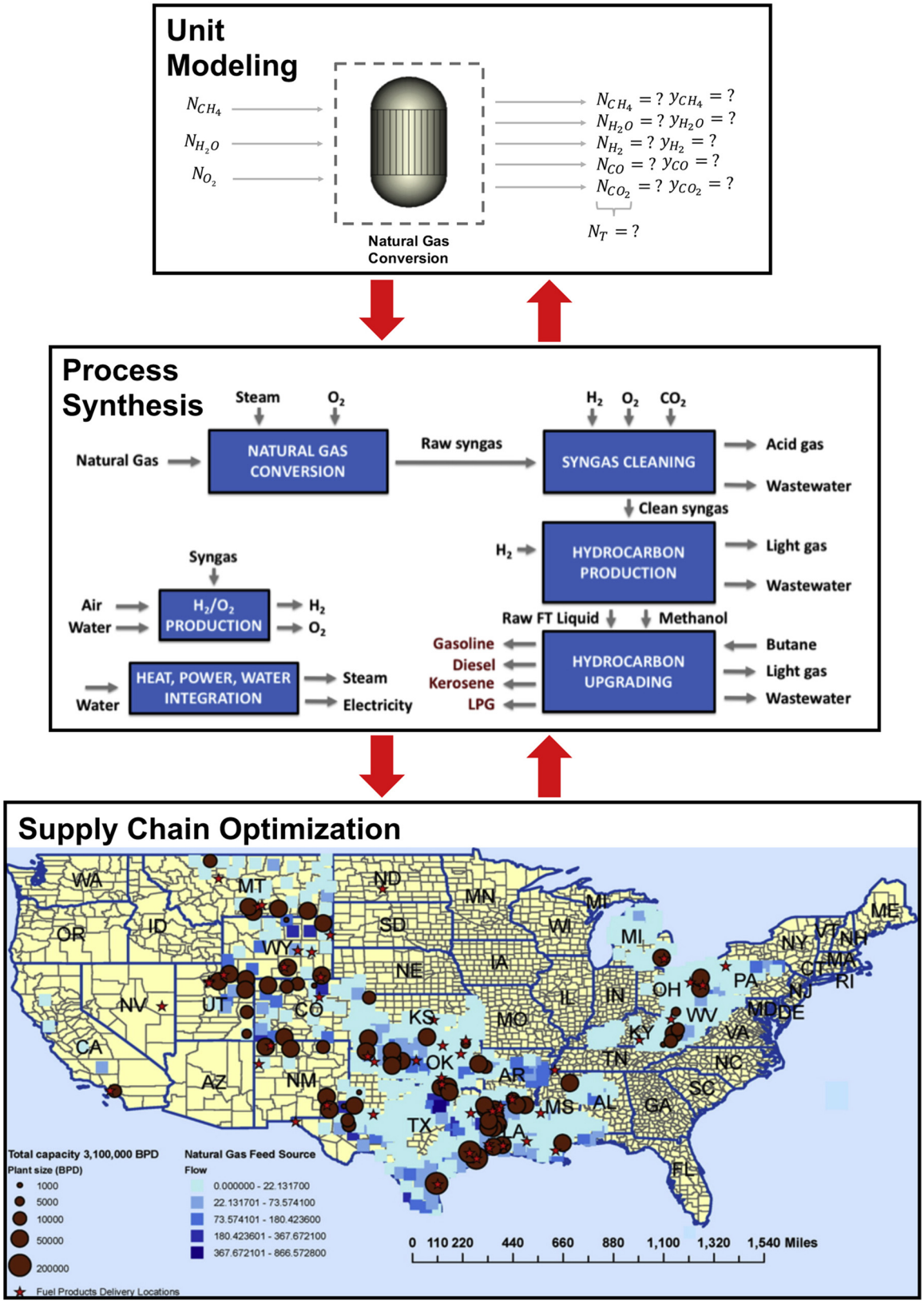

Fig. 10. Multi-scale energy systems engineering for the conversion of natural gas to liquid transportation fuels at the unit, process, and supply chain levels.

natural gas, decisions on the lower levels may have reverberating effects that could materialize into significant consequences on the upper levels. Accurate modeling is required at every stage of the multi-scale strategy to avoid this.

