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Probing the Impact of an Energy and Transportation Paradigm Shift on the Petrochemicals Industry

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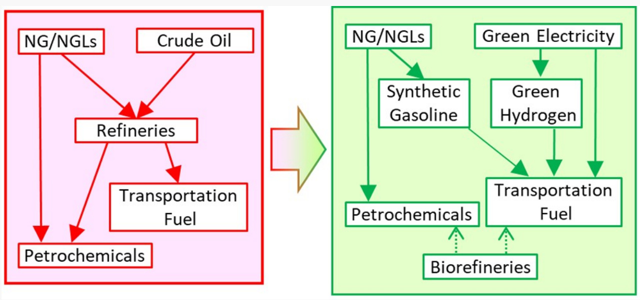
ABSTRACT: A paradigm shift in energy and transportation, away from fossil fuels and toward renewables, has begun. Driven by climate and sustainability considerations, consumer preferences and corporate aspirations favoring electric vehicles, powered by electricity generated renewably, are accelerating. As a result, the long-term future outlook for fossil-based fuels and the petroleum refining industry is subject to significant uncertainty. Since the production of petrochemicals is closely connected to petroleum refining, it is also likely to be impacted by this paradigm shift. In this paper, these potential impacts are probed using an optimization-based, network superstructure model of the U.S. petrochemicals industry. The model is used to investigate the response of the industry under extreme-case scenarios involving complete loss of demand for liquid transportation fuels and/or complete loss of crude oil supply and petroleum refining capacity. The model is also used to perform an assessment of new, natural-gas-based technologies that might be implemented in the context of a residual, limited-demand market for liquid transportation fuels. The production of green hydrogen for use in this context is also considered.



1. INTRODUCTION

A paradigm shift in the energy industry is underway. Under the old paradigm, renewable sources of energy (e.g., solar, wind, biomass) were dismissed as expensive (relative to fossil-based energy) and unlikely to account for more than a small fraction of satisfying overall energy usage. However, today, renewables are undercutting fossil fuels economically, especially in the context of electricity generation, and their usage is increasing rapidly.[1] This shift is being driven by technological advances, often motivated by concerns about climate change and sustainability (fossil fuels are a finite resource), and, in some cases, by favorable government policies.

This paradigm shift is becoming particularly apparent in the transportation sector, with the increasing adoption of electric vehicles (EVs), which can be regarded as zero emission if powered by electricity generated from renewables. The U.S. Energy Information Administration predicts[1] that the internal combustion engine fleet will peak in 2023 in OECD counties overall and in 2038 globally, as road-going vehicles are replaced by EVs. This is occurring due to changing consumer preferences and corporate aspirations, and this is supported by government policies and initiatives. For example, General Motors has announced aims to produce only EVs by 2035[2−4] and other automakers have announced similar plans.[5−7] Consumer preferences can be both sustainability driven and economic, with the cost of operation of EVs estimated as about half that of a gasoline-powered vehicle.[8] Furthermore, with similar motivations, companies that operate large vehicle fleets[9,10] have announced the purchase or use of EVs or other "greener" vehicles. There are currently programs in most U.S. states to support the adoption of EVs.[11] For example, California and other states have adopted plans to support the transition to zero-emissions light vehicles[12] and clean trucks.[13] At a national level, the White House has announced a plan aiming for at least 50% of all new vehicles sold in 2030 to be zero-emission vehicles.[14] Similar programs and policies are also being implemented in the European Union.[15,16]

The electrification of light vehicles is already well underway; it is starting in heavy vehicles[17] and developing in freight-duty rail.[18] The high energy density of liquid fuels is still required for long-distance air and sea transport, but there are growing efforts to make these fuels biobased and renewable.[19−21] This prompts a question: Will there be fossil-based transportation

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fuels and a viable petroleum refining industry in the future? Furthermore, since the petrochemicals industry is closely connected, and sometimes directly integrated with petroleum refining, it is also likely to be significantly affected by these changes in the transportation sector. Thus, we must consider the impact on the petrochemicals industry of the energy paradigm shift described above. In this paper, we aim to probe this impact, using a computational model of the U.S. petrochemicals industry.

The model used for this study is the optimization-based, superstructure model described by Skouteris et al.,[22] enhanced with a greater resolution of refinery-based processes. As a base case, we first identify the optimal (minimum total cost) network configuration of the current industry. We then consider three limit-case scenarios. The first involves a complete loss of demand for fossil-based transportation fuels, but with refinery-based processes remaining available. The second represent a situation in which petroleum refineries have become economically nonviable and are completely shut down, but demand for some liquid transportation fuels remains. The third scenario then considers the case of both no demand for fossil-based liquid fuels and no capacity for refining. In all three cases, it is assumed that demand for petrochemical products remains unchanged. In each scenario, we determine the optimal industry structure and analyze how it has changed relative to the base case. Also, in the context of the second scenario, we consider two alternative sources for liquid transportation fuels to meet remaining demand. First, the potential adoption of new pathways to produce synthetic gasoline from natural gas liquids (NGLs), specifically ethane, is studied. Then, we investigate whether green hydrogen production can be a cost-effective solution to meeting demand.

In summary, the main contributions of this work are as follows:

○ A novel study probing the effect on the U.S. petrochemicals industry of today's incipient paradigm shift away from fossil-based transportation fuels is presented, based on a minimum-cost, superstructure model of the industry.

○ Multiple case studies, based on modeling limit-case scenarios for the industry's future are presented, with comparisons to a base case representing the current industry:

- No demand for fossil-based transportation fuels, but petroleum refining processes remain available and demand for petrochemical products remains unchanged
- No capacity for petroleum refining, but some demand for liquid transportation fuels remains and demand for petrochemical products remains unchanged
- A combination of the previous two scenarios

○ For the scenario of no refining capacity, novel studies are presented that address the potential for alternative sources of liquid transportation fuels as a means to meet the remaining demand:

- New pathways that transform an ethane or ethylene feed to liquid transportation fuel are assessed
- The potential of green hydrogen production to meet demand is investigated

It is hoped that this work will help identify future petrochemicals industry processing needs and guide research and development efforts as the industry finds a path through this paradigm shift.

In the next section, a brief summary of network superstructure models applied to the petrochemicals industry is given and the specific model formulation used is presented. Next, in Sections 3 and 4, we provide details of the case studies noted above and present and discuss results. Finally, concluding remarks are provided in Section 6.

2. INDUSTRY NETWORK MODELING

2.1. Background. The petrochemicals industry can be viewed as a complex, integrated network of individual refining and chemical manufacturing processes that are interconnected via material and energy flows.[23] This network system acts to convert a relatively small number of primary raw materials (e.g., natural gas, NGLs, petroleum) into a large and diverse array of intermediates and end products, including polymer products.[22,24] Often, intermediates and final products can each be produced through multiple different processes, utilizing different types and amounts of feedstocks and energy sources, while also producing different byproducts. Thus, this industry network involves multiple competing pathways for transforming the primary raw materials into the desired final products.

Optimization-based network models of the petrochemicals industry originated with the work of Stadtherr and Rudd,[25] who initially focused on minimization of resource usage and subsequently on minimization of industry cost.[26] Many variations and extensions of this initial work, with different applications, have appeared since, as reviewed by Skouteris et al.[22] and DeRosa and Allen.[27] Such network models represent the industry as a directed graph, in which nodes correspond to chemical processes that are connected by edges that correspond to flows between nodes. Each process node is characterized by a set of input−output coefficients that represent its material and energy balances. Additional properties such as capacity or geographic location may also be used, depending on the desired application of the model. The directed graph edges are then characterized by material and energy flow rates, and (for some applications) transportation capacities and cost. The model is then formulated as a superstructure of commercially viable processes[28] that allows for determining the optimal configuration of the industry network by solving an optimization problem to minimize a given industry-wide objective, subject to material balance constraints, as well as supply limitations and demand requirements. The solution of the optimization problem determines the optimal production levels for each process technology, as well as material flows in the network. In this paper, we use a production cost minimization objective, but alternative or multiple objectives can be used. For example, Giannikopoulos et al.[29] have developed a multiobjective industry network model that considers the minimization of both the total industry cost, as well as the total carbon loss (e.g., as CO_2 emissions) in the network, which accounts for both feedstock carbon and fuel carbon consumed to cover energy needs. Studies performed using network models often focus on the industry response to some perturbation, such as evaluation of the impact of adding new technology, changes in supply and demand, or variations in materials pricing or production costs.

