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Systems Analysis of Natural Gas Liquid Resources for Chemical Manufacturing: Strategic Utilization of Ethane

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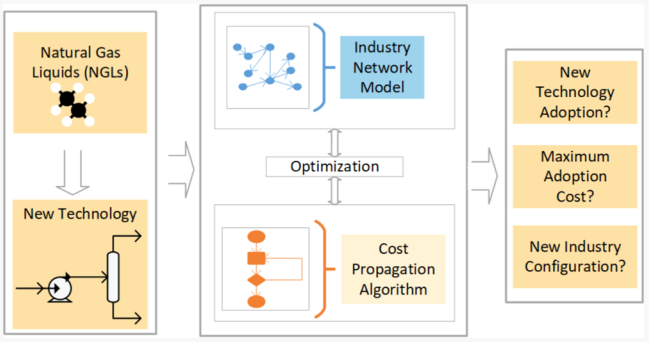
ABSTRACT: The increasing production of shale gas and, consequently, natural gas liquids (NGLs) provides opportunities to expand the U.S. chemical industry, leading to questions about how to best use these resources. We consider targets for the strategic use of ethane, the most abundant of the NGLs, by evaluating the impact of a potential, new catalytic dehydrogenation technology for converting ethane to ethylene and then evaluating potential, new catalytic oligomerization processes for converting ethylene to 1-butylene and to 1-octene. To conduct these evaluations, we introduce a new, nonlinear, industry-wide, optimization-based network model of the U.S. petrochemical and refining industries. Unlike previous linear models of this type, the nonlinear model accounts for changes in intermediate prices and, thus, process costs as new technology is added to the industry network. A method for propagating cost and price changes, permitting the solution of the nonlinear optimization problem as a sequence of linear problems, is developed and utilized. Using network models for this study, we account for and identify the direct and secondary consequences of introducing new technology on the rest of the industry. For each new technology evaluated, we determine the production level of the technology in the optimal industry network. By doing this over a wide range of net process cost points, a maximum adoption cost (the net process cost beyond which the technology would not be adopted) can be identified, and its sensitivity to the assumed product yield determined for each new technology can be studied. The maximum adoption costs can be viewed as targets for future catalyst research, reaction engineering, and process development work. Scenarios in which the ethane supply is constrained to current values and in which it is unconstrained are considered.



1. INTRODUCTION

The United States has experienced a significant increase in the production of crude oil, natural gas, and natural gas liquids (NGLs). Natural gas is one of the fastest growing energy sources in the world,[1] with its U.S. 2019 dry (consumer-grade) production at 33.97 trillion cubic feet (Tcf), the highest annual value to date.[2] The rapid increase in natural gas production since 2005 is the result of advancements in technologies, such as hydraulic fracturing and horizontal drilling, that facilitate the exploitation of unconventional gas and oil sources and which today are widely applied in the fossil fuel extraction industry.[3,4] The most important unconventional sources are oil- and gas-rich shale formations that were previously economically unfavorable to exploit.

Unlike gas from conventional sources, gas produced from shale formations is typically rich in NGLs (primarily C2−C5), most of which must be removed to produce consumer-grade ("dry") natural gas. Given the rapid increase in natural gas production from unconventional sources, there is now an abundance of NGLs available for use,[3] with the U.S. production in 2020 at about 5 million barrels per day, compared to less than 2 million barrels per day in 2010.[5] While some NGLs may be used directly as fuels (propane and butane), their primary use (especially for ethane) is as a feedstock for petrochemical manufacturing (through cracking to ethylene) and the ultimate production of a wide variety of consumer goods (plastics, synthetic fibers, rubbers, and other products). The boom in the production of shale gas and, consequently, NGLs is thus providing a unique opportunity to expand the U.S. chemical industry[6] and is motivating the development of new technologies for using NGLs. This has

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prompted a number of studies on how to best exploit natural gas and NGL resources for chemical and/or fuel production.[6−10]

In this paper, we focus specifically on the evaluation of targets for the strategic use of ethane, through its catalytic dehydrogenation to ethylene.[11] Ethane is the most abundant of the NGLs but, unlike propane or butane, has no direct use as fuel (a small amount is allowed in consumer-grade natural gas). Its production rate (Figure 1) mirrors that of NGLs overall.

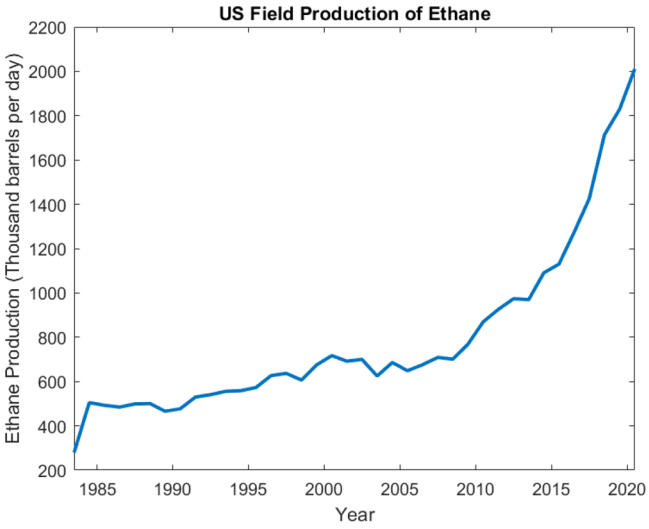

Figure 1. Annual U.S. production of ethane. Data from the U.S. Energy Information Administration.[15]

The abundance of ethane has driven the development of multiple new cracking facilities for the production of ethylene. An alternative approach, as suggested by Ridha et al.,[8] is that ethane and/or other NGLs may be converted through catalytic dehydrogenation to their more reactive olefin counterparts, followed by oligomerization of the olefins to hydrocarbons suitable for use as liquid transportation fuels or in chemical applications.[12] This may be advantageous compared to traditional steam cracking processes, due to the latter having high capital and energy demands, a high environmental impact, and a tendency to produce many byproducts.[8] Moreover, the catalytic dehydrogenation process can potentially be operated on a much smaller and modular scale, perhaps allowing for the placement of plants near natural gas-processing plants or gas-gathering stations. In order to evaluate this type of technology for producing ethylene and its oligomers from ethane, it is necessary to consider the implications across the entire petrochemical industry, since ethylene and its oligomers are widely used as feedstocks and/or intermediates for the production of other materials. The existence of different technologies for the production of the same intermediates leads to many competing chemical pathways to end products and, consequently, to several possible configurations of the future industry as a whole. Production routes to end products may change depending on the production costs of intermediate chemicals. To simulate this system, we will use a new industry network superstructure model evolved from the model previously used by DeRosa and Allen.[13,14] A key feature in the new model that differentiates it from previous models of this type is that intermediate prices and thus downstream chemical process costs are explicitly considered as variables (rather than assuming that they are constant). From a mathematical point of view, this renders the resulting problem nonlinear.

The main contributions of this work are as follows:

- We formulate and demonstrate a new nonlinear network superstructure model for the petrochemical industry with variable intermediate and production costs.
- We apply the model to evaluate the adoption by the industry of a new, potential catalytic dehydrogenation process for conversion of ethane to ethylene. The optimal production level for this process, over a wide range of net production costs, is determined, leading to identification of a maximum adoption cost (net production cost above which the process will not be adopted into the optimal industry configuration). This sets a target for future catalyst and process development work.
- Similarly, we apply the model to evaluate the potential adoption of new oligomerization technology with 1-butylene and 1-octene as target products. Again, the optimal production levels, over a wide range of net processing costs, are determined, thereby establishing maximum adoption costs and process development targets.
- We examine the direct and secondary effects of the adoption of these processes, by determining how the new processes alter the optimal industry configuration.
- We perform sensitivity analyses to quantify the impact of the yield of the new processes on their adoption rate and maximum adoption cost.
- We compare production levels and market share for the new processes using both the current ethane supply levels and in a scenario involving an unconstrained supply of ethane.

