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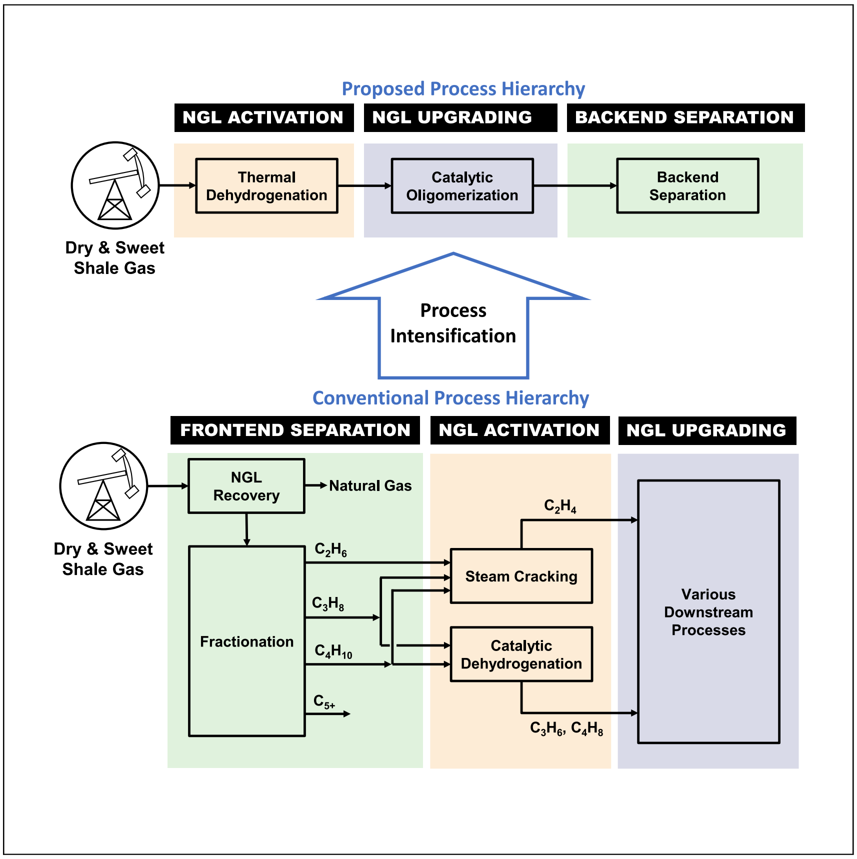

Chen et al. propose a potential solution to reduce wastage of shale resources and greenhouse gas emission by introducing an alternative process hierarchy for the natural gas liquid-to-liquid fuel process at a small scale near the wellhead. The intensified and simplified process has the potential for >30% cost reduction as compared to the established process hierarchy.

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Highlights

Alternative process hierarchy is proposed for natural gas liquid-to-liquid fuel process

Processes via direct shale gas dehydrogenation followed by oligomerization are presented

Intensified and simplified flowsheets for distributed shale gas processing are presented

The processes are shown to have potential for up to 30% cost reduction

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Alternative ordering of process hierarchy for more efficient and cost-effective valorization of shale resources

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SUMMARY

In the past 2 decades, natural gas flaring and venting have increased due to the lack of transforming or transportation infrastructure in emerging shale-gas-producing regions. To reduce carbon emissions and wastage of shale resources, here, we report an alternative process hierarchy for natural gas liquid (NGL) to liquid fuel processes, which enables efficient valorization of shale resources on a small scale near the wellhead. While the conventional shale gas process follows a front-end separation, NGL activation, NGL upgrading hierarchy, our process introduces a hierarchy of NGL activation, NGL upgrading, back-end separation. This proposed hierarchy intensifies and simplifies the entire process by eliminating repeated or unnecessary unit operations and associated equipment. We illustrate the benefit of the proposed process hierarchy through synthesis, simulation, and analysis of an exemplary process via dehydrogenation followed by oligomerization. For small-scale plants, detailed simulation and economic analysis demonstrate this process to be economically attractive.