7. Future challenges

Today, multi-scale energy systems engineering is largely carried out in a sequential manner due to the increasing complexity and

computational intractability that often exists with simultaneous approaches [52]. The examples outlined here were mostly sequential. Information from unit level simulations were passed to the process level through surrogate models. Input parameters to the supply chain model were determined from the lower process synthesis results. Ideally, the molecular, unit, process, and supply chain scales would all be modeled and optimized simultaneously since combining together sequential optimal solutions may not necessarily lead to the true optimum. Therefore, two challenges that exist are: (1) the construction of more accurate and computationally inexpensive surrogate models and (2) the development of an integrated framework to analyze multiple scales and efficient solution algorithms. The former would lead to better approximations of the optimal solution, and the latter would give the true optimum if successful. Much progress has taken place in surrogate modeling, an area that also receives interest from other disciplines like operations research, computer science, applied mathematics, and statistics. We envision that interest in surrogate modeling will continue to grow, and there are great opportunities in simultaneous methods [53].

Another challenge for multi-scale energy systems engineering is the uncertainty inherently associated with energy from both resource and technology standpoints. For example, resource-wise, the supply and demand of natural gas fluctuate geographically and throughout the year. This is reflected in the spot price of natural gas which varies by location and peaks in the winter months. In terms of technology, performance of catalysts, reactors, and plants do not always reach their designed specifications, and they often are not steady operations. Process control systems are in place to take care of disturbances and keep the system stable near its performance criteria. While we have not touched upon the process control here due to scope, it is also an integral part of multi-scale energy systems engineering. There are challenges with resolving the dynamics between different temporal and spatial systems [54]. For example, the time characteristic of a catalyst is on the order of seconds and minutes, while the time characteristic of the supply chain might be weeks or months. It is an issue to assess how a strategic decision made on the supply chain level will affect the kinetics of a catalyst and the reactor performance. Toward addressing this challenge, Pistikopoulos et al. [55] have developed a multi-parametric programming framework for integrating the dynamics of different scales together in designing and controlling energy systems. Ogumerem et al. [56] extended this to analyze natural gas solid oxide fuel cells for distributed electricity generation. We observe that the much work remains on the integration of dynamics and control of energy systems across different scales, and it is an important topic that does not receive as much attention as system design problems do.

Actual realizations of the uncertainty also affect a model's solution quality. In other words, depending on what values uncertain parameters such as prices or demand actualize to, a solution to the optimization problem may no longer be optimal or even feasible because the parameter has actually taken a different value from that assumed when the model was first solved. Therefore, it is important to account for these sources of uncertainty within the multi-scale energy systems engineering methodology during the model development phase, especially since the uncertainty could propagate across the different scales into a larger value. This is a challenging task because there is no agreed upon standard method, and the right model depends on the problem being studied. From a modeling perspective, uncertainty can be handled either stochastically or probabilistically [57]. Stochastic approaches treat the uncertain parameters as random variables that combine together to generate different scenarios upon which to model and optimize. Probabilistic strategies bound parameters within uncertainty sets containing all possible realizations and assigns probabilities to parameters violating their bounds. The former results in a stochastic optimization model, typically solved using Monte Carlo or stage-wise decomposition techniques, and the latter remains a deterministic optimization through reformulation. As an example of a probabilistic approach, Matthews et al. [58] utilized robust optimization to study GTL plants under feedstock price uncertainty and concluded that 80% of the time they have a profit margin of $0.65/GJ or greater over a five year period from June 2011 to May 2016. While robust optimization may be suitable for addressing feedstock price uncertainty, it may not be appropriate for dealing with uncertainties that have nonlinear effects. We believe that standardization of approaches is needed for addressing different types of uncertainty.