2.2. Model Formulation. The data used for the model (e.g., process stoichiometries and costs) have been obtained from the *IHS 2012 Process Economic Yearbook*.[28] The current model contains 893 processes, 895 materials and 7 utility types, aiming to represent a superstructure of the commercially viable processes available to the bulk petrochemicals and refining industry, including polymer products.

The core model consists of balance equations for all materials, plus supply and demand constraints. The balance equation for each material i (including utility types) are

$$F_i + \sum_j a_{i,j}X_j - Q_i = 0 \tag{1}$$

where F_i is the exogenous flow rate of material i into the network as a primary feedstock, $a_{i,j}$ is the input−output coefficient for material i in process j (negative if material i is consumed in process j, positive if it is produced; unity if i is the main product of process j), X_j is the utilization level of process j (in terms of flow rate of main product), and Q_i is the exogenous flow rate of material i out of the network as a final product. The supply and demand constraints limit the flow rates of primary feedstocks into the network to be less than their exogenous supply rates S_i and requires the flow rates of final products out of the network to meet their exogenous demand D_i:

$$0 \leq F_i \leq S_i \tag{2}$$

$$Q_i \geq D_i \geq 0 \tag{3}$$

The decision variables in this model are X_j, F_i, and Q_i and are all constrained to be non-negative.

The objective function in this optimization-based model is the minimization of the total industry cost C_{tot}:

$$\min_{X_j,F_i,Q_i} C_{\text{tot}} = \sum_j C_jX_j \tag{4}$$

where C_j is the net unit cost of process j (per amount of main product). The process cost C_j consists of a fixed component and variable component.[28] The fixed component includes the capital investment, expressed as straight-line depreciation over a 10-year period, as well as fixed operating costs, such as maintenance, labor, overhead, and taxes, based on an average scale plant. The variable component includes raw material costs, byproduct credits, and utilities cost. If the cost coefficients are assumed to be constant (independent of the X_j), then this optimization problem is a linear program (LP). However, in some situations, this assumption is not appropriate. Such a situation may arise, for example, if a new, less costly process k for producing an intermediate or byproduct species i is added to the model as a perturbation to be studied. If this process is used (X_k is nonzero), then the price for species i may be reduced, thus affecting the net costs for all processes in which species i is a raw material or byproduct. In this type of situation, the net process costs are dependent on the process utilization levels, and so the problem becomes nonlinear. To deal with this issue, Skouteris et al.[22] have described a successive linear programming (SLP) approach that alternates between solving a constant-cost LP and a special cost-propagation algorithm that updates process costs and material prices based on the LP results. This approach is used in the case studies below in which new synthetic gasoline processes are added to the industry network and a variable-cost electrolysis process for green hydrogen is studied. We claim no guarantee that the SLP approach will find a global optimum to the nonlinear problem. However, in recent preliminary studies comparing the SLP approach to an MINLP problem formulation with standard solvers,[30] we find empirical evidence that globally optimal solutions are found.

We also note the following:

(1) The technology matrix $A = [a_{i,j}]$ in the model can be considered to be independent of location. However, the process costs (C_j), supply rates (S_i), and demand rates (D_i) are values based on U.S. data. Thus, all case studies presented below are done in the context of the U.S. industry.

(2) There is no geospatial resolution in this model. That is, the variable X_j represents the combined production rate of the main product for process j from *all* facilities in the United States using process j. However, as shown by Giannikopoulos et al.[31] and DeRosa et al.,[32] it is possible to add geospatial resolution to this type of model, so that production rates from individual facilities at specific locations are considered, along with relevant material transportation costs.

(3) This is a static model. There will be supply chain, infrastructure, and other issues that will limit the speed of the transition to a transportation system powered only by renewable energy sources. However, we are not attempting here to model the dynamics of this transition. We are instead interested in finding the optimal "steady state" that will result at the end of this transition.

3. CASE STUDIES

In Section 1, a series of case studies was introduced, motivated by the incipient paradigm shift in energy and transportation away from fossil-based energy toward renewables. In this section, we present details of these case studies and discuss their results.

3.1. Base Case. This case represents the U.S. industry under its present conditions. Supply and demand levels for all raw materials and final products, respectively, represent current values. All commercially proven technologies appear in the network model superstructure as potential processes that can be selected as part of the minimum-cost network configuration. The process superstructure is that used by Skouteris et al.,[22] but with some additional processes and components used in the superstructure to provide greater resolution of refining processes and products. Because petroleum refineries have flexibility in adjusting their product mix, the demands for gasoline, diesel, and kerosene (jet fuel) are lumped into a single liquid transportation fuel demand constraint.

Results for petrochemicals from the base case optimization appear in the comparisons presented in the subsequent case studies. Results for production of transportation fuels appear in Figure 1, with comparison to actual data for 2019 and 2020. Even though demands based on these data for the individual fuels (gasoline, diesel, jet fuel) were not used as constraints in the model (only the sum of their demands was constrained, to a value that was a slight underestimate of the final 2020 data), the model still captures the relative distribution of these products remarkably well.

3.2. Case Study 1: No Transportation Fuels Demand. The case study considers a limit-case scenario in which all demand for fossil-based liquid transportation fuels (gasoline, diesel, jet fuel) is set to zero. This implies a future in which the need for fossil-fueled vehicles will be eliminated due to a complete adoption of electric or other renewably fueled vehicles. As discussed in Section 1, this will happen on different time scales for different transportation modes. In this scenario, it is assumed that (i) the current supply of crude oil remains available, as do the current refinery processes represented in the industry model, and (ii) the demand for petrochemical products remains unchanged.

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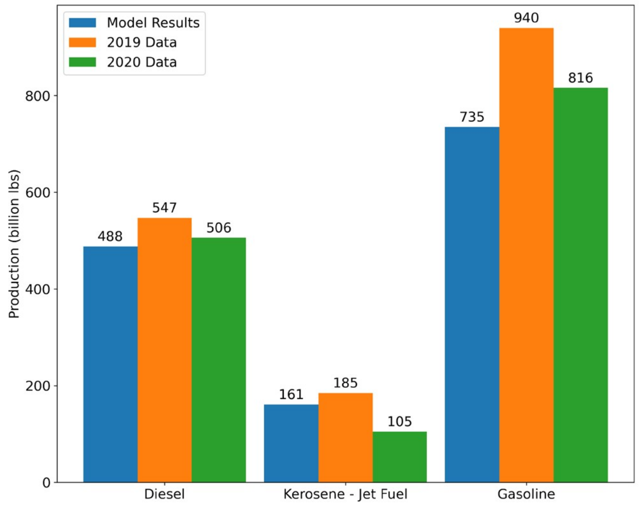

Figure 1. Yearly production of transportation fuels in the base case model and in years 2019 and 2020. Data adapted from EIA.[33] Production levels in 2020 are lower than 2019 levels, primarily because of the impact of the COVID-19 pandemic, and the associated local lockdowns and work-from-home policies, on transportation fuel demand.

The energy paradigm shift away from fossil fuels considered in this scenario represents a massive change in how transportation is powered. To put this in perspective, consider the U.S. motor vehicles fleet (this includes automobiles and other light-duty vehicles as well as medium/heavy trucks and buses). In 2019, there were 276 million motor vehicles registered[34] in the United States; this means that the United States (4.25% of global population[35]) accounts for ∼19% of all vehicles in the world.[36] The total annual mileage traveled by U.S. motor vehicles was 3.27 trillion miles[37] in 2019. Fuel consumption[38] (almost all gasoline and diesel) by these vehicles was 172 billion GGE (gallons of gas equivalent, with 0.904 gallon diesel/GGE) (this is 2018 information, which is assumed to be little changed for 2019), for an average fuel efficiency of ∼19 miles/gallon (mpg). EVs are much more efficient than fossil-fueled vehicles at converting fuel energy into motion on the road,[39] say by a factor of ∼3.5.[40] Thus, for 2019, 172/3.5 = 49.1 billion GGE of electricity would have been required to power an all-electric U.S. motor vehicle fleet; at 33.7 kWh/GGE,[38] this is 1.65 trillion kWh of electricity. The total U.S. generation of electricity in 2019 was 4.13 trillion kWh, so powering an all-electric motor vehicle fleet would have required the generation of ∼40% more electricity.