In the next section, some background on the use of network models of the petrochemical industry is provided. This is followed in Section 3 with details about the model used here and its formulation. Then, in Section 4, relevant case studies and results are presented and discussed.

2. BACKGROUND

A common approach for determining the competitiveness of a new process relative to existing processes that generate the same product or for comparing alternative new processes with one another is to employ a techno-economic analysis, that is, a model is used to simulate, design, and optimize a potential new process, and direct comparisons are then performed using selected economic criteria and cost correlations. This approach has been followed for various applications, including the development of processes using NGLs as raw materials (e.g., Yang and You[6,7] and Ridha et al.[8]). Despite being effective in comparing different processes on a consistent basis, this approach does not account for follow-on effects that may be caused by inserting a new process into the existing industrial ecosystem. These effects can often be substantial and could significantly alter the conclusions of simple techno-economic comparisons when taken into consideration. A representative example is given in the work of DeRosa and Allen,[14] who studied the adoption of a methane to aromatics process. Given that processes in the refining and petrochemical industry are interconnected, such an adoption will have a ripple effect on the optimal choice of other processes and their utilization. As

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shown in Figure 2, the adoption of a new methane-to-aromatics process leads to adjustments in the whole network

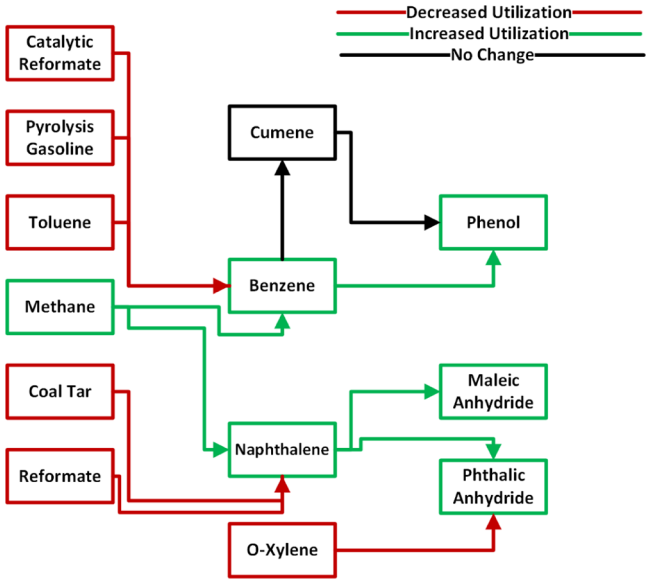

Figure 2. Impact of the adoption of a new methane to aromatics process on naphthalene and benzene reaction pathways. Red pathways experience a decrease in utilization, and green pathways experience an increase in utilization, whereas black pathways are not affected. Figure adapted from DeRosa and Allen.[14]

configuration, something that could not have been predicted without the use of the network model. Therefore, it is essential to capture such follow-on effects when studying the introduction and adoption of new technology.

The petrochemical industry itself is a highly complex, interconnected system of refining and chemical manufacturing processes. A relatively small number of primary raw materials enter the network and undergo a sequence of transformations in order to produce a large array of final products.[14,16] A simplified representation of this network is shown in Figure 3a. Note that many intermediate and final products can be produced via several different processes, which will require different amounts and types of energy and raw materials and result in dissimilar amounts and types of byproducts. This leads to several competing pathways between primary raw materials and final products, reflecting the complexity of the network. An example of this is presented in Figure 3b, where four different chemical pathways for the production of ethylene are depicted. In practice, the number of competing pathways for the production of an intermediate or final product can be much larger. Moreover, these pathways may be more intertwined than in this simple example. This results in the aforementioned network complexity. Understanding and accounting for these interconnections can lead to more realistic conclusions about the eventual adoptability of a potential new process, answering questions related to its successful adoption in the long term and the related secondary effects on the future industry as a whole. Hence, network models of the U.S. chemical manufacturing and refining industries are employed in this work.

As explained in more detail below, network models represent the industry as a directed graph. A production process appears as one type of node in the graph, characterized by its material and energy balances and perhaps by other features such as capacity or geographic location. Flows of materials from one process to another appear as edges in the graph, characterized by a flow rate and perhaps by a transportation cost. Once formulated, perturbations can be imposed on the graph, which enables the performance of various types of response studies. Examples include studying the response of the industry to the insertion of a new process, to a change in the price or availability of a primary raw material, or to the demand for a final product. Responses are generally evaluated by the optimization of some specified objective function.

The network model approach for representing the hydrocarbon processing industry was pioneered by Stadtherr and Rudd[17−20] and colleagues, who focused initially on minimization of resource usage as a driving force and subsequently on minimization of industry cost,[21] with studies on industrial development,[17,18] impact of new technologies,[19,22] future trends and planning,[20,23] and the effect of chemical toxicity regulations.[24] Many variations, extensions, and applications of

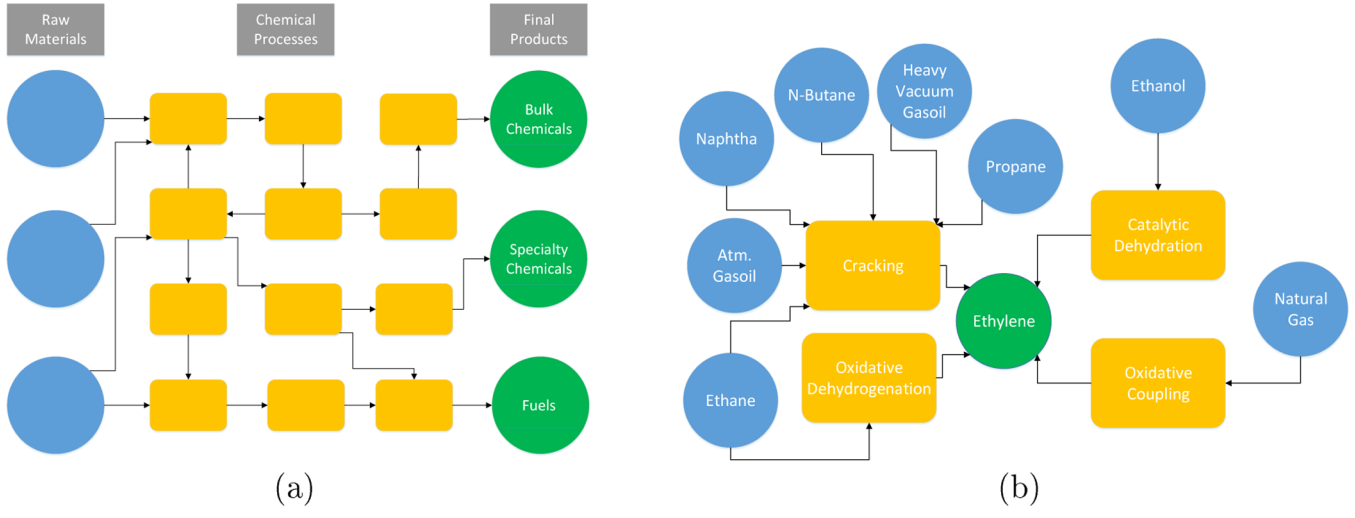

Figure 3. (a) Simplified representation of the petrochemical industry network. (b) Example of competing chemical pathways in chemical manufacturing: four pathways for the production of ethylene.

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this initial work have subsequently appeared, a selection of which are noted here. Fathi-Afshar and Yang[25] developed a multi-objective model that combined cost and toxicity objectives, with the goal of compromising between the two objectives. Chang and Allen[26] formulated a network model focusing on the impact of minimizing chlorine use in the petrochemical industry. Grossman and Santibanez[27] developed a mixed-integer linear programming (MILP) framework with multiple time periods, aiming to optimally design chemical complexes, that is, sections of the chemical industry. Jiménez et al.[28] formulated a similar MILP model for the Mexican petrochemical industry, while Al-Qahtani et al.[29] expanded this framework to account for uncertainty in several model parameters, such as process yield and forecasted demand. Sahinidis et al.[30,31] developed MILP network models for the long-term planning of industries with specific investment decisions, both for dedicated (fixed product distribution) and flexible (varying product distribution) plants. More recently, Elia et al.[10] used network models as part of a multi-scale systems analysis of the energy industry.