8. Conclusion

We emphasize that a multi-scale strategy is not only useful for discovering the interactions between energy systems of varying temporal and spatial scales, but also critical for investigating the optimal design of the overall system. For natural gas, we have discussed examples at the unit, process, and supply chain levels where multi-scale energy systems engineering provided key insights into the optimal natural gas conversion technologies, integrated process synthesis, and supply chain networks. When chemical looping and microchannel reactors were modeled together with other units, it was shown that the collective optimal operation deviated from that of the individual ones. Next, coproduction of ammonia and methanol gave economic results that were not achievable through single production. Finally, the GTL supply chain network did not necessarily construct plants where natural gas was plentiful. These unintuitive discoveries are the direct results of the multi-scale strategy. While several challenges will continue to exist with the exact modeling techniques for energy systems under different settings, multi-scale energy systems engineering will remain a proven methodology for analyzing and developing efficient, reliable, profitable, and sustainable energy systems. Numerous opportunities exist for utilizing natural gas, but a multi-scale approach is essential toward determining its optimal utilization.

Acknowledgments

The authors declare no competing interests and acknowledge financial support from the Texas A&M Energy Institute and the Shell Oil Company.

References

[1] United Nations DESA/Population Division, World Population Prospects 2017, http://esa.un.org/unpd/wpp/Download/Standard/Population/, 2017.
[2] International Energy Agency, World Energy Outlook 2017, http://www.iea.org/weo2017/, 2017.
[3] U.S. Energy Information Administration, Annual Energy Outlook 2018 with projections to 2050, http://www.eia.gov/outlooks/aeo/pdf/AEO2018.pdf, 2018.
[4] ExxonMobil, 2018 Outlook for Energy: A View to 2040, http://cdn.exxonmobil.com//media/global/files/outlook-for-energy/2018/2018-outlook-for-energy.pdf, 2018.
[5] BP, BP Energy Outlook: 2018 Edition, http://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/energy-outlook/bp-energy-outlook-2018.pdf, 2018.
[6] Shell, Energy Transition Report, http://www.shell.com/energy-and-innovation/the-energy-future/shell-energy-transition-report.html, 2018.
[7] U.S. Energy Information Administration, June 2019: Monthly Energy Review, http://www.eia.gov/totalenergy/data/monthly/pdf/mer.pdf, 2019.
[8] BP, BP Statistical Review of World Energy: June 2018, http://www.eia.gov/totalenergy/data/monthly/pdf/mer.pdf, 2018.
[9] U.S. Energy Information Administration, Henry Hub Natural Gas Spot Price, http://www.eia.gov/dnav/ng/hist/rngwhhdm.htm, 2018.
[10] International Energy Agency, Global Energy & CO < *ce* : *inf* > 2 < / *ce* : *inf* > Status Report: 2017, https://www.iea.org/publications/freepublications/publication/GECO2017.pdf, 2018.
[11] GE Power, Breaking the Power Plant Efficiency Record, https://www.ge.com/power/about/insights/articles/2016/04/power-plant-efficiency-record, 2016.
[12] U.S. DOE, Combined Heat and Power Installation Database, https://doe.icfwebservices.com/chpdb/, 2019.
[13] N.A. Diangelakis, E.N. Pistikopoulos, A multi-scale energy systems engineering approach to residential combined heat and power systems, Computers & Chemical Engineering 102 (2017) 128–138.
[14] J. Ross, A. Van Keulen, M. Hegarty, K. Seshan, The catalytic conversion of natural gas to useful products, Catalysis Today 30 (1996) 193–199.
[15] G. Keller, M. Bhasin, Synthesis of ethylene via oxidative coupling of methane: I.