With no demand for liquid transportation fuels, the use of the available refinery processes in the minimum-cost industry is very limited. Some operations are maintained in order to produce naphthalene, since its production in refinery processing is the only route in the model to meet its need (to produce and satisfy the demand for anthraquinone). More significantly, additional light naphtha is now available from refinery operations, and its increased use in the Asahi aromatization (Alpha) process has an impact on the usage of other processes in the industry, as depicted in Figure 2, which shows the key changes relative to the base case. With more

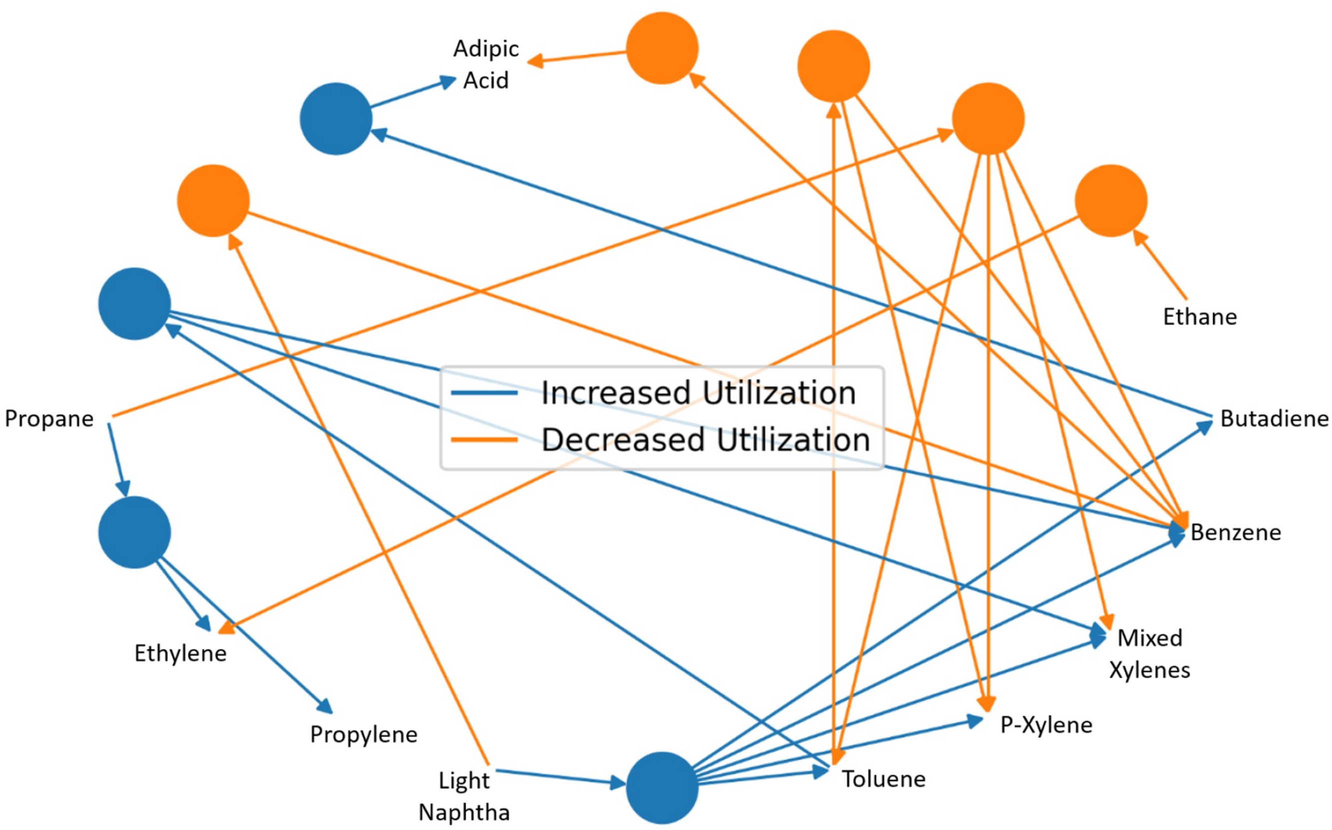

Figure 2. Major changes in process utilization for the no transportation fuels demand scenario (Case Study 1) when compared to the base case. Circles represent chemical processes with arrows showing primary inputs and outputs. Blue indicates a process with increased utilization and orange decreased utilization. [Figure created using NetworkX.[41]]

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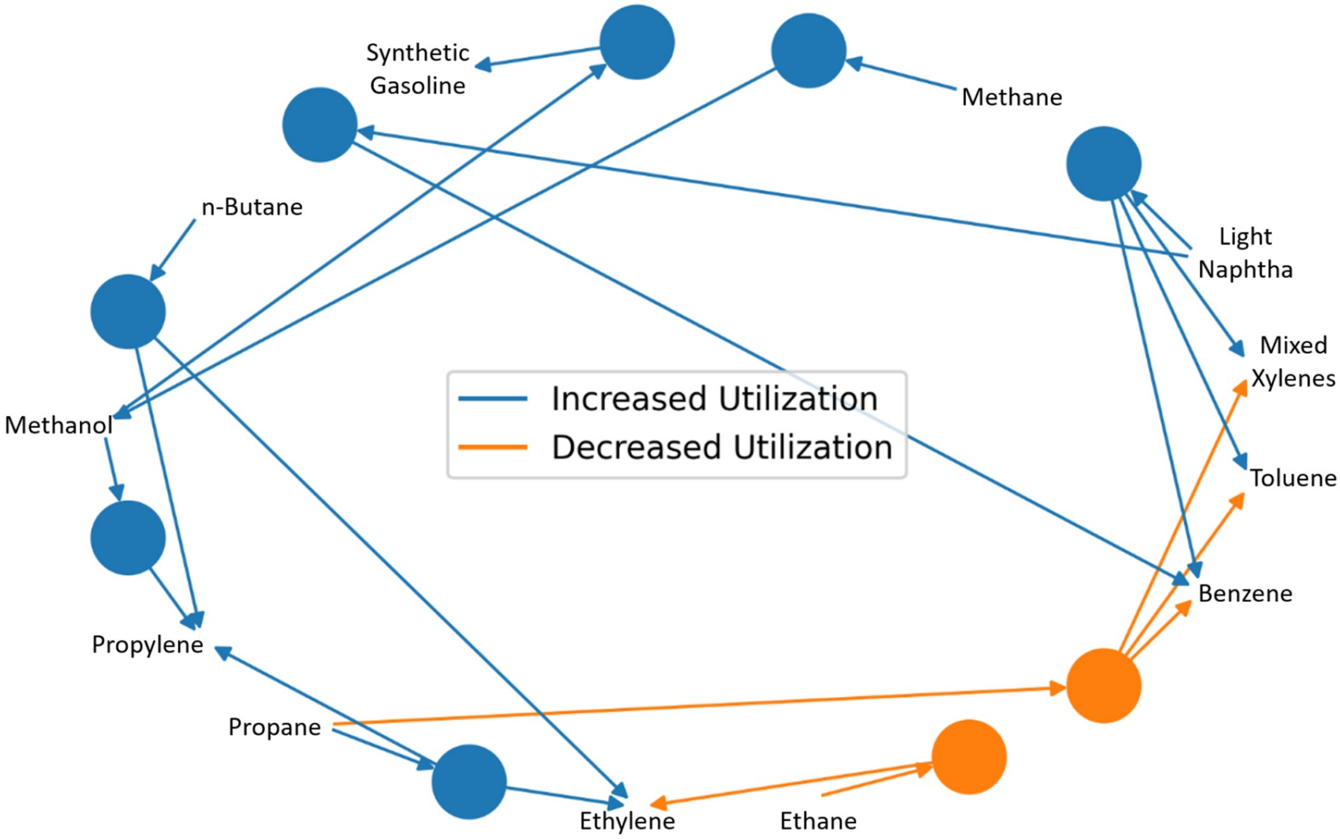

Figure 3. Major changes in process utilization for the no refining scenario (Case Study 2), when compared to the base case. Circles represent chemical processes with arrows showing primary inputs and outputs. Blue indicates a process with increased utilization, and orange features represent decreased utilization. [Figure created using NetworkX.[41]]

BTX from naphtha, there is reduced usage of propane for BTX (BP/UOP Cyclar process) and increased use of propane as cracker feed for olefins production. Of course, refining crude to produce only light naphtha and naphthalene would not be a viable operation, as, at least with the refining processes currently in the model, this would lead to significant overproduction of materials for which there is no longer a demand. However, given the current degree of flexibility in refinery processing, it is not unreasonable to think that these processes could be modified, and new processes developed, that would focus refinery output on petrochemical feedstocks rather than fuels, albeit at a greatly reduced throughput.