For this study, the starting point is an industry network model that was developed by DeRosa and Allen.[13,14,16] This model, in contrast to previously published work, provided a mechanism for propagating changes in primary raw material prices beyond their initial use into the prices of downstream intermediates and final products. In this work, we extend this model to also propagate price changes due to adding new processes to the network. This means that material prices and thus intermediate raw material costs incurred by a process node are not necessarily constant and may depend on production levels at other process nodes. A review of the entire process database used by DeRosa and Allen[13,14,16] was carried out, and some technologies that were considered obsolete were removed. Refinements to uncertainties and/or approximations in the database were made in order to meet the needs of the specific case studies reported here, as noted below:

- One focal point for this work will be assessing oligomerization processes for producing 1-butylene and 1-octene. In the DeRosa and Allen formulation of the model, mixed C4 streams were used as feedstocks and/or products at the production unit nodes. To resolve the resulting uncertainties, these mixed streams were replaced with feedstocks and products with well-defined compositions.
- The level of detail of the model was further increased by classifying and accounting for C4 components (*n*-butane, isobutane, *n*-butylene, isobutylene, and butadiene) by grade (polymer and chemical grades).
- The market for linear α-olefins (LAO) is growing rapidly,[32] and LAO-producing processes were added to the model.

In the next section, details about the network model formulation used here are presented, along with a procedure for propagating prices changes within the model.

3. MODEL DETAILS

3.1. Model Formulation. In the network model, the industry is represented by a directed graph, with each chemical process or technology represented by a node and each edge representing a material flow. The current model contains 887 processes, 892 materials, and 7 utility types (which are used for evaluating process costs). The model represents an industry superstructure in which all commercially viable manufacturing routes to the desired products are represented. Process stoichiometries and costs have been obtained from the IHS 2012 Process Economic Program Yearbook.[33] For the purpose of this study, it is assumed that this information is sufficiently up-to-date. This assumption is based on the fact that major technology changes often take substantial time to develop, and thus, the data have likely not changed to a significant extent since 2012.

The base model is formulated as an optimization problem, with material balance constraints for each material included in the network and the objective of minimizing the total industry production cost C_{tot}

$$\min_{X_j,F_i,Q_i} C_{tot} = \sum_j C_j X_j \tag{1}$$

Here, C_j is the net production cost for process j (per unit mass of the main product) and X_j is the production level of process j (annual mass flow rate of the main product). The net production cost C_j includes[33] the fixed capital investment, expressed as straight-line depreciation over a 10-year period, variable costs related to raw material usage, byproduct credits and cost of utilities, and other fixed operating costs, such as maintenance, labor, overhead, and taxes, based on an average scale plant (economy of scale is not considered). Each process is a separate entity, and the flow of the material from one process to another represents a raw material cost to the receiving entity, at the unit prices obtained from the database[33] (these are average market prices, so in the case of intracorporate flows, it is assumed that the intracorporate transfer prices emulate the external market).

The material balance for a material i in the network, with all terms expressed as annual mass flow rates, is

$$F_i + \sum_j a_{i,j} X_j - Q_i = 0, \qquad \forall\, i \tag{2}$$

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 i is produced; and unity if i is the main product), and Q_i is the exogenous flow rate of material i out of the network as a final end product. This optimization problem includes two additional sets of constraints, one limiting the flow rates of primary feedstocks into the network to be less than their exogenous supply rates S_i and the other bounding the flow rates of final end products out of the network based on their exogenous demand rates D_i

$$F_i \le S_i, \qquad \forall\, i \tag{3}$$

$$Q_i \ge D_i, \qquad \forall\, i \tag{4}$$

Finally, all decision variables, X_j, F_i, and Q_i, are constrained to be non-negative. If the net production costs C_j are constants, then, this optimization problem is a linear program (LP). However, as discussed in the next section, the C_j may actually depend on certain decision variables and thus not be constant. This means that the optimization problem of interest is nonlinear. For materials that are produced only as main products, eq 4 will be an active constraint, since excess production will increase the value of the objective function, which represents the total cost. However, for materials

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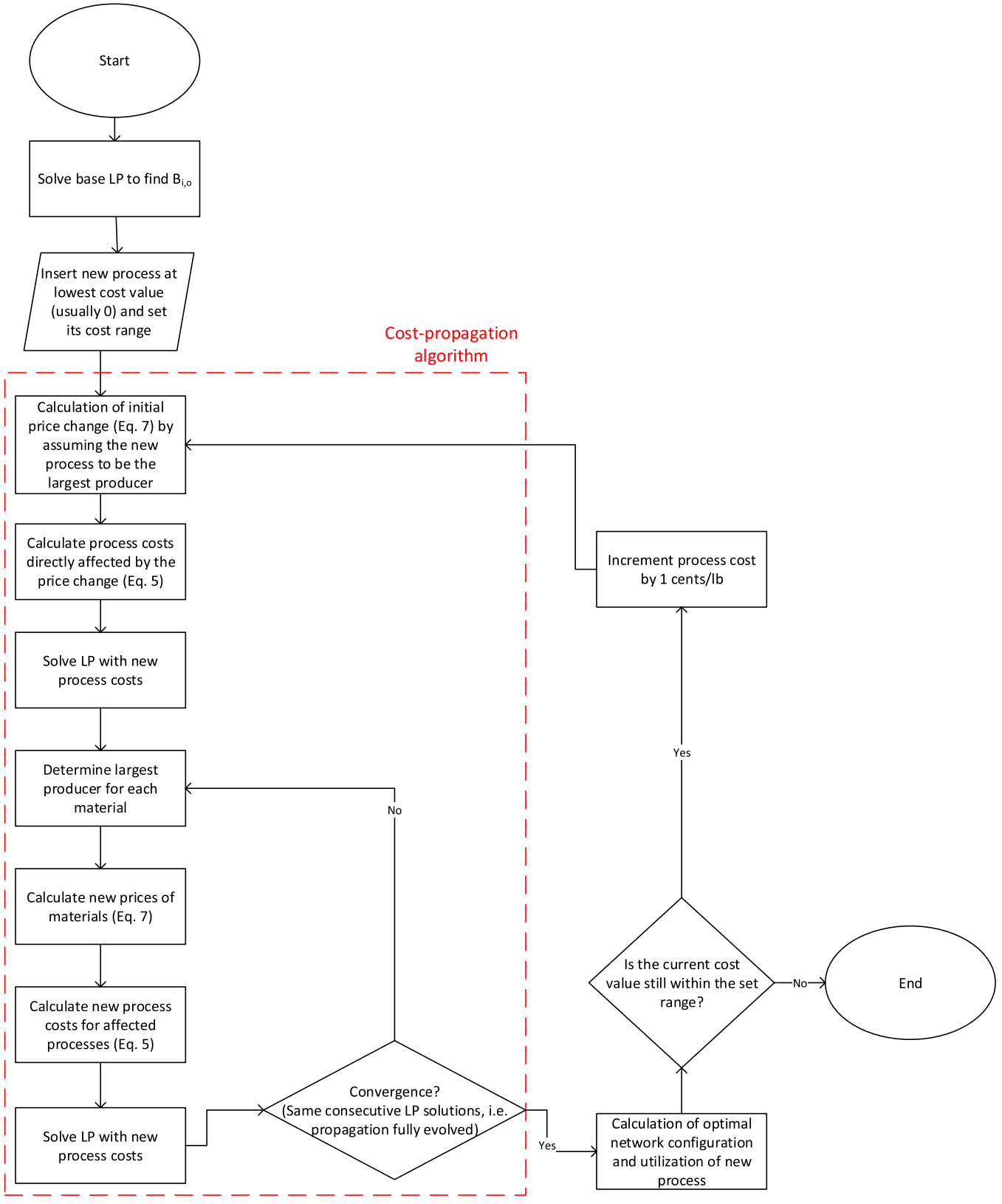

Figure 4. Flowchart showing the overall workflow for the investigation of the adoption of new processes, including cost propagation algorithm steps.

produced as byproducts, excess production is possible. In our experience, when this occurs, the byproducts are of value (e.g., fuel gas, hydrogen, and pyrolysis gasoline) but do not have a readily specified demand value. As needed, excess production could be addressed by modifying the objective function to include a penalty term, such as an inventory or disposal charge.