Determination of active catalysts, Journal of Catalysis 73 (1982) 9–19.
[16] K. Otsuka, K. Jinno, A. Morikawa, Active and selective catalysts for the synthesis of C_2H_4 and C_2H_6 via oxidative coupling of methane, Journal of Catalysis 100 (1986) 353–359.
[17] J.H. Lunsford, The catalytic oxidative coupling of methane, Angewandte Chemie International Edition in English 34 (1995) 970–980.
[18] J.R. Rostrup-Nielsen, Catalysis and large-scale conversion of natural gas, Catalysis Today 21 (1994) 257–267.
[19] J. Lee, S. Oyama, Oxidative coupling of methane to higher hydrocarbons, Catalysis Reviews Science and Engineering 30 (1988) 249–280.
[20] J. Xu, G.F. Froment, Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics, AIChE journal 35 (1989) 88–96.
[21] W.W. Tso, A.M. Niziolek, O. Onel, C.D. Demirhan, C.A. Floudas, E.N. Pistikopoulos, Enhancing natural gas-to-liquids (GTL) processes through chemical looping for syngas production: Process synthesis and global optimization, Computers & Chemical Engineering 113 (2018) 222–239.
[22] K.-U. Klatt, W. Marquardt, Perspectives for process systems engineering: Personal views from academia and industry, Computers & Chemical Engineering 33 (2009) 536–550.
[23] I.E. Grossmann, A.W. Westerberg, Research challenges in process systems engineering, AIChE Journal 46 (2000) 1700–1703.
[24] C.A. Floudas, A.M. Niziolek, O. Onel, L.R. Matthews, Multi-scale systems engineering for energy and the environment: Challenges and opportunities, AIChE Journal 62 (2016) 602–623.
[25] R. Wang, D. Rohr, Natural gas processing technologies for large scale solid oxide fuel cells, Abstracts of Papers of the American Chemical Society (2002) U562–U562.
[26] S. Luo, L. Zeng, D. Xu, M. Kathe, E. Chung, N. Deshpande, L. Qin, A. Majumder, T.-L. Hsieh, A. Tong, et al., Shale gas-to-syngas chemical looping process for stable shale gas conversion to high purity syngas with a H2:CO ratio of 2:1, Energy & Environmental Science 7 (2014) 4104–4117.
[27] H. Butcher, C.J. Quenzel, L. Breziner, J. Mettes, B.A. Wilhite, P. Bossard, Design of an annular microchannel reactor (AMR) for hydrogen and/or syngas production via methane steam reforming, International Journal of Hydrogen Energy 39 (2014) 18046–18057.
[28] G. Arzamendi, P. Diéguez, M. Montes, J. Odriozola, E.F. Sousa-Aguiar, L. Gandía, Computational fluid dynamics study of heat transfer in a microchannel reactor for low-temperature Fischer-Tropsch synthesis, Chemical Engineering Journal 160 (2010) 915–922.
[29] M. Karakaya, A.K. Avci, Microchannel reactor modeling for combustion driven reforming of iso-octane, International Journal of Hydrogen Energy 36 (2011) 6569–6577.
[30] I. Iliuta, R. Tahoces, G.S. Patience, S. Rifflart, F. Luck, Chemical-looping combustion process: Kinetics and mathematical modeling, AIChE Journal 56 (2010) 1063–1079.
[31] H. Kruggel-Emden, S. Rickelt, F. Stepanek, A. Munjiza, Development and testing of an interconnected multiphase CFD-model for chemical looping combustion, Chemical Engineering Science 65 (2010) 4732–4745.
[32] X. Yao, Y. Zhang, L. Du, J. Liu, J. Yao, Review of the applications of microreactors, Renewable and Sustainable Energy Reviews 47 (2015) 519–539.
[33] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, F. Luis, Progress in chemical-looping combustion and reforming technologies, Progress in Energy and Combustion Science 38 (2012) 215–282.
[34] F. Boukouvala, M.F. Hasan, C.A. Floudas, Global optimization of general constrained grey-box models: New method and its application to constrained PDEs for pressure swing adsorption, Journal of Global Optimization 67 (2017) 3–42.
[35] O. Onel, A.M. Niziolek, H. Butcher, B.A. Wilhite, C.A. Floudas, Multi-scale approaches for gas-to-liquids process intensification: CFD modeling, process synthesis, and global optimization, Computers & Chemical Engineering 105 (2017) 276–296.
[36] A. Bhosekar, M. Ierapetritou, Advances in surrogate based modeling, feasibility analysis and and optimization: A review, Computers & Chemical Engineering 108 (2018) 250–267.