INTRODUCTION

Shale gas has significantly transformed the energy landscape in the United States. However, processing shale gas at remote locations is still challenging due to the lack of transportation infrastructure.[1,2] Some remote shale basins remain unexploited, and even worse, large amounts of associated gas are directly flared on-site,[3–5] which contributes toward the wastage of shale resources and increased greenhouse gas emissions. Economical valorization of remote shale basins is also hindered by the current low price of natural gas and natural gas liquids (NGLs) in the market.[6,7] NGLs, which mainly consist of light hydrocarbons such as C_2H_6, C_3H_8, and C_4H_{10}, can serve as high-value feedstock for chemicals and fuels. However, the market prices of these alkanes are low as their production gradually overwhelmed their domestic consumption after the shale gas boom.[7] Therefore, economic strategies for small-scale on-site transformation of NGLs are needed for remote shale basins.

One promising route to valorize remote NGLs is converting NGLs into value-added and easy-to-transport liquid fuels.[8] It not only increases product market value but it also relaxes transportation infrastructure requirement constraints, as liquid fuels can be easily transported by rail or truck. A modular plant designed near shale and other natural gas gathering stations would be a perfect option for this application. Gas gathering stations typically gather shale gas from 2 to 5 wellheads and their

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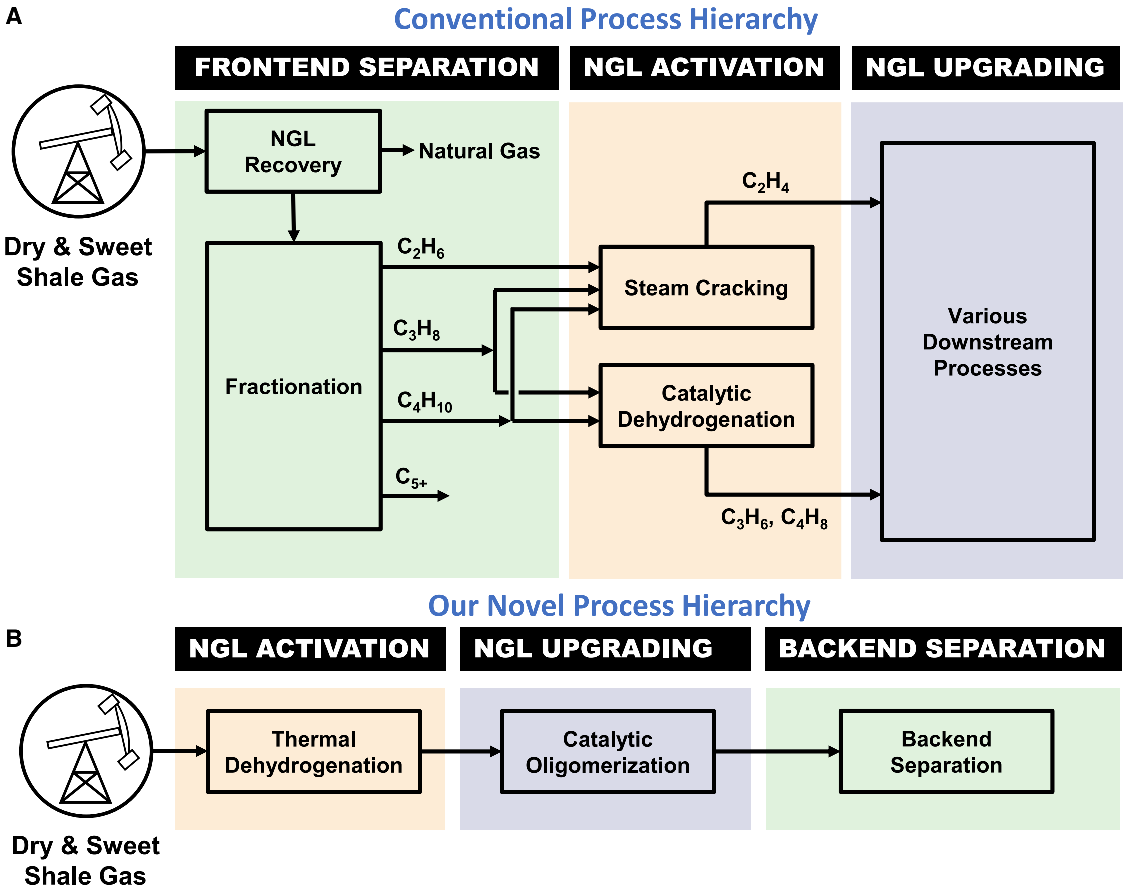

Figure 1. The conventional and alternative process hierarchy

(A) The conventional processes consist of NGL recovery and fractionation, steam cracking, catalytic dehydrogenation, and downstream processes. They follow a front-end separation, NGL activation, NGL upgrading hierarchy.