3.3. Case Study 2: No Crude Oil Refining. The previous case study suggests that, as demand for liquid transportation fuels wanes, crude oil refineries will need to be largely reinvented and operated at a much smaller scale to remain viable. In Case Study 2, we consider a limit-case scenario in which petroleum refining has become economically nonviable and is completely shut down. Thus, all refinery processes are removed from the model and the crude oil supply is set to zero (a small supply of coal present in the base case is also set to zero). This implies a future where heavy hydrocarbon utilization has been eliminated due to environmental and climate concerns, together with governmental policies. The heaviest hydrocarbon typically produced from refineries that is still available to the industry network is light naphtha, albeit at a much lower supply level compared to the base case, corresponding only to the amount produced[42] in the United States from NGL fractionation in 2020 (light naphtha from NGL fractionation is also called natural gasoline or pentanes plus). However, for this extreme-case scenario, we assume that demand for transportation fuels has remained at its current level, and thus alternative means of production must be utilized (in Case Study 3, we consider the case in which transportation fuel demand has also been eliminated). As in Case Study 1, the demand for petrochemical products is assumed to be unchanged.

In contrast to the earlier scenario, this case proved to be initially infeasible. That is, it was impossible to meet all final product demands with the given array of available processing technologies and supplied hydrocarbons. Further investigation showed that the infeasibility was due mainly to the inability of the network to meet the demand for anthraquinone, a relatively low volume final product in the network model with uses in dye manufacture, paper pulp production, and other applications. The only route provided in the model to produce anthraquinone uses naphthalene and butadiene, and the only source of naphthalene in the model is recovery from refinery processes. Thus, without the refinery processes that were removed, there is no route to anthraquinone, and so an alternative route, not based on refinery derivatives, is needed. Such routes are available;[43] e.g., one route is based on a styrene feedstock. However, to remedy this situation in the model used, the demand for anthraquinone was simply set to zero, as the volume of its demand is several orders of magnitude lower than most other demand levels in the model.

With crude oil refining not available, alternative technologies must be utilized to meet the demand for transportation fuels. For the minimum-cost industry, the model shows this demand to be almost fully (~98.5%) met by synthetic gasoline

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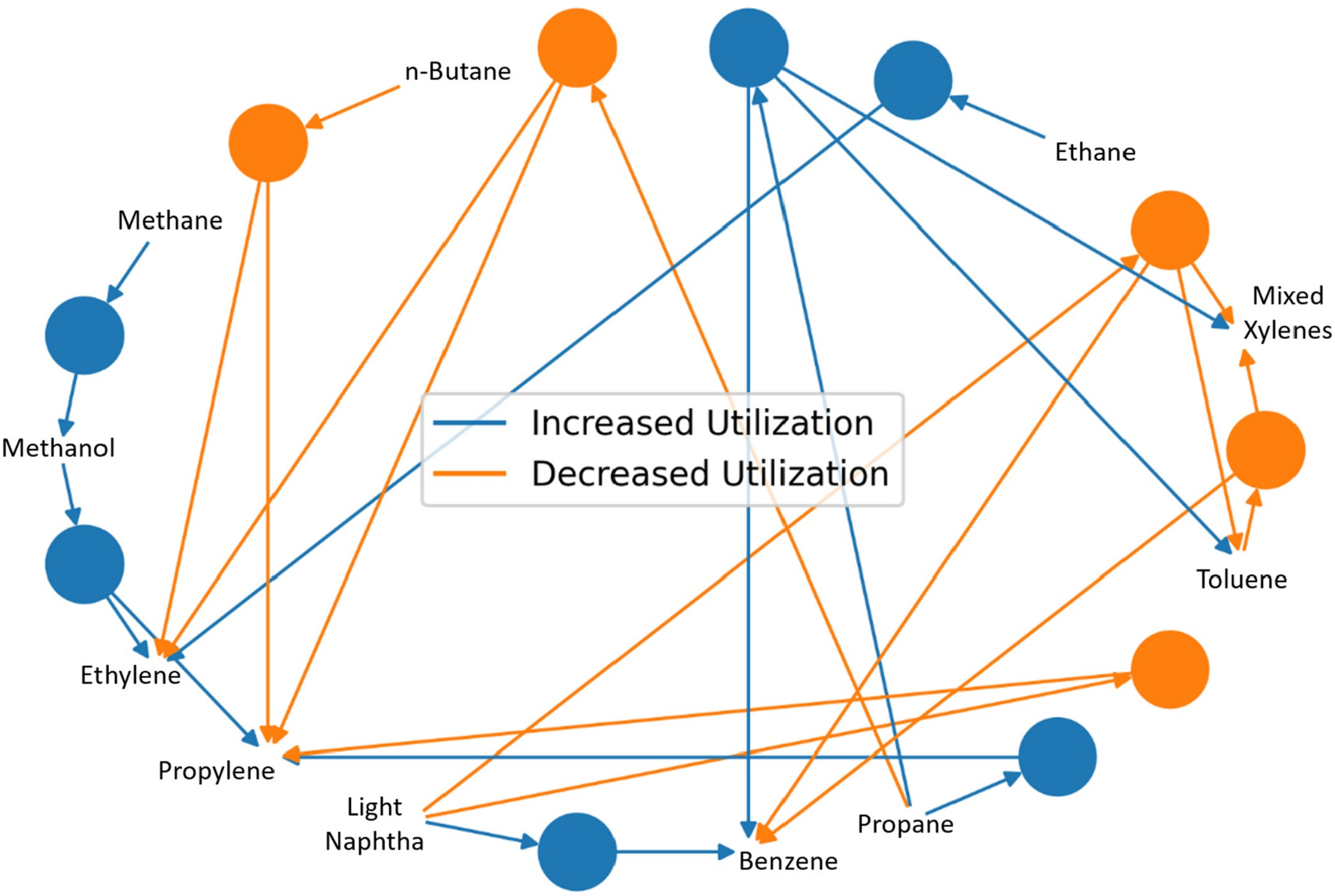

Figure 4. Major changes in process utilization for the no refining and no transportation fuels demand scenario (Case Study 3) when compared to the base case. Circles represent chemical processes with arrows showing primary inputs and outputs. Blue indicates a process with increased utilization, and orange features indicate decreased utilization. [Figure created using NetworkX.[41]]

produced from natural gas via methanol to gasoline technology. Additional much smaller amounts are produced as byproducts in large-volume olefins (ethylene, propylene) production processes such as steam cracking. This shift to a natural-gas-based route as the primary producer of liquid transportation fuels comes at a large overall cost. The total U.S. industry minimum-cost objective function for this case study (with all crude-oil and crude-oil refining processes removed) is approximately $681 billion/yr. In the base case, the same processes available in this case study (all except the removed crude-oil refining processes) have an optimal cost of about $187 billion/yr. Thus, the shift from crude-oil-based processes for liquid transportation fuels to natural-gas-based processes comes at a cost of about $494 billion/yr, assuming that both must supply the current demand.

The major pathway shifts in the overall network relative to the base case are depicted in Figure 3. In this scenario, there is much less light naphtha available, since it is now obtained only from fractionation of NGLs, and the most cost-efficient use for this resource is BTX production. This reduces usage of propane for BTX and allows for increased use of propane as cracker feed for olefins production. Use of heavier alkanes for cracker feed also results in increasing amounts of a gasoline byproduct, thereby lessening the use of the relatively expensive methanol to gasoline process.