3.2. Cost Propagation Algorithm. Previous work in this context (e.g., Rudd et al.,[21] Fathi-Afshar and Rudd,[22] and

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Floudas et al.[34]) has assumed the net process costs C_j to be constant and independent of the production levels X_j. However, this is not entirely accurate and leads to the model being unresponsive toward upstream price changes of exogenous raw materials or changes caused in the prices of intermediates by the insertion and adoption of a new process in the network. The first issue was successfully addressed by DeRosa and Allen,[13,16] who developed a cost propagation algorithm that is capable of propagating changes in the upstream prices of exogenous raw materials throughout the whole network. In this work, the second isssue is addressed. This issue is substantially more challenging to deal with, as now, the process costs C_j are also dependent on the production levels $X_{k\neq j}$, giving rise to nonlinearity and discontinuity in the objective function (the relationship between the C_j and X_k may not be continuous). This issue may arise, for example, if a new, more efficient process k for producing an intermediate species i is inserted in the model; if this process is adopted (X_k is nonzero), then, the price for species i may be reduced, thus reducing the costs for all processes using species i as a raw material.

A new cost propagation algorithm for dealing with this issue will be described here. The key idea is to decompose the nonlinear and potentially discontinuous problem into a series of LPs, with all the price adjustments and cost calculations and their propagation taking place "externally", that is, as a separate iterative process outside the optimization program. An important decision in implementing the algorithm is how to perform the price adjustments. In the optimal industry configuration, most materials are produced using a single process. For such a material, it is clear that changes in the production cost for the single active process should be used in determining the price adjustment for the material. However, some materials are produced by multiple active processes, typically with one process type accounting for most of the production. For these materials, we adopt a dominant-producer price leadership model.[35] In this economic model, there is a dominant producer of a material, and this producer is the price leader (i.e., has sufficient market influence to effectively be able to set the material's price). This situation tends to arise in markets where there are only a small number of producers and there is little product differentiation (i.e., the product is a commodity), characteristics that reasonably describe the situation of interest here. Thus, we use the cost change in the largest producer of a material in determining its price adjustment. Note that in the context of this model, a "producer" is a process technology, not a company. Other options for effecting price adjustments may be investigated in future work. It should be emphasized that in propagating costs, we are not attempting to model economic market dynamics, that is, we are neither trying to account for the impacts of supply, demand, corporate competition, and other market factors in determining prices nor are we attempting to model price evolution over time. Our goal is simply to ensure that cost changes in processes appearing upstream in the industry are accounted for in downstream processes, something that has not been considered in previous studies.

We now outline the cost propagation procedure. First, a baseline LP is solved using baseline net process costs $C_{j,0}$ (determined from the IHS database[33]). The solution to this LP represents the situation prior to external perturbations such as adding a new process and is used to set initial material prices $B_{i,0}$ for the cost propagation iteration (we will investigate the addition of a profit margin in future work). This is done by first determining the largest producer of each material i in the baseline LP solution and then using the net cost of producing i in that process as the initial price $B_{i,0}$. During the cost propagation process, updated costs due to material price changes are then calculated relative to these baseline values

$$\Delta C_j = C_j - C_{j,0} = \sum_{i\cap j} -a_{i,j}\Delta B_i \tag{5}$$

$$\Delta B_i = B_i - B_{i,0} \tag{6}$$

Here, the notation $i \cap j$ indicates summation over those species i occurring in process j. Note that if material i is consumed in process j, then, $a_{i,j} < 0$, and a price increase in i ($\Delta B_i > 0$) will result in a net cost increase for process j ($\Delta C_j > 0$). Conversely, if material i is a byproduct in process j, then, $a_{i,j} > 0$, and a price increase in i will result in a net cost decrease (byproduct credit) for process j. At the beginning of each iteration of the cost propagation procedure, ΔB_i, the price change for material i is assumed equal to the cost change in the largest producer of material i. If this process is denoted by j_i^*, then

$$\Delta B_i = \Delta C_{j_i^*} \tag{7}$$

The overall iterative procedure is described next, followed by a simple example calculation.

After an external perturbation to the network (new process inserted or cost of the new process changed), the cost propagation algorithm is started by assuming that the new process will be the largest producer j_i^* of its main product i (this may change in subsequent iterations) and that its cost has an initial value $C_{j_i^*,0}$ that is equal to the initial price of its main product $B_{i,0}$. A price change for i is then determined from eq 7, followed by an update of all the affected process costs using eq 5. The LP model is now solved using the updated cost values. Based on the results (optimal network configuration) of this LP, the largest producer for all materials is determined. Then, updated material prices can be determined from eq 7 and process costs updated using eq 5. The LP is solved again, and if its solution is the same as that of the previous LP, the cost propagation algorithm is considered to be converged. Otherwise, the next iteration starts by again determining the largest producer of all materials. A flowchart for this procedure is shown as part of Figure 4.

For example, assume that in the baseline LP, the largest producer j_i^* of material i has a net cost of $C_{j_i^*,0} = 40$ ¢/lb, so that the baseline price of i is set to $B_{i,0} = C_{j_i^*,0} = 40$ ¢/lb. Now, a new process j_{new} is introduced for the production of material i, with $C_{j_{\text{new}}} = 15$ ¢/lb. To start the cost propagation procedure, it is assumed that the new process will be the largest producer of i, so that $j_i^* = j_{\text{new}}$, and now, $C_{j_i^*} = C_{j_{\text{new}}} = 15$ ¢/lb. Now, a price update for i is done using eq 7, $\Delta B_i = \Delta C_{j_i^*} = C_{j_{\text{new}}} - C_{j_i^*,0} = 15 - 40 = -25$ ¢/lb. This price change for i is now propagated to all existing processes in which i is a raw material or byproduct. For example, say that process P5 uses i as a raw material with a stoichiometric coefficient $a_{i,\text{P5}} = -0.2$ and has a baseline net cost $C_{\text{P5},0} = 50$ ¢/lb. A net cost update for this process is then done using eq 5, $C_{\text{P5}} = 50 - (-0.2 \times -25) = 45$ ¢/lb (in subsequent iterations, there may be price changes in more than one material). After all affected net process costs have been updated in this way, the

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LP is solved again with the updated net cost values, the largest producers for each material are again determined, and a new cost propagation iteration begins using the updated net cost values.

For example, in the new LP solution, say that process P5 is the largest producer of its main product, material M10 (as P5 also was in the baseline LP); thus, j^*_{M10} = P5. A price update for material M10 is now done using eq 7, $\Delta B_{M10} = \Delta C_{j_i^*} = C_{j^*_{M10}} - C_{j^*_{M10},0} = C_{P5} - C_{P5,0} = 45 - 50 = -5$ ¢/lb. Other material price updates may also need to be done, if for any other materials k, there were changes in $C_{j_k^*}$ (these changes may occur due to a process cost update in the previous iteration, as in the case of M10 or due to a switch in the largest producer of a material). Next, all material price changes are propagated to affected net process costs using eq 5. Therefore, if there is a process P20 that uses M10 as a raw material with a stoichiometric coefficient $a_{M10,P20} = -0.6$, P20 has a baseline cost $C_{P20,0}$ = 80 ¢/lb, and M10 is the only material in P20 with a price change, its current net cost will be updated to $C_{P20} = 80 - (-0.6 \times -5) = 77$ ¢/lb. After all net process costs are updated to reflect the material price updates, the LP is solved again with the updated net cost values, and cost propagation iterations are continued until no further cost changes occur.