(B) The proposed process consists of thermal dehydrogenation, catalytic oligomerization, and back-end separation. It follows a NGL activation, NGL upgrading, back-end separation hierarchy.

flowrates are ~10 million standard cubic feet per day (MMSCFD) containing 1–4 MMSCFD NGLs. Due to limited allowable capital expenditure, processes designed at such a small scale must be highly intensified and simplified.

The shale gas industry typically follows a front-end separation, NGL activation, NGL upgrading hierarchy to process NGLs. Existing processes in the literature, although making significant progress in process intensification (PI) and simplification, still exclusively follow the same hierarchy.[9–12] As shown in Figure 1A, the front-end separation section includes NGL recovery, whereby methane and NGLs are separated through a cryogenic demethanizer,[13] and a fractionation train, where individual NGL component streams are recovered through a series of distillation columns. The main use of NGL components is to produce olefins, which are crucial building blocks for polymers, lubricants, fuels, and so forth. Therefore, the NGL activation section activates these NGL components into their corresponding olefins. Steam cracking and catalytic dehydrogenation are two major technologies used in this section.[14,15] While steam cracking of C_2-C_4 light hydrocarbons produces almost exclusively ethylene, the catalytic dehydrogenation of propane and butane selectively produces propylene and butene, respectively.[15] The conversion of NGL components into olefins is an activation step in the sense that a double bond is introduced into the molecule and various subsequent reactions could be conducted through the resulting double bond. The olefins produced can be then upgraded into valuable products in the downstream NGL upgrading section. This conventional NGL processing network consists of several well-known complex steps such as cryogenic separation, steam cracking, and catalytic dehydrogenation. These unit operations are not economically attractive for a small-scale plant. Furthermore, the composition of shale gas varies spatially and temporally from well to well, especially the C_2H_6, C_3H_6, C_3H_8, and C_4H_{10} relative concentration. When processed on a small scale, namely, at the scale of a gas gathering station, it is challenging to mitigate the composition variation by simply mixing the gas from several wells. If complicated processing steps such as cryogenic separation are used, then sizing of equipment and rigorous operation will become difficult for varying stream compositions. Therefore, simplified processes with less complicated unit operations are needed to make the process economically attractive; at the same time, such processes should tolerate the relative composition variation of C_2H_6, C_3H_8, and C_4H_{10} in the shale gas stream.

In this work, an alternative process hierarchy to NGL activation, NGL upgrading, back-end separation is created (Figure 1B). This process hierarchy distinguishes our work from all previous PI studies on this topic in the literature, which have focused mainly on combining two or more adjacent unit operations into one unit operation, such as using thermal coupling and dividing wall configurations to achieve the recovery and fractionation of NGLs,[16,17] and using a membrane reactor for steam cracking and catalytic dehydrogenation.[18,19] Furthermore, all of these literature studies still stick to the conventional process hierarchy, while the process hierarchy in our work opens up an unprecedented opportunity to intensify the entire NGL to the liquid fuel process. Although several systematic approaches for PI, which are not limited to shale gas valorization, such as the building block-based optimization method[20–22] and the phenomena-based method,[23–25] have been proposed and successfully applied to many applications, the process hierarchy proposed in this work has not been identified previously. The proposed process hierarchy is applied to an exemplary process via dehydrogenation followed by oligomerization and results in much simpler and intensified process configurations. The simplified process configurations are demonstrated, through detailed process simulation and economic analysis, to be economically attractive for small-scale installations.