3.4. Case Study 3: No Crude Oil Refining and No Transportation Fuels Demand. This case study considers a combination of the two extreme-case scenarios used in Case Studies 1 and 2. As in Case Study 2, there is no availability of crude oil or refinery processes, and, as in Case Study 1, there is no demand for liquid transportation fuels. The demand for petrochemical products is again unchanged, except that the demand for anthraquinone is set to zero, for reasons discussed in connection with Case Study 2. For this combination of scenarios, the key pathway shifts in the minimum-cost industry network relative to the base case are depicted in Figure 4. With no demand now for the gasoline byproduct from heavier alkanes cracking to olefins, there is a shift toward lighter alkane cracker feeds. Production of heavier olefins such as propylene is now supplemented with increased use of propane dehydrogenation to propylene (Catofin process) and methanol to olefins (UOP/Hydro process). BTX production is now from both propane and light naphtha.

4. ALTERNATIVE SYNTHETIC FUELS TECHNOLOGY

In the next two case studies, we assess the potential adoption of two new synthetic fuel processes for use in the no-crude-oil-refining scenario (Case Study 2). Recall that in that limit-case scenario, a demand for liquid transportation fuels remains, but crude oil and crude oil refining processes are assumed to be unavailable. It was found in Case Study 2 that the primary alternative for production of liquid transportation fuels using current technology would be via the route natural gas (methane) → synthesis gas → methanol → gasoline. Future technology may involve conversion of CO_2 to synthesis gas or directly to methanol and thence to gasoline. Various other new

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technologies for liquid fuels production have also been proposed, and here we consider two such possibilities based on use of NGLs and derivatives. These are an ethylene-to-gasoline oligomerization process (Case Study 4) and a coupled dehydrogenation−oligomerization process that transforms ethane to gasoline (Case Study 5). Relevant process design studies have been performed by Ridha et al.,[44] both for the dehydrogenation of NGLs, as well as for the oligomerization of their corresponding olefins. Moreover, there has been significant recent research on catalysts for both the dehydrogenation of ethane (e.g., Ko et al.,[45] Wu et al.,[46] Wegener et al.[47]) and the oligomerization of ethylene (e.g., Agapie,[48] Finiels et al.,[49] Metzger et al.,[50] Joshi et al.[51]), targeting higher selectivities and conversions. For each of these two new processes, we will determine the production level in the minimum-cost industry configuration over a range of net process cost points, and identify the maximum adoption cost (net process cost above which the process would not be adopted by the optimal industry network for Case Study 2). This will be done for realistic current process yields, with sensitivity analysis to determine the effect of higher or lower yields.

4.1. Case Study 4: Ethylene-to-Gasoline Oligomerization Process.

In their process design studies, Ridha et al.[44] assume an almost 100% conversion of ethylene and slightly higher than 50% selectivity toward gasoline. These assumptions are based on the experimental studies of Toch et al.[52,53] Therefore, we insert the ethylene to gasoline oligomerization process into the Case Study 2 model at a nominal 50% yield, and also consider 40% and 60% yields for sensitivity analysis. The adoption rates of this process as a function of the net production cost and process yield are shown in Figure 5. At the nominal 50% yield, the process is not adopted into the optimal industry network configuration for net processing costs of 25 ¢/lb of gasoline or higher. Thus, the maximum adoption cost (net cost at or below which the process is adopted) of the process is 24 ¢/lb of gasoline. The level of gasoline production (~6.27 billion lbs/yr) is a very small fraction (~0.45%) of the current gasoline demand as used in Case Study 2, and because it is such a small perturbation in ethylene, its use does not cause any significant changes to the optimal industry configuration determined in Case Study 2. However, in a future with a much lower gasoline demand, and if cost targets for adoption can be met, this process could capture a significant market share, displacing methanol to gasoline.

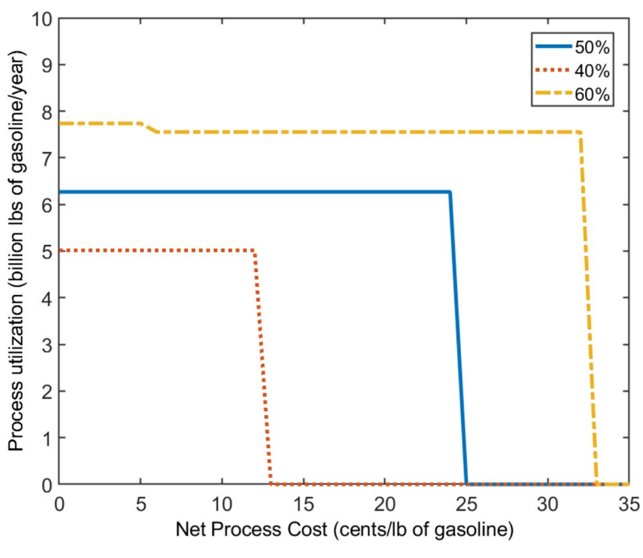

Figure 5. Utilization of an ethylene-to-gasoline oligomerization process (Case Study 4) in the optimal industry network, as a function of net production cost and gasoline yield.

The effect of process yield is as expected, with the maximum adoption cost and production levels decreasing with decreasing yield and increasing with increasing yield. The production levels below the maximum adoption cost show only a small change, and only for the 60% yield case, even as the process cost reaches the zero cost limit. Even at zero cost, the optimal utilization levels vary significantly for different yields. This occurs because, depending on the yield, more or less ethylene will be required to produce the same amount of gasoline. An increase in the amount of ethylene needed for gasoline will require ethylene-producing processes to produce more ethylene, causing the total industry cost to increase. Thus, in the minimum-cost industry, production of gasoline from ethylene is suppressed at lower yields, even at zero process cost.

4.2. Case Study 5: Ethane-to-Gasoline Coupled Process.

For this case study, we must consider the yield parameters of both the dehydrogenation and oligomerization parts of this coupled transformation process. Ridha et al.[44] have assumed a 45% conversion of ethane and 95% selectivity toward ethylene in their process design studies, based on experimentally determined dehydrogenation catalyst parameters.[54] This results in an overall ethylene yield of 40%, which, when combined with the 50% ethylene-to-gasoline yield[44] used above, results in a 20% ethane to gasoline yield for the coupled process. Thus, the coupled process is added to the Case Study 2 model at a nominal gasoline yield of 20%, and yields of 15% and 30% are used for sensitivity analysis. Results showing the adoption rate of the coupled process as net production cost and gasoline yield are varied are shown in Figure 6. At 20% yield, the maximum adoption cost is 48 ¢/lb gasoline, with a production level that, as in the previous Case Study, is only a very small fraction of the gasoline demand level imposed in Case Study 2. The response to changes in gasoline yield are

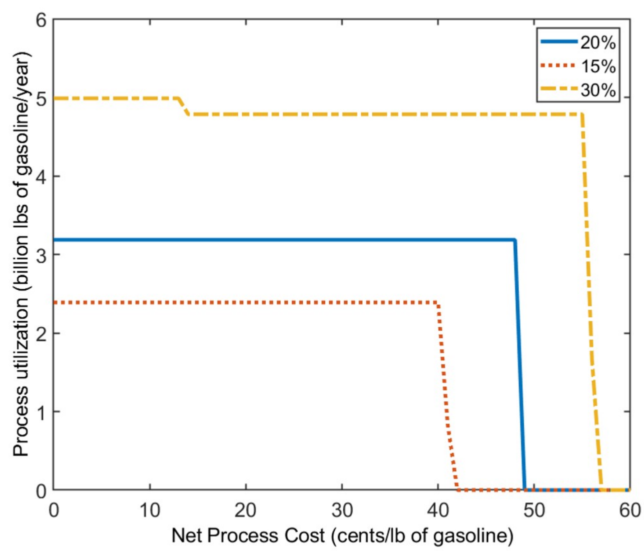

Figure 6. Utilization of an ethane-to-gasoline process (Case Study 5) in the optimal industry network, as a function of net production cost and gasoline yield.