In the overall workflow for investigating the adoption of new processes (Figure 4), the baseline LP is first solved, establishing the baseline material prices as described above. Then, a new process of interest is added to the model, and a cost range for the process is set. The model is then solved for the case of the lowest net cost value (usually zero), employing the cost propagation algorithm described above. In the optimal solution for this net cost point, the level of adoption of the new process is noted, along with other changes in the optimal industry configuration. This procedure is then repeated, incrementing the net cost of the new process by 1 ¢/lb of the main product for each new net cost point case, until the maximum net cost level is reached (typically chosen to be slightly higher than the net cost point at which the utilization becomes zero). As a result, the utilization of the new process as a function of its net cost is obtained, among other information related to the optimal industry configuration. The net cost point above which the process utilization is zero is the maximum adoption cost for the new process.

The model was implemented and solved in the General Algebraic Modeling System (GAMS),[36] using the CPLEX solver to solve the LP problems and determine the optimal industry configuration (i.e., the optimal material flows and process utilizations). The computation time required for the solution of the model varies, from 10 s to 2 min for each net cost point, depending on the number of iterations of the cost propagation algorithm.

4. CASE STUDIES

The focus of this work is to assess the economic viability of chemical processing technologies that can transform ethane, the most prevalent NGL component, to more valuable products, by evaluating their potential adoption by the current chemical manufacturing industry. This will be done by conducting case studies using the industry model described above. The first process that will be examined is the catalytic dehydrogenation of ethane to ethylene. Relevant process design studies have been performed by Ridha et al.,[8] and there has been significant recent research on catalysts for this process (e.g., Ko et al.,[11] Wu et al.,[37] and Wegener et al.[38]). This would provide an alternative to the widely used ethane to ethylene cracking process, potentially reducing energy and capital demands and enabling strategic deployment on a smaller and modular scale.

It is also important to then assess potential processes that will utilize ethylene for the production of chemicals. Of particular interest are oligomerization products. Two such cases are 1-butylene and 1-octene. 1-Butylene is a bulk intermediate chemical used as a raw material in various other industry processes,[33] including as a co-monomer in producing linear low-density polyethylene (LLDPE); 1-octene has a smaller niche market, mostly as an alternative co-monomer in LLDPE production. New processes for ethylene oligomerization have been the focus of substantial interest in recent years, mainly on the development of new catalysts that achieve higher selectivities and ethylene conversion.[12,39−41]

For each new process studied, we will determine the production level for the process in the optimal industry network. This will be done over a wide range of net process cost points and lead to identification of the maximum adoption cost (the net process cost above which the process would not be adopted into the optimal industry configuration). This sets targets for future catalyst and process development work. Each new process inserted in the model is initially assumed to have a 100% yield to the main product. A sensitivity analysis is also carried out to determine how results change as yields are decreased.

4.1. Case Study 1: Ethane to Ethylene Catalytic Dehydrogenation. An ethane to ethylene catalytic dehydrogenation process is inserted into the base case model, carrying out the reaction

$$CH_3CH_3 \rightarrow CH_2{=}CH_2 + H_2$$

Assuming initially an overall process yield to ethylene of 100%, the adoption rates of this process as a function of the net production cost are shown in Figure 5. When the net process cost is 20 ¢/lb of ethylene or higher, the process is not adopted into the optimal industry network configuration. The maximum adoption cost of the process is 19 ¢/lb of ethylene, at which it captures a 73% share of ethylene production in the

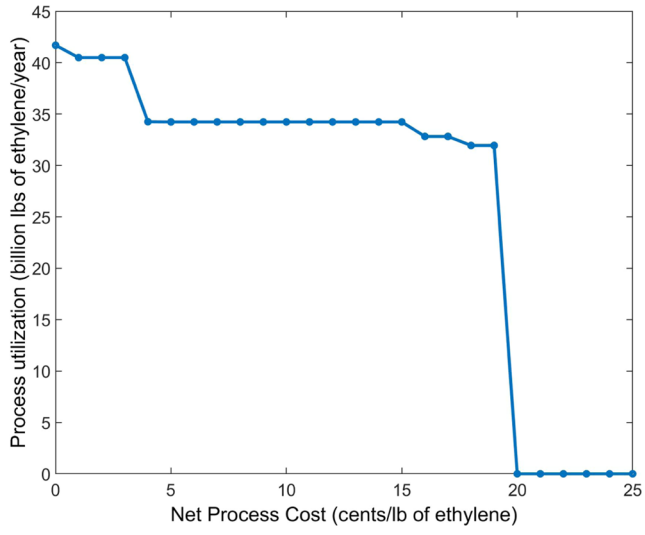

Figure 5. Process adoption plot for an ethane to ethylene catalytic dehydrogenation process at 100% ethylene yield.

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optimal network. As the net cost decreases, the production level increases to 32.8 billion lbs of ethylene/year for net process costs of 16 and 17 ¢/lb of ethylene, representing 73.7% of ethylene production. For net process costs between 15 and 5 ¢/lb, the production level is 34.2 billion lbs of ethylene/year and a 75.4% share of production. Ultimately, in the limit of zero net process cost, an 81.4% share of production is reached, limited by a constraint on the ethane supply (based on 2019 EIA data[15]). The rest of the ethylene at the zero net cost point comes mostly from processes in which ethylene is produced as a byproduct.

The step changes in process utilization observed in Figure 5 are due to changes in the industry configuration. An important advantage of the network optimization approach is that not only does it identify the level of adoption of a new process but also it determines the consequences of that adoption on the entire industry configuration. Thus, secondary "ripple" effects in the network can be identified. Some of these effects will be described here. When the new process is first adopted, at a net process cost of 19 ¢/lb of ethylene, it takes over a significant share of ethylene production from ethane steam cracking, with its share decreasing from 81.8% (at 20 ¢/lb of ethylene or higher) to just 18.5%. With further net cost reductions and as the predicted utilization increases, the new process keeps replacing ethane steam cracking to a larger and larger extent, resulting in steam cracking accounting for only 2.8% of the total ethylene production at the zero net cost point limit, and vinyl acetate production shifts to a process that uses ethylene, due to its now lower net cost. At a net process cost of 17 ¢/lb, butylene production is shifted partially to a process based on ethylene. As the cost of the new process further decreases and ethylene becomes even less expensive, part of vinyl chloride production shifts to a process that uses ethylene from a process that uses ethane. In general, as the cost of the new process decreases and cheaper ethylene becomes available, shifts to downstream processes that take advantage of the lower cost ethylene occur.

The results mentioned above are for the case of a 100% yield of ethylene from the new dehydrogenation process, which is an ideal case. Thus, the sensitivity of these results to the ethylene yield was investigated by repeating the study mentioned above for different yield values. Results are shown in Figure 6. As the achieved yield decreases, the maximum adoption cost also decreases, indicating that a lower net process cost must be achieved for the process to be utilized. Also, production levels from the new process decrease with ethylene yield. This is due in part simply to the lower ethylene yield of the process but also in part because the lower production levels of less-expensive ethylene are insufficient to allow for as many downstream shifts to ethylene-based technologies as in the higher yield cases. Both these effects contribute to the limiting behaviors at zero net process cost, which do not converge to the same value, primarily because the limited ethane supply is depleted at a faster rate with lower yield to ethylene. In terms of sensitivity, it is observed in Figure 7 that for reductions of ethylene yield down to about 80%, the drop in the maximum adoption cost is fairly small, but further reduction of yield results in more severe drops in the maximum adoption cost. The significant impact of yield is not unexpected. However, it should be noted that in the less-than-100% yield cases, no attempt was made to quantify byproduct or fuel credits for unconverted ethane or other reaction products. When the industry network is optimized at a particular cost point for the inserted new process, that cost represents the net process cost after byproduct and fuel credits (as is true for all other process cost coefficients in the network), so for the less-than-100% yield cases, the gross process cost will be higher by some undetermined amount. Thus, if the maximum adoption cost was determined on a gross process cost basis, the impact of product yield would be less pronounced.