RESULTS

NGL process development using alternative hierarchy

As shown in Figure 1, the process hierarchy introduced in this work for NGL-based processes includes three sections: NGL activation, NGL upgrading, and back-end separation. In such a hierarchy, the entire shale gas stream, without any front-end separation, is directed to an NGL activation section. The activated NGL is sent to the NGL upgrading section for production of desired products. All of the necessary separations, including separation of methane, unreacted NGL components, and synthesized products, are at the back end of the process. Although our hierarchy has the potential for application to many gas-to-liquid processes, a specific process route via dehydrogenation (NGL activation) and oligomerization (NGL upgrading) is chosen as an example in this work to better illustrate the benefit of the proposed hierarchy. The low-cost process developed via this route consists of three sequential processing blocks: dehydrogenation, oligomerization, and liquid hydrocarbon recovery. These three processing blocks are described in sufficient detail in the next few subsections.

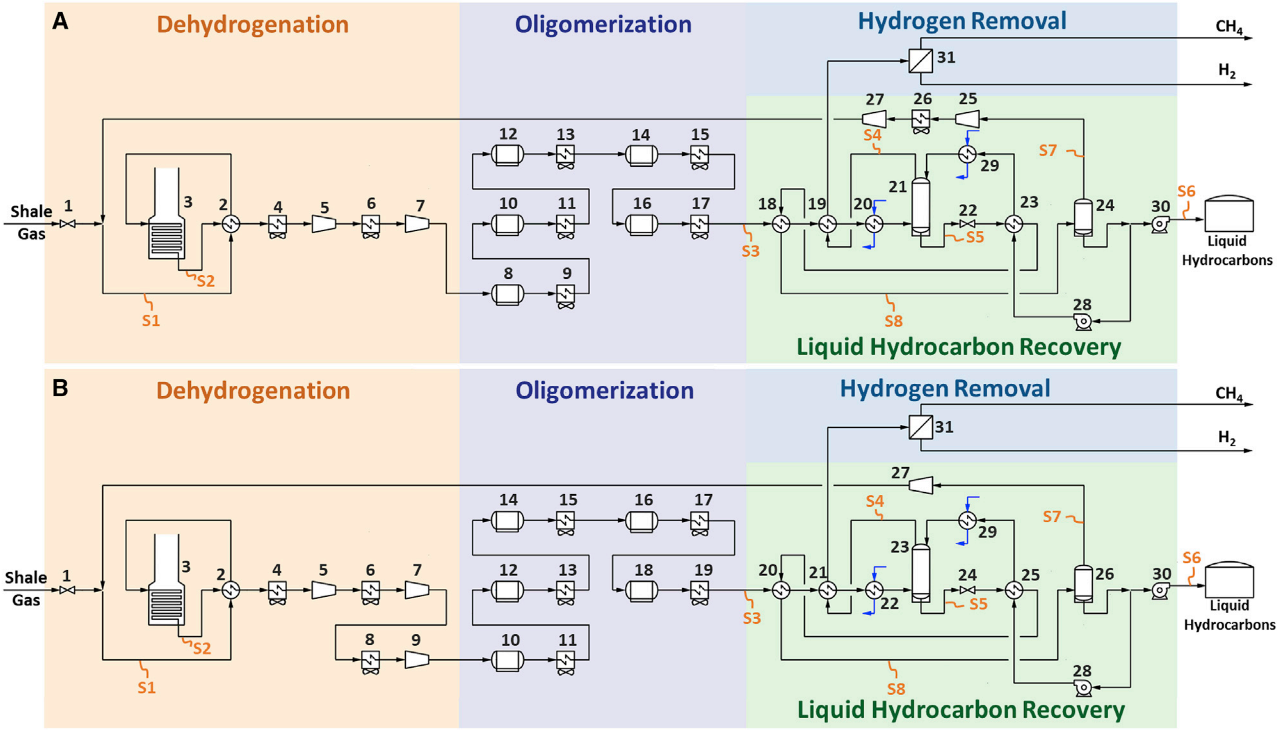

Figure 2. Two processes with the proposed hierarchy

(A) Process I, the configuration with a high-pressure dehydrogenation reactor operated at 6 bar.