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similar to what was observed in Case Study 4. However, the production levels at zero-cost are now determined by the amount of the ethane supply that can be diverted from steam cracking to ethylene while maintaining a minimum total industry cost. This amount depends on the gasoline yield from ethane, and is about one-third of the ethane supply when the yield is 30%. In the minimum-cost model, this is compensated by using a methanol-to-olefins process and a light-naphtha-to-olefins process. Given such low yields of gasoline from ethane, the relatively high cost at which the process would be adopted is somewhat surprising, and reflects the high cost of the competing methanol-to-gasoline process that would be displaced. In the context of a residual, limited-demand market for liquid transportation fuels, this process could be attractive, especially if yields could be pushed higher by advances in the dehydrogenation and oligomerization catalysts used.

5. GREEN HYDROGEN

In the final case study, we analyze the potential adoption of a renewably powered electrolysis process for the production of green hydrogen as a substitute transportation fuel for use in the no-crude-oil-refining scenario (Case Study 2). With appropriate infrastructure and continuing improvements in fuel cell and electrolysis technology, hydrogen may be an attractive transportation fuel, and there is much interest in this possibility.[55,56] Hydrogen is quite energy-dense (on a per mass unit basis): the energy contained in 6.2 lbs of gasoline is equivalent to that in only 2.2 lbs of hydrogen.[57] Therefore, for this case study, in the transportation fuel demand constraint, we have added a green hydrogen term (mass/time) as an option but weighted by a factor of 6.2/2.2 = 2.82 to convert the hydrogen term to an equivalent amount (mass/time) of gasoline (i.e., a gasoline demand of 2.82 lb/yr can be satisfied by 1 lb/yr of hydrogen).

5.1. Case Study 6: Electrolysis Technology. An electrolysis process for production of hydrogen is already provided in the IHS technology database[28] used to construct the superstructure model used here. The hydrogen produced from this process is designated as green hydrogen, which is treated as a component different from hydrogen produced by other means. However, when the green hydrogen from this process is designated as a transportation fuel and its production added to the demand constraint as described above, this process is not adopted to produce transportation fuel, since, evidently, its production cost is too high. Thus, in this case study, we have considered the extent to which the electrolysis production cost would need to be reduced in order for its green hydrogen product to be adopted as a transportation fuel. Such cost reduction could be achieved by increasing the efficiency of converting electrical energy to hydrogen energy in the electrolysis process from the 60% (based on lower heating value of hydrogen) assumed in the database, or by use of less expensive electricity. Since electrolysis efficiencies approaching 90% are projected for the long-term[55] and the cost of electricity from renewables is already undercutting fossil-fueled power,[1] significant green hydrogen production cost reductions seem likely.

The adoption rates for the electrolysis process and for the production of synthetic gasoline as the net electrolysis process cost is varied are shown in Figure 7 for the scenario described here. This indicates a small level of adoption (~6% of the total transportation fuel demand) when the electrolysis process cost falls below \$2/lb hydrogen. At this cost point, green hydrogen

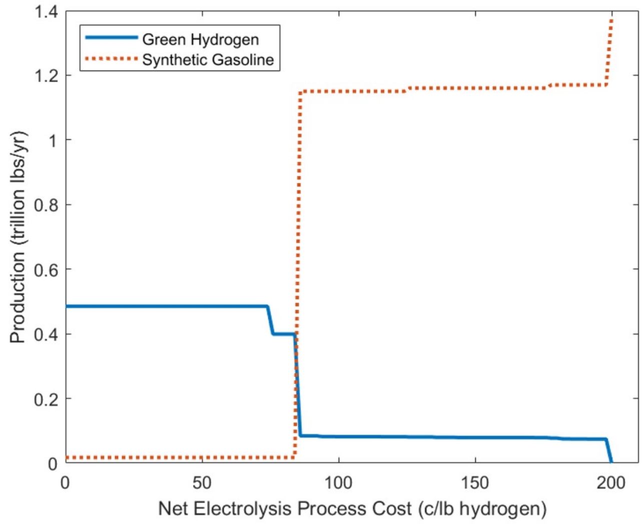

Figure 7. Synthetic gasoline production and utilization of a electrolysis process to produce green hydrogen (Case Study 6) in the optimal network, as a function of green hydrogen net production cost from electrolysis.

from electrolysis replaces synthetic gasoline from the more expensive of two methanol-to-synthetic-gasoline processes used. As the cost drops below \$0.85/lb (\$1.87/kg) hydrogen, there is a more significant shift, with green hydrogen from electrolysis covering ~96% of the total transportation fuel demand. At this cost point, green hydrogen from electrolysis replaces synthetic gasoline from the less expensive of the two methanol-to-synthetic-gasoline processes. To put this cost point into perspective, the U.S. Department of Energy's "Hydrogen Shot" initiative has a goal of reducing the price of clean hydrogen by 80%, to \$1/kg hydrogen in 10 years.[58] Therefore, there may be good prospects for the future adoption of this technology.

6. CONCLUDING REMARKS

In this work, we probed the effects of potentially disruptive scenarios in petrochemicals manufacturing that may arise from the incipient paradigm shift in energy and transportation away from fossil fuels and toward renewables. These are limit-case scenarios in which petroleum refineries are no longer economically viable and thus shut down and/or the demand for fossil-based liquid transportation fuels has entirely disappeared. Case studies involving these scenarios were analyzed using a minimum-total-cost network model of the petrochemicals industry. Results show that the petrochemicals industry can respond by using current technology based on natural gas and natural gas liquids (NGLs), although the pathways to several large-volume products may shift. Residual demands for liquid transportation fuels could also be met by using natural gas, based on methanol-to-gasoline technology, or by using NGLs as implemented in new technology for which adoption cost targets were investigated or by green hydrogen production, especially if set goals for technological advancements are met, leading to a significant decrease in the price of hydrogen. But by switching to a petrochemicals industry based on natural gas and NGLs, a nonrenewable, fossil-based resource is still being used. An alternative is the use of renewable, bio-based resources as raw materials for both chemicals and transportation fuels. This possibility has been

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widely studied,[59−69] often in the context of an integrated "biorefinery". As a practical matter, the structure of the industry and the resources it uses will evolve based on many factors, including economics, sustainability and life cycle analysis, and government policies.

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Notes

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REFERENCES

(1) *International Energy Outlook 2021*; U.S. Energy Information Administration, 2021. Available via the Internet at: https://www.eia.gov/outlooks/ieo/, accessed Jan. 3, 2022.

(2) Wayland, M. *General Motors plans to exclusively offer electric vehicles by 2035*, 2021. Available via the Internet at: https://www.cnbc.com/2021/01/28/general-motors-plans-to-exclusively-offer-electric-vehicles-by-2035.html, accessed Jan. 14, 2022.

(3) *Electrification*. General Motors, 2021; Available via the Internet at: https://www.gm.com/commitments/electrification.html, accessed June 23, 2021.

(4) *Our Path to an All-Electric Future*. General Motors, 2021; Available via the Internet at: https://www.gm.com/electric-vehicles, accessed Dec. 16, 2021.

(5) Woods, B. *GM, Ford are all-in on EVs. Here's how their dealers feel about it*. CNBC, 2021. Available via the Internet at: https://www.cnbc.com/2021/06/13/gm-ford-are-all-in-on-evs-heres-how-dealers-feel-about-it-.html, accessed Jan. 14, 2022.

(6) *Bentley and Electrification: The Journey Starts Here*. Bentley Motors, 2020. Available via the Internet at: https://www.bentleymotors.com/en/world-of-bentley/the-bentley-story/future/bentley-and-electrification-the-journey-starts-here.html, accessed Jan. 14, 2022.

(7) *Future is Electric*. Volvo, 2021. Available via the Internet at: https://group.volvocars.com/company/innovation/electrification, accessed Dec. 16, 2021.

(8) *eGallon*. U.S. Department of Energy, 2021. Available via the Internet at: https://www.energy.gov/maps/egallon, accessed March 25, 2021.

(9) *Join us on the ride toward a green future*. Uber, 2021. Available via the Internet at: https://www.uber.com/us/en/ride/ubergreen/, accessed Dec. 16, 2021.

(10) *U.S. Postal Service Awards Contract to Launch Multi-Billion-Dollar Modernization of Postal Delivery Vehicle Fleet*. U.S. Postal Service, 2021. Available via the Internet at: https://about.usps.com/newsroom/national-releases/2021/0223-multi-billion-dollar-modernization-of-postal-delivery-vehicle-fleet.htm, accessed Dec. 16, 2021.