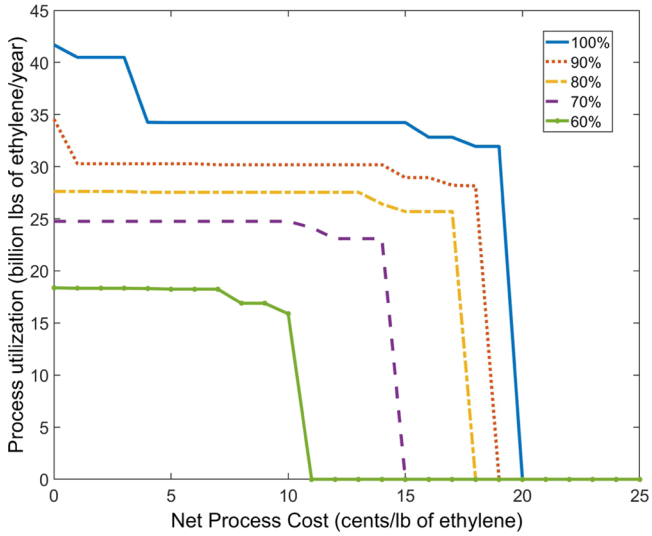

Figure 6. Process adoption plot for an ethane to ethylene catalytic dehydrogenation process, showing the effect of ethylene percentage yield.

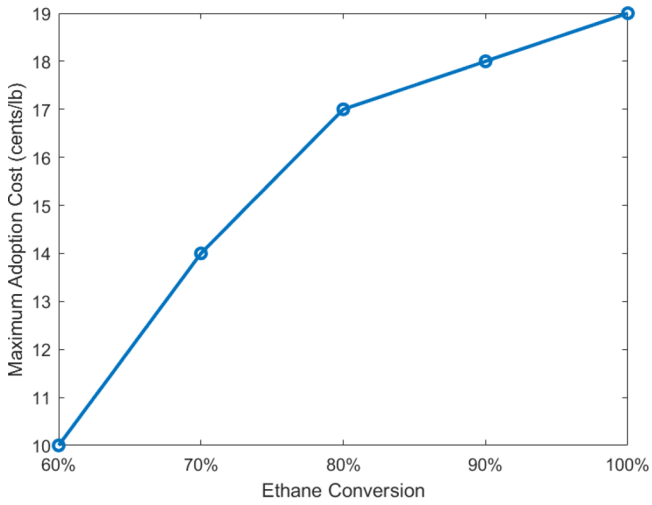

Figure 7. Maximum adoption cost as a function of ethylene yield for the new ethane to ethylene catalytic dehydrogenation process.

4.2. Case Study 2: Ethylene to 1-Butylene Oligomerization. An ethylene to 1-butylene oligomerization process is inserted into the base case model, carrying out the reaction

$$2CH_2{=}CH_2 \rightarrow CH_2{=}CHCH_2CH_3(\text{polymer grade})$$

Assuming 100% 1-butylene yield, the magnitude of utilization of the new oligomerization process is shown in Figure 8. At a net process cost of 72 ¢/lb of 1-butylene or higher, the new oligomerization process is not part of the optimal configuration of the network. For net costs of 71 (maximum adoption cost) and 70 ¢/lb of 1-butylene, the process does become part of the optimal industry network, producing almost 0.7 billion lbs/year 1-butylene. As the net

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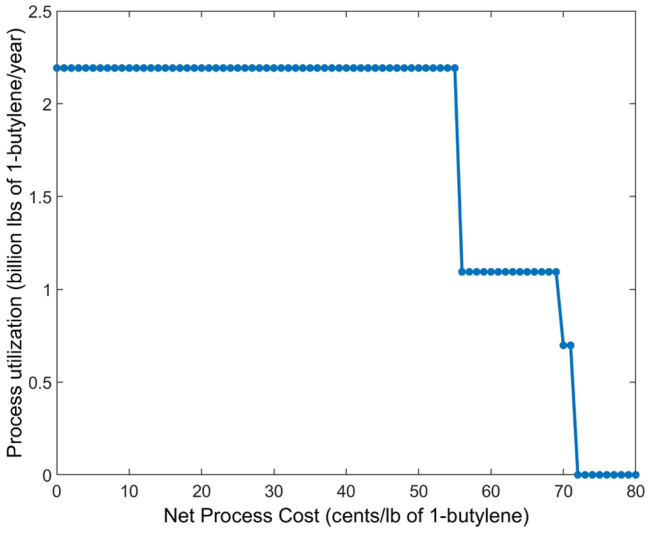

Figure 8. Ethylene to 1-butylene oligomerization process adoption plot.

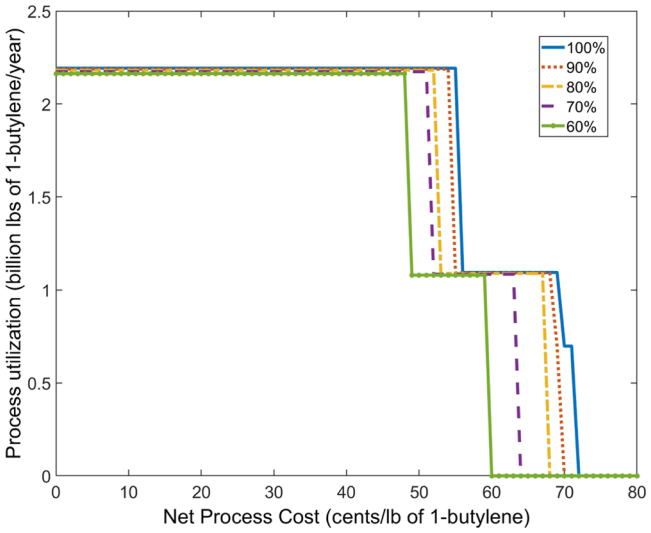

Figure 9. Ethylene to 1-butylene oligomerization process adoption plot for different 1-butylene percentage yield values.

process cost drops to 69 ¢/lb, its utilization increases to about 1.10 billion lbs/year 1-butylene. The maximum process utilization occurs for net process costs less than or equal to 55 ¢/lb at 2.19 billion lbs/year 1-butylene. At all net cost points where it is adopted, the new process accounts for 100% 1-butylene production in the optimal network, replacing older ethylene oligomerization processes with net process costs in the range of 70−85 ¢/lb of 1-butylene.[33] Thus, if a net process cost of 71 ¢/lb of 1-butylene or less could be achieved for the new oligomerization process, older processes may be rendered obsolete. As in the previous case study, the step changes in utilization observed in Figure 8 are due to changes in the industry configuration, and use of the network model allows us to identify these secondary effects of adopting the new oligomerization process. For example, when the net process cost is reduced to 55 ¢/lb, linear low-density polyethylene (LLDPE) processes using 1-hexene and 1-octene as co-monomers are replaced by a process using 1-butylene as a co-monomer, thus increasing the 1-butylene production from the new process, as shown in Figure 8, and reducing the production of 1-hexene and 1-octene from other oligomerization processes in the network.