(B) Process II, the configuration with a low-pressure dehydrogenation reactor operated at 2 bar.

Two configurations with different dehydrogenation reactor pressures are simulated, which are called process I and process II for the high-pressure and the low-pressure case, respectively (Figure 2). The process feed is taken to be 10 MMSCFD shale gas from the Bakken field at 30 bar and ambient temperature. Its composition is listed in Table 1. The Bakken field is of special interest since its shale gas has a high NGL concentration, the wells are in a remote location, and there is substantial flaring.[26] General simulation assumptions are described in Table S1.

In our example processes shown in Figure 2, thermal dehydrogenation is adopted for NGL activation. Dehydrogenation is generally operated at high temperature and low pressure to achieve high equilibrium conversion and selectivity toward dehydrogenation,[27] instead of cracking. The conventional cracking process introduces steam as a diluent to the cracker, but equipment associated with steam handling, including water conditioning for steam generation, water boiling, steam superheating, and steam condensation, contributes significantly to the process complexities and the process costs.[28–30] Similar to the steam, other gases can be introduced to the dehydrogenation reactor as diluent gas. For example, the introduction of CH_4, N_2, or H_2 to the feed of a catalytic propane dehydrogenation process has been suggested by Leonard et al.[31] Sundaram and Fernandez-Baujin[28] studied the effect of the addition of CH_4 and H_2 to an ethane cracker. Gami[30] recycled the light-reaction products for the cracking of ethylbenzene to styrene. However, the intentional introduction of diluents requires additional equipment to separate these diluents. These complex designs are unlikely to be economically attractive on a small scale, as the allowable capital expenditure is limited.

Table 1. The representative shale gas conditions of Bakken field

Component	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	CO_2	N_2
Composition mol%	57.81	19.98	11.35	3.79	1.26	0.57	5.22

The mole concentrations of CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, CO_2, and N_2 are listed.

In process I and process II configurations, the treated shale gas, which is free of acid gases and other undesirable components, is directly fed to a dehydrogenation reactor without any preseparation of CH_4 from NGLs. Since NGLs are already diluted with CH_4 in the shale gas stream, high conversion and selectivity can be achieved without introducing extra diluents such as steam and the associated process equipment for its handling. Furthermore, since thermal dehydrogenation is usually accompanied by cracking, which generates CH_4 as a by-product,[32–34] an additional demethanizer unit following dehydrogenation is necessary. This demethanizer is a duplication of the front-end demethanizer if CH_4 is separated from NGL before dehydrogenation as in the conventional process hierarchy. Therefore, using CH_4 as a "natural" diluent that is already present in the shale gas dramatically simplifies the process by eliminating duplicated CH_4/C_{2+} separation. Lower energy consumption is achieved by reducing energy-intensive distillation, and lower capital expenditure is realized by using fewer pieces of equipment.

The dehydrogenation reactor is operated at 850°C to achieve a reasonably high conversion of ethane. Two operating pressures, 6 bar and 2 bar, are chosen to represent a high-pressure case process I (Figure 2A) and a low-pressure case process II (Figure 2B), respectively. In process I, the partial pressure of C_{2+} is ~2 bar, which is at the upper limit of the applicable pressure of the kinetic model developed by Sundaram and Froment[34], while the total pressure is ~6 bar. In process II, the total pressure of the dehydrogenation reactor is 2 bar, but the partial pressure of C_{2+} is much lower (0.8 bar), leading to high equilibrium conversion and selectivity, as dehydrogenation favors low pressure. However, compared to process I, this process requires one more compression stage to compress effluent stream back to high pressure for oligomerization. Because of the competing economic trade-offs, without detailed simulation and economic analysis of both cases, it is not possible to tell which operating pressure is more beneficial. Hence, both cases are simulated and analyzed in this work. A further description of the combined kinetic model is given in Note S1.