(11) Hartman, K.; Shields, L. *State Policies Promoting Hybrid and Electric Vehicles*. 2021. Available via the Internet at: https://www.ncsl.org/research/energy/state-electric-vehicle-incentives-state-chart.aspx, accessed Dec. 16, 2021.

(12) *Zero-Emission Vehicle Program*. California Air Resources Board, 2022. Available via the Internet at: https://ww2.arb.ca.gov/our-work/programs/zero-emission-vehicle-program/about, accessed Jan. 14, 2022.

(13) *Advanced Clean Trucks Fact Sheet: Accelerating Zero-Emission Truck Markets*. California Air Resources Board, 2021. Available via the Internet at: https://ww2.arb.ca.gov/resources/fact-sheets/advanced-clean-trucks-fact-sheet, accessed Jan. 14, 2022.

(14) *President Biden Announces Steps to Drive American Leadership Forward on Clean Cars and Trucks*. The White House, 2021. Available via the Internet at: https://www.whitehouse.gov/briefing-room/statements-releases/2021/08/05/fact-sheet-president-biden-announces-steps-to-drive-american-leadership-forward-on-clean-cars-and-trucks/, accessed Jan. 14, 2022.

(15) *New agreements on urban deliveries without CO_2 emission*. Government of the Netherlands, 2021. Available via the Internet at: https://www.government.nl/latest/news/2021/02/11/new-agreements-on-urban-deliveries-without-co2-emission, accessed Jan. 14, 2022.

(16) *Overview−Electric vehicles: tax benefits & purchase incentives in the European Union*. European Automobile Manufacturers Association (ACEA), 2020. Available via the Internet at: https://www.acea.auto/fact/overview-electric-vehicles-tax-benefits-purchase-incentives-in-the-european-union/, accessed January 14, 2022.

(17) Alvarez, S. *First 15 Tesla Semi units to be delivered to PepsiCo by end of January: report*. 2022. Available via the Internet at: https://www.teslarati.com/tesla-semi-first-customer-deliveries-date-pepsico/, accessed January 14, 2022.

(18) *FLXdrive*. Wabtec Corporation, 2021. Available via the Internet at: https://www.wabteccorp.com/locomotive/alternative-fuel-locomotives/flxdrive, accessed January 14, 2022.

(19) *Sustainable Aviation Fuels*. U.S. Department of Energy, 2021. Available via the Internet at: https://www.energy.gov/eere/bioenergy/sustainable-aviation-fuels, accessed January 14, 2022.

https://doi.org/10.1021/acs.iecr.2c00309
Ind. Eng. Chem. Res. 2022, 61, 12169−12179

(20) *United Airlines' First Passenger Flight Using 100% Sustainable Aviation Fuel is Officially Off the Ground!*. U.S. Department of Energy, 2021. Available via the Internet at: https://www.energy.gov/energysaver/articles/united-airlines-first-passenger-flight-using-100-sustainable-aviation-fuel, accessed Jan. 14, 2022.
(21) *Anchors Aweigh: Examining Biofuels for Maritime Shipping*. U.S. Department of Energy, 2021. Available via the Internet at: https://www.energy.gov/eere/bioenergy/articles/anchors-aweigh-examining-biofuels-maritime-shipping, accessed Jan. 14, 2022.
(22) Skouteris, A.; Giannikopoulos, I.; Edgar, T. F.; Baldea, M.; Allen, D. T.; Stadtherr, M. A. Systems Analysis of Natural Gas Liquid Resources for Chemical Manufacturing: Strategic Utilization of Ethane. *Ind. Eng. Chem. Res.* **2021**, *60*, 12377−12389.
(23) Rudd, D. F.; Fathi-Afshar, S.; Treviño, A. A.; Stadtherr, M. A. *Petrochemical Technology Assessment*; Wiley: New York, 1981; pp 1−157.
(24) DeRosa, S. E.; Allen, D. T. Impact of New Manufacturing Technologies on the Petrochemical Industry in the United States: A Methane-to-Aromatics Case Study. *Ind. Eng. Chem. Res.* **2016**, *55*, 5366−5372.
(25) Stadtherr, M. A.; Rudd, D. F. Systems study of the petrochemical industry. *Chem. Eng. Sci.* **1976**, *31*, 1019−1028.
(26) Fathi-Afshar, S.; Maisel, D. S.; Rudd, D. F.; Treviño, A. A.; Yuan, W. W. Advances in petrochemical technology assessment. *Chem. Eng. Sci.* **1981**, *36*, 1487−1511.
(27) DeRosa, S. E.; Allen, D. T. Impact of natural gas and natural gas liquids supplies on the United States chemical manufacturing industry: Production cost effects and identification of bottleneck intermediates. *ACS Sustainable Chem. Eng.* **2015**, *3*, 451−459.
(28) IHS, *IHS Process Economics Program yearbook*. IHS, 2012. Available via the Internet at: https://ihsmarkit.com/products/chemical-technology-pep-index.html/, accessed April 5, 2022.
(29) Giannikopoulos, I.; Skouteris, A.; Allen, D. T.; Baldea, M.; Stadtherr, M. A. Multi-objective Optimization of Production Cost and Carbon Loss in the U.S. Petrochemicals Industry. In *Proceedings of the 14th International Symposium on Process Systems Engineering (PSE2021)*, Kyoto, Japan, 2022; Elsevier B.V.: Amsterdam, in press.
(30) Skouteris, A.; Giannikopoulos, I.; Allen, D. T.; Baldea, M.; Stadtherr, M. A. MINLP Framework for Systems Analysis of the Chemical Manufacturing Industry Using Network Models. In *Proceedings of the 32nd European Symposium on Computer Aided Process Engineering (ESCAPE32)*, Toulouse, France, 2022; Elsevier B.V.: Amsterdam, in press.
(31) Giannikopoulos, I.; Skouteris, A.; Edgar, T. F.; Baldea, M.; Allen, D. T.; Stadtherr, M. A. Geospatial Network Approach for Assessing Economic Potential of Ethylene-to-Fuel Technology in the Marcellus Shale Region. *Ind. Eng. Chem. Res.* **2021**, *60*, 14801−14814.
(32) DeRosa, S. E.; Kimura, Y.; Stadtherr, M. A.; McGaughey, G.; McDonald-Buller, E.; Allen, D. T. Network Modeling of the U.S. Petrochemical Industry under Raw Material and Hurricane Harvey Disruptions. *Ind. Eng. Chem. Res.* **2019**, *58*, 12801−12815.
(33) *Refinery & Blender Net Production*; U.S. Energy Information Administration, 2021. Available via the Internet at: https://www.eia.gov/dnav/pet/pet_pnp_refp_dc_nus_mbbl_a.htm, accessed April 25, 2021.
(34) *Highway Statistics Series: State Motor-Vehicle Registrations−2019*. U.S. Department of Transportation, 2020. Available via the Internet at: https://www.fhwa.dot.gov/policyinformation/statistics/2019/mv1.cfm, accessed March 16, 2022.
(35) *United States Population*. Worldometer, 2022. Available via the Internet at: https://www.worldometers.info/world-population/us-population/, accessed April 5, 2022.
(36) *How Many Cars Are There in The World in 2022?*; Worldometer, 2022. Available via the Internet at: https://hedgescompany.com/blog/2021/06/how-many-cars-are-there-in-the-world/, accessed April 5, 2022.
(37) *Annual Vehicle Miles Traveled in the United States*. U.S. Department of Energy, Alternative Fuels Data Center, 2021. Available via the Internet at: https://afdc.energy.gov/data/10315, accessed March 16, 2022.
(38) *Energy Use by Transportation Mode and Fuel Type*. U.S. Department of Energy, Alternative Fuels Data Center, 2021. Available via the Internet at: https://afdc.energy.gov/data/10661, accessed March 16, 2022.
(39) *All-Electric Vehicles*. U.S. Department of Energy, 2022. Available via the Internet at: https://www.fueleconomy.gov/feg/evtech.shtml, accessed March 16, 2022.
(40) *Average Range and Efficiency of U.S. Electric Vehicles*. U.S. Department of Energy, Alternative Fuels Data Center, 2021. Available via the Internet at: https://afdc.energy.gov/data/10963, accessed March 16, 2022.
(41) Hagberg, A. A.; Schult, D. A.; Swart, P. J. Exploring Network Structure, Dynamics, and Function using NetworkX. In *Proceedings of the 7th Python in Science Conference*, Pasadena, CA, USA, 2008; pp 11−15, DOI: 10.25080/issn.2575-9752.
(42) *Natural Gas Plant Field Production*. U.S. Energy Information Administration, 2021. Available via the Internet at: https://www.eia.gov/dnav/pet/PET_PNP_GP_DC_NUS_MBBL_M.htm, accessed Dec. 13, 2022.
(43) Vogel, A. Anthraquinone. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley−VCH: Weinheim, Germany, 2000, DOI: 10.1002/14356007.a02_347.
(44) Ridha, T.; Li, Y.; Gençer, E.; Siirola, J. J.; Miller, J. T.; Ribeiro, F. H.; Agrawal, R. Valorization of shale gas condensate to liquid hydrocarbons through catalytic dehydrogenation and oligomerization. *Processes* **2018**, *6*, 139.
(45) Ko, J.; Muhlenkamp, J. A.; Bonita, Y.; LiBretto, N. J.; Miller, J. T.; Hicks, J. C.; Schneider, W. F. Experimental and Computational Investigation of the Role of P in Moderating Ethane Dehydrogenation Performance over Ni-Based Catalysts. *Ind. Eng. Chem. Res.* **2020**, *59*, 12666−12676.
(46) Wu, Z.; Wegener, E. C.; Tseng, H. T.; Gallagher, J. R.; Harris, J. W.; Diaz, R. E.; Ren, Y.; Ribeiro, F. H.; Miller, J. T. Pd-In intermetallic alloy nanoparticles: Highly selective ethane dehydrogenation catalysts. *Catal. Sci. Technol.* **2016**, *6*, 6965−6976.
(47) Wegener, E. C.; Wu, Z.; Tseng, H. T.; Gallagher, J. R.; Ren, Y.; Diaz, R. E.; Ribeiro, F. H.; Miller, J. T. Structure and reactivity of Pt−In intermetallic alloy nanoparticles: Highly selective catalysts for ethane dehydrogenation. *Catal. Today* **2018**, *299*, 146−153.
(48) Agapie, T. Selective ethylene oligomerization: Recent advances in chromium catalysis and mechanistic investigations. *Coord. Chem. Rev.* **2011**, *255*, 861−880.
(49) Finiels, A.; Fajula, F.; Hulea, V. Nickel-based solid catalysts for ethylene oligomerization - a review. *Catal. Sci. Technol.* **2014**, *4*, 2412−2426.
(50) Metzger, E. D.; Comito, R. J.; Wu, Z.; Zhang, G.; Dubey, R. C.; Xu, W.; Miller, J. T.; Dincǎ, M. Highly Selective Heterogeneous Ethylene Dimerization with a Scalable and Chemically Robust MOF Catalyst. *ACS Sustainable Chem. Eng.* **2019**, *7*, 6654−6661.
(51) Joshi, R.; Saxena, A.; Gounder, R. Mechanistic insights into alkene chain growth reactions catalyzed by nickel active sites on ordered microporous and mesoporous supports. *Catal. Sci. Technol.* **2020**, *10*, 7101−7123.
(52) Toch, K.; Thybaut, J.; Marin, G. Ethene oligomerization on Ni-SiO_2-Al_2O_3: Experimental investigation and Single-Event Micro-Kinetic modeling. *Appl. Catal. A: Gen.* **2015**, *489*, 292−304.
(53) Toch, K.; Thybaut, J.; Arribas, M.; Martínez, A.; Marin, G. Steering linear 1-alkene, propene or gasoline yields in ethene oligomerization via the interplay between nickel and acid sites. *Chem. Eng. Sci.* **2017**, *173*, 49−59.
(54) Cybulskis, V. J.; Bukowski, B. C.; Tseng, H.-T.; Gallagher, J. R.; Wu, Z.; Wegener, E.; Kropf, A. J.; Ravel, B.; Ribeiro, F. H.; Greeley, J.; Miller, J. T. Zinc Promotion of Platinum for Catalytic Light Alkane Dehydrogenation: Insights into Geometric and Electronic Effects. *ACS Catal.* **2017**, *7*, 4173−4181.