[37] IHS Markit, The changing face of the global methanol industry, http://www.methanol.org/wp-content/uploads/2016/07/IHS-ChemicalBulletin-Issue3-Alvarado-Jun16.pdf, 2016.
[38] Ammonia Industry, What drives new investments in low-carbon ammonia production? One million tons per day demand, http://ammoniaindustry.com/what-drives-new-investments-in-low-carbon-ammonia/, 2018.
[39] IHS Markit, Driven by China, global methanol demand rises 23 percent in two years, unprecedented demand growth expected for 2012 to 2022, Says New IHS Study, http://news.ihsmarkit.com/press-release/country-industry-forecasting/driven-china-global-methanol-demand-rises-23-percent-two-/, 2013.
[40] G.A. Olah, Beyond oil and gas: the methanol economy, Angewandte Chemie International Edition 44 (2005) 2636–2639.
[41] C.H. Christensen, T. Johannessen, R.Z. Sørensen, J.K. Nørskov, Towards an ammonia-mediated hydrogen economy? Catalysis Today 111 (2006) 140–144.
[42] Oil & Gas Journal, New integrated methanol/NH_3 plant starts up in Western Oklahoma, http://www.ogj.com/articles/print/volume-92/issue-32/in-this-issue/petrochemicals/new-integrated-methanol-nh3-plant-starts-up-in-western-oklahoma.html, 1994.
[43] Q. Chen, I. Grossmann, Recent developments and challenges in optimization-based process synthesis, Annual Review of Chemical and Biomolecular Engineering 8 (2017) 249–283.
[44] W.W. Tso, C.D. Demirhan, J.B. Powell, E.N. Pistikopoulos, Toward optimal synthesis of renewable ammonia and methanol processes (RAMP), Computer Aided Chemical Engineering 44 (2018) 1705–1710.
[45] O. Onel, A.M. Niziolek, C.A. Floudas, Optimal production of light olefins from natural gas via the methanol intermediate, Industrial & Engineering Chemistry Research 55 (2016) 3043–3063.
[46] A.M. Niziolek, O. Onel, C.A. Floudas, Production of benzene, toluene, and xylenes from natural gas via methanol: Process synthesis and global optimization, AIChE Journal 62 (2016) 1531–1556.
[47] L.G. Papageorgiou, Supply chain optimisation for the process industries: Advances and opportunities, Computers & Chemical Engineering 33 (2009) 1931–1938.
[48] J.A. Elia, C.A. Floudas, Energy supply chain optimization of hybrid feedstock processes: a review, Annual Review of Chemical and Biomolecular Engineering 5 (2014) 147–179.
[49] M.T. Melo, S. Nickel, F. Saldanha-Da-Gama, Facility location and supply chain management – a review, European Journal of Operational Research 196 (2009) 401–412.
[50] J.A. Elia, R.C. Baliban, C.A. Floudas, Nationwide, regional, and statewide energy supply chain optimization for natural gas to liquid transportation fuel (GTL) systems, Industrial & Engineering Chemistry Research 53 (2013) 5366–5397.
[51] J.A. Elia, J. Li, C.A. Floudas, Strategic planning optimization for natural gas to liquid transportation fuel (GTL) systems, Computers & Chemical Engineering 72 (2015) 109–125.
[52] D.G. Vlachos, Multiscale modeling for emergent behavior, complexity, and combinatorial explosion, AIChE Journal 58 (2012) 1314–1325.
[53] L.T. Biegler, Y.-d. Lang, W. Lin, Multi-scale optimization for process systems engineering, Computers & Chemical Engineering 60 (2014) 17–30.
[54] J. Li, W. Ge, W. Wang, N. Yang, X. Liu, L. Wang, X. He, X. Wang, J. Wang, M. Kwauk, From Multiscale Modeling to Meso-Science, Springer, 2013.
[55] E.N. Pistikopoulos, N.A. Diangelakis, R. Oberdieck, M.M. Papathanasiou, I. Nascu, M. Sun, PAROC An integrated framework and software platform for the optimisation and advanced model-based control of process systems, Chemical Engineering Science 136 (2015) 115–138.
[56] G.S. Ogumerem, E.N. Pistikopoulos, N.A. Diangelakis, Natural gas based SOFC in distributed electricity generation: modeling and Control, Natural Gas Processing from Midstream to Downstream Vol. 1 Wiley, 2018.
[57] N.V. Sahinidis, Optimization under uncertainty: state-of-the-art and opportunities, Computers & Chemical Engineering 28 (2004) 971–983.
[58] L.R. Matthews, Y.A. Guzman, O. Onel, A.M. Niziolek, C.A. Floudas, Natural gas to liquid transportation fuels under uncertainty using robust optimization, Industrial & Engineering Chemistry Research 57 (2018) 11112–11129.