For lower 1-butylene yields, the process adoption plots are shown in Figure 9. For the case of 90% 1-butylene yield, process adoption occurs when the net process cost is 69 ¢/lb of 1-butylene or less. For still lower 1-butylene yields, process adoption requires even lower net process costs. The maximum adoption costs for each case are shown in Figure 10. The form of the process plot for each case is similar but with shifts toward a lower net process cost requirement. The utilization levels do not vary significantly; for example, the maximum production level for each case varies only from 2.19 (for the 100% yield case) to 2.16 billion lbs/yr 1-butylene (for the 60% yield case), a 1.32% difference. This behavior is different from that seen in the first case study, in which the yield of ethylene from ethane had a significant impact on the process utilization rates. The key difference between the two situations is that in the first case study, there was a limited supply of raw material (ethane), and at lower product yields, this supply was more quickly depleted. In the current case study, there is sufficient raw material (ethylene) to keep the process operational even at

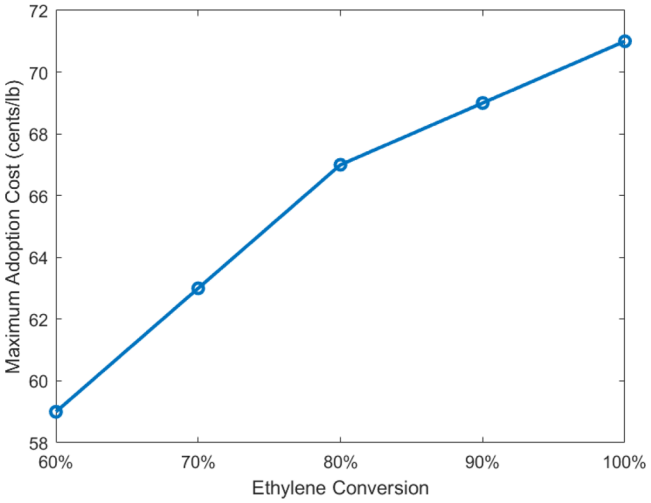

Figure 10. Maximum adoption cost as a function of ethylene conversion for the ethylene to 1-butylene oligomerization process.

lower product yields. However, as the yield of 1-butylene decreases, ethylene consumption will increase, requiring more ethylene to be produced. Increasing ethylene production results in increasing amounts of C4 byproducts, including butadiene. The final consequence is that less 1-butylene is needed for the production of butadiene, and thus, the utilization of the oligomerization process is reduced somewhat as the 1-butylene yield decreases.

4.3. Case Study 3: Ethylene to 1-Octene Oligomerization. An ethylene to 1-octene oligomerization process is inserted into the base case model, carrying out the reaction

$$4CH_2{=}CH_2 \rightarrow CH_2{=}CH(CH_2)_5CH_3(\text{polymer grade})$$

Assuming 100% 1-octene yield, the adoption curve for this process is presented in Figure 11, which indicates that the process is not adopted into the optimal industry for net process costs of 64 ¢/lb of 1-octene or higher (i.e., the maximum adoption cost is 63 ¢/lb of 1-octene). Once adopted, the new oligomerization process accounts for 100% 1-octene production in the optimal network. Current oligomerization processes for 1-octene in the model have a net cost range of 75−85 ¢/lb

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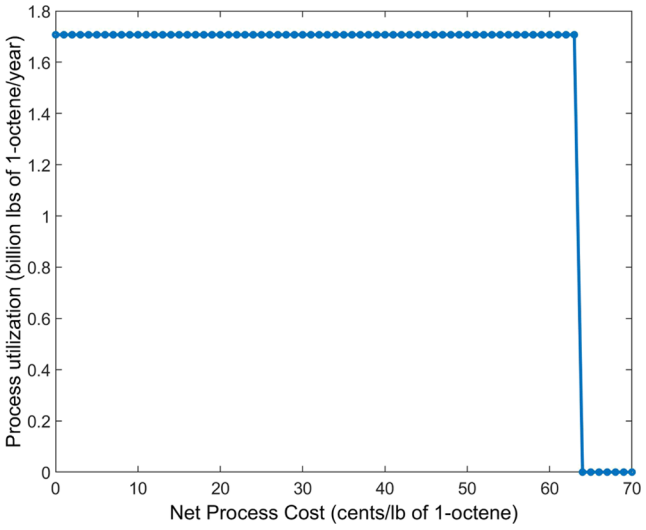

Figure 11. Ethylene to 1-octene oligomerization process adoption plot.

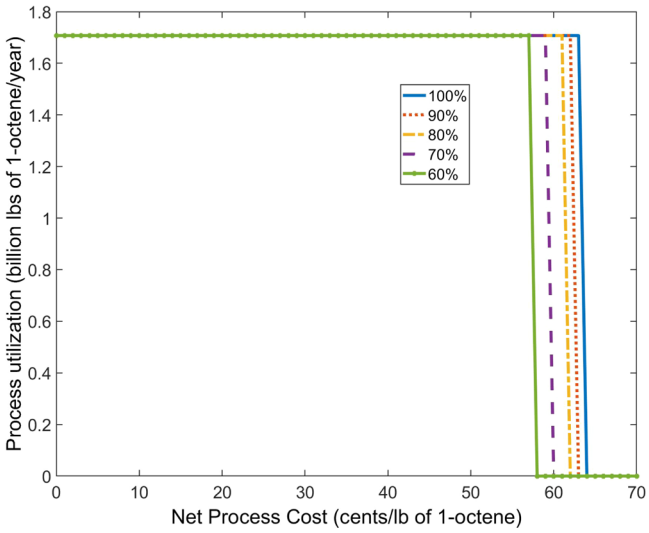

Figure 12. Ethylene to 1-octene oligomerization process adoption plot for different ethylene conversions.

of 1-octene,[33] meaning that the new process would have to achieve a significant net cost reduction relative to the current ones, in order to be adopted by the optimal industry. The process adoption plot in Figure 11 is different from that seen in the previous two case studies in that there is only a single level of utilization once adopted. This occurs because 1-octene's sole role in the network model is as an intermediate used as a co-monomer in processes for LLDPE production.

This case study provides a good example for the need to treat the process net cost coefficients C_j as dependent on the production levels X_j. In the base-case optimal industry configuration, there is no production of 1-octene because all LLDPE is produced from processes using 1-butylene or 1-hexene as a co-monomer. Processes using 1-octene for LLDPE are not chosen because they have high net process costs due to the high cost of 1-octene, which is reflected in the process net cost coefficient. When a new process for 1-octene is inserted in the model with a low net process cost, one would expect that it would become an attractive co-monomer for LLDPE. However, this will not happen if the net process costs are regarded as constant, since the lower net production cost of 1-octene will not be reflected in the constant net cost of 1-octene-based processes for LLDPE. It is necessary for the net costs of the LLDPE processes using 1-octene to depend on the production level of the lower cost 1-octene. Use of the cost propagation method discussed above deals with this nonlinearity and accomplishes the adjustment of the LLDPE net process costs when using 1-octene. Without accounting for this, the new oligomerization process would not be adopted even at very low net cost points, which is clearly unrealistic.

As in the previous case studies, the sensitivity of the adoption of the new oligomerization process to the achieved product yield also has to be examined. The process adoption plots for conversions 100, 90, 80, 70, and 60% are presented in Figure 12, and the effect on the maximum process adoption cost is shown in Figure 13. Here, it appears that the effect of product yield on process adoption is much less pronounced than in the first two case studies. In this case, neither of the factors that drove greater sensitivity to product yield in the first two studies is present. The raw material is not scarce (as in case study 1), and there are no network interactions between

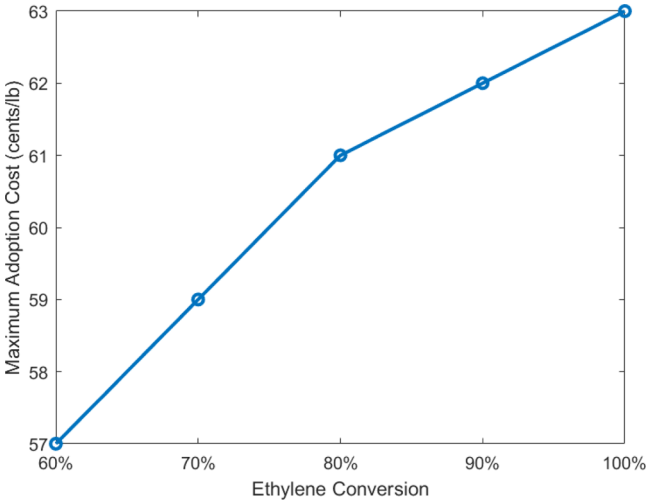

Figure 13. Maximum adoption cost as a function of ethylene conversion for the ethylene to 1-octene dehydrogenation process.

ethylene byproducts and uses of 1-octene (as in case study 2 with 1-butylene). The reduction in the maximum adoption cost with product yield here appears to be due solely to the cost of the additional ethylene that must be used as product yield is decreased.