(55) *Future of Hydrogen*. International Energy Agency, 2019. Available via the Internet at: https://www.iea.org/reports/the-future-of-hydrogen, accessed March 22, 2022.
(56) Li, Z.; Gao, D.; Chang, L.; Liu, P.; Pistikopoulos, E. N. Hydrogen infrastructure design and optimization: A case study of China. *Int. J. Hydrogen Energy* **2008**, *33*, 5275−5286.
(57) *Alternative Fuels Data Center: Hydrogen Basics*. U.S. Department of Energy, 2016. Available via the Internet at: https://afdc.energy.gov/fuels/hydrogen_basics.html, accessed March 22, 2022.
(58) *Hydrogen Shot*. U.S. Department of Energy, Hydrogen and Fuel Cell Technology Office, 2021; https://www.energy.gov/eere/fuelcells/hydrogen-shot, accessed March 22, 2022.
(59) Fernando, S.; Adhikari, S.; Chandrapal, C.; Murali, N. Biorefineries: Current Status, Challenges, and Future Direction. *Energy Fuels* **2006**, *20*, 1727−1737.
(60) Dodds, D. R.; Gross, R. A. Chemicals from Biomass. *Science* **2007**, *318*, 1250−1251.
(61) Marshall, A.-L.; Alaimo, P. Useful Products from Complex Starting Materials: Common Chemicals from Biomass Feedstocks. *Chem.−Eur. J.* **2010**, *16*, 4970−4980.
(62) Kim, J.; Sen, S. M.; Maravelias, C. T. An optimization-based assessment framework for biomass-to-fuel conversion strategies. *Energy Environ. Sci.* **2013**, *6*, 1093−1104.
(63) Wang, B.; Gebreslassie, B. H.; You, F. Sustainable design and synthesis of hydrocarbon biorefinery via gasification pathway: Integrated life cycle assessment and technoeconomic analysis with multiobjective superstructure optimization. *Comput. Chem. Eng.* **2013**, *52*, 55−76.
(64) Martín, M.; Grossmann, I. E. On the Systematic Synthesis of Sustainable Biorefineries. *Ind. Eng. Chem. Res.* **2013**, *52*, 3044−3064.
(65) Santibañez-Aguilar, J. E.; González-Campos, J. B.; Ponce-Ortega, J. M.; Serna-González, M.; El-Halwagi, M. M. Optimal planning and site selection for distributed multiproduct biorefineries involving economic, environmental and social objectives. *J. Cleaner Prod.* **2014**, *65*, 270−294.
(66) Stichnothe, H.; Meier, D.; de Bari, I. Biorefineries: Industry Status and Economics. In *Developing the Global Bioeconomy*; Lamers, P., Searcy, E., Hess, J. R., Stichnothe, H., Eds.; Elsevier: Amsterdam, 2016; pp 41−67.
(67) Panteli, A.; Giarola, S.; Shah, N. Supply chain mixed integer linear program model integrating a biorefining technology superstructure. *Ind. Eng. Chem. Res.* **2018**, *57*, 9849−9865.
(68) Hingsamer, M.; Jungmeier, G. Biorefineries. In *The Role of Bioenergy in the Bioeconomy*; Lago, C., Caldés, N., Lechón, Y., Eds.; Elsevier: Amsterdam, 2019; pp 179−222.
(69) Thongchul, N.; Charoensuppanimit, P.; Anantpinijwatna, A.; Gani, R.; Assabumrungrat, S. 1—Overview of biorefinery. In *A−Z of Biorefinery*; Thongchul, N., Kokossis, A., Assabumrungrat, S., Eds.; Elsevier: Amsterdam, 2022; pp 3−32.

https://doi.org/10.1021/acs.iecr.2c00309
Ind. Eng. Chem. Res. 2022, 61, 12169−12179