4.4. Case Study 4: Unconstrained NGL Supply. In the previous case studies, the primary raw material supplies, including the NGL supply, were constrained to their 2019 values.[15] However, as discussed in Section 1, it is likely that the NGL supply will continue to expand. Therefore, it is useful to also consider the situation in which there is an unconstrained supply of ethane and other NGLs. We do this here by removing the supply constraints on ethane and other NGLs and then considering again the insertion into the industry network of the new processes considered in the previous case studies.

The adoption plots for the ethane to ethylene catalytic dehydrogenation process for the base case (NGL supply constrained as in case study 1 with 100% product yield) and for the unconstrained NGL supply case are presented in Figure 14. The utilization level of the new process is significantly

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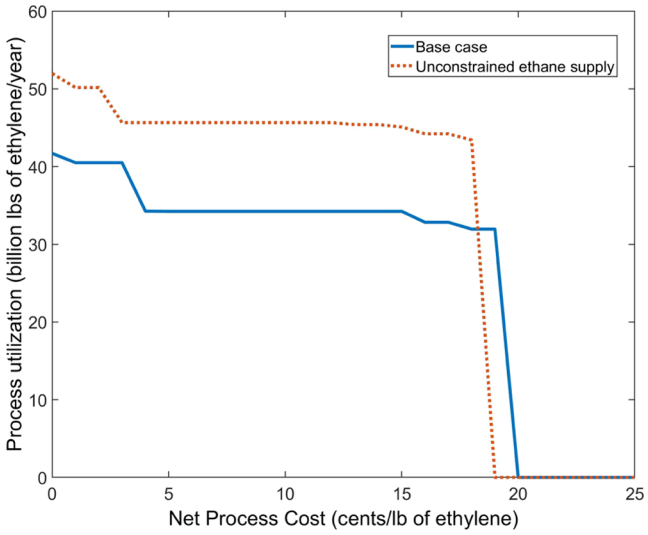

Figure 14. Ethane to ethylene dehydrogenation process adoption plot for the base case and unconstrained ethane supply.

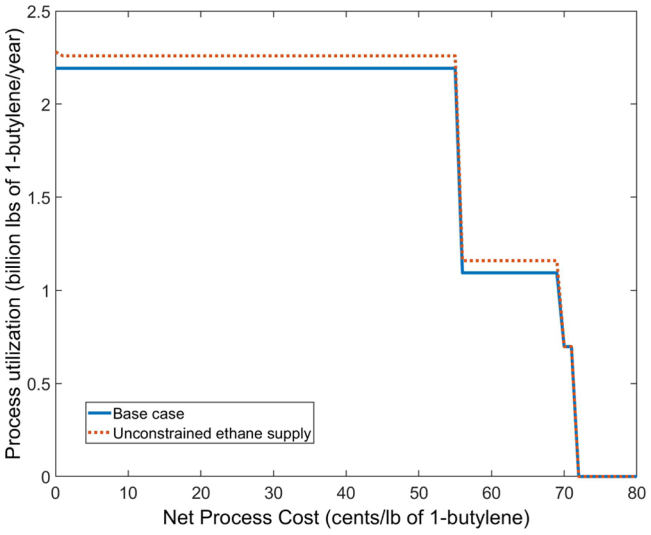

Figure 15. Ethylene to 1-butylene oligomerization process adoption plot for the base case and unconstrained ethane supply.

higher for the unconstrained NGL case once the net process cost is reduced to the maximum adoption cost or below. More specifically, in the limit of zero cost, the utilization level rises from 41.7 to 51.9 billion lbs of ethylene per year, which represents 100% of the on-purpose ethylene production in the network. This increase is not surprising, as we have previously noted in case study 1 that adoption of the process was constrained by the ethane supply. A more surprising and counterintuitive feature of the process adoption curves is that by relaxing the ethane supply constraint, the maximum adoption cost is reduced by 1 ¢/lb of ethylene, making it slightly more difficult for the new process to enter the industry ecosystem. This occurs because the supply constraints on other NGLs (propane and *n*-butane) have also been relaxed, and at the 19 ¢/lb net process cost point, this enables the use of additional routes in the network, leading to an optimal network without the use of the new process. With the NGL supply constraints in place, however, as in the base case, the new process is adopted into the optimal network at this net cost point.

The adoption plots for the new ethylene to 1-butylene oligomerization process for the base case (NGL supply constrained as in case study 2 with 100% product yield) and for the unconstrained NGL supply case are presented in Figure 15. Unlike the dehydrogenation process result, the adoption plots for the two cases are very similar, with only a small difference in utilization levels. This is because the raw material here (ethylene) is not directly constrained in the base case, and so removing the constraint on NGL supply has no direct impact. However, there is a small indirect impact, seen in the slight increase in the process utilization at the lower net cost points (≤69 ¢/lb of 1-butylene). This occurs because relaxing the supply constraint on ethane results in more ethane cracking to produce ethylene and less cracking of heavier alkanes. This results in less byproduct butadiene (from cracking of heavier alkanes), the production of which is then replaced with a 1-butylene to butadiene process, thus requiring more 1-butylene and increasing utilization of the new oligomerization process.

Finally, for the ethylene oligomerization to 1-octene case, no difference was observed in the process adoption curves between the base case and the unconstrained NGL case. Both are the same, as shown in Figure 11. As in the 1-butylene case, there is no direct constraint on the raw material, and now, since 1-octene occurs in the model only as a feedstock for a final end product (LLDPE), there are no indirect impacts either.

5. CONCLUDING REMARKS

The increased production of shale gas and, consequently, NGLs is providing opportunities to expand the U.S. chemical industry, leading to questions about how to best exploit these resources. In this paper, we considered new strategies for the use of ethane, the most abundant of the NGLs, by evaluating a new catalytic dehydrogenation process (e.g., Wu et al.,[37] Ridha et al.,[8] Wegener et al.,[38] and Ko et al.[11]) for converting ethane to ethylene and then evaluating new catalytic oligomerization processes (e.g., Agapie,[39] Finiels et al.,[40] Metzger et al.,[41] and Joshi et al.[12]) for converting ethylene to 1-butylene and to 1-octene. To conduct these evaluations, we developed a new, nonlinear, industry-wide network model of the U.S. petrochemical and refining industries. Unlike previous linear models of this type, the nonlinear model accounts for changes in material prices and, thus, process costs, as new technology is added to the industry network. A method for propagating cost and price changes, permitting the solution of the nonlinear optimization problem as a sequence of linear problems, was developed and utilized. Using network models for this study, we were able to account for and identify the direct and ancillary consequences of introducing a new technology on the rest of the industry.

For each new process evaluated, we determined the production level for that process in the optimal industry network. This was done over a wide range of net process cost points for each new process and led to the identification of a maximum adoption cost (the net process cost beyond which the process would not be adopted into the optimal industry). The sensitivity of the maximum adoption cost to the assumed product yield in the new processes was also studied. The maximum adoption costs can be viewed as setting targets for future catalyst and process development work. These are the values of the net process costs (accounting for byproduct and fuel credits) at or below which the process is predicted to be

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competitive. A low maximum adoption cost, especially if it has little or no margin above the anticipated raw material costs, suggests a process that may be difficult to be competitive, while a large maximum adoption cost, with a significant margin above raw material costs, indicates a process that provides opportunities. The processes studied here fall into the latter category.

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Author Contributions

¶A.S. and I.G. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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NOTATION

Variables

C_{tot} total industry production cost
C_j net production cost for process j (per unit mass of the main product)
F_i exogenous flow rate of material i into the network as the primary feedstock
Q_i exogenous flow rate of material i out of the network as a final end product
X_j production level of process j (annual mass flow rate of the main product)

Parameters

$a_{i,j}$ input−output coefficient for material i in process j
B_i current price of material i
$B_{i,0}$ baseline price of material i
$C_{j,0}$ baseline unit net production cost of process j
D_i exogenous demand for final end product i
j_i^*, largest producer of material i
S_i exogenous supply of primary feedstock i

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