In both cases, the outlet stream of the thermal dehydrogenation reactor contains exclusively H_2, CH_4, C_2, H_6, and C_2H_4, with few C3 or C4 hydrocarbons (see Tables S2 and S3 for stream composition), which indicates that the predominantly produced olefin from the thermal dehydrogenation is ethylene. Simulations are performed on three different feed compositions from Bakken, Eagle Ford, and Barnett, representing rich, medium, and lean shale gas compositions as shown in Table S9. The C_2H_6 conversions are 77.5%, 79.7%, and 84.8%; the C_{3+} conversions are >99%. While the ratio of C_2:C_{3+} varies between these feeds, the conversion of C_{3+} from the dehydrogenation reactor exceeds 99% for all 3 cases, and the predominant olefin product in each case is ethylene (Table S10). This implies that the dominant olefin feed to the downstream oligomerization reactor will be somewhat insensitive to the relative quantities of various hydrocarbons in the C_{2+} fraction of the shale gas feed. This could serve as a method to overcome feed composition variations at small-scale shale gas processing. This is another advantage of our process hierarchy over the conventional one for small-scale installation.

A furnace with no convection section is used as the dehydrogenation reactor in our proposed processes. A conventional steam cracking furnace consists of a convection section and a radiation section.[35,36] The convection section houses complex heat exchanger networks to recover heat in the effluent gas and generate steam for the rest of the plant, while the radiation section provides high-temperature heat directly to the steam cracker. In our proposed processes, however, the only heating needs are the preheating of dehydrogenation feed and the heat of reaction required in the dehydrogenation reactor. As shown in Figure 2, the shale gas feed is preheated against the effluent stream **S2** from the dehydrogenation reactor (unit **3**), and the heat of reaction required is supplied by the radiation section of the furnace. No steam is needed for other parts of the process, and the convection section is no longer needed in the furnace. Therefore, the furnace without convection section has simplified heat management of the process and further reduces the capital cost. The furnace is primarily fueled by the H_2-rich stream from the membrane (unit **31**) to reduce carbon emissions.

Due to the exothermic character of the oligomerization reaction, efficient removal of heat from the reactor to maintain the reaction temperature is the key to a low-cost oligomerization design. In our proposed processes, a five-stage adiabatic reactor sequence with intermediate air cooling is used for oligomerization. The temperature is maintained at 200°C–250°C in all of the reactor stages and the pressure is $\sim$30 bar to achieve a high conversion. Different from typical oligomerization reactors, which take pure olefin as feed and require a paraffin/olefin separation before the reactor,[37,38] our oligomerization reactor sequence directly takes the entire outlet stream of dehydrogenation without paraffin/olefin separation or hydrogen removal before the reactor. As a result, paraffins and H_2 in the feed can serve as thermal mass and mitigate the temperature increase in the reactors.

It is worth noting that the new process flowsheets in Figure 2 require a H_2-tolerant catalyst. Although some lab work has shown evidence that the oligomerization catalyst can be H_2 tolerant,[39] industrial application of such a catalyst requires further investigations and experiments. Therefore, although our work highlights the possible benefits that would result from the availability of such oligomerization catalysts, we provide an alternative flowsheet in Figure S1, whereas H_2 is removed through a H_2 membrane before the oligomerization in case such a catalyst is economically not available.

The liquid hydrocarbon recovery system is aimed at separating the outlet stream of the oligomerization reactor into three portions: a fuel gas stream containing H_2, N_2, and CH_4; a recycle stream containing unreacted NGLs and their unconverted olefin derivatives; and a liquid fuel product stream containing liquid hydrocarbons. The new process hierarchy has delayed all of the separation steps to the end of the process. We take advantage of this fact to create a simple yet powerful separation system using the liquid product as a separating agent.

The outlet stream **S3** from the oligomerization reactor contains CH_4, H_2, NGL, NGL's olefin derivatives, and C_{5+} liquid hydrocarbons. This stream is cooled to -20°C and sent to an absorption column (unit **21** in Figure 2A and unit **23** in Figure 2B), where a portion of the liquid product is used as the absorbent. We adjust the liquid flowrate at the top of the absorption column to ensure high recovery of not only liquid hydrocarbons in the gas stream but also all of the light components starting from C_2. This results in the absorption of a portion of CH_4 into the liquid phase leaving the bottom of the absorption column. The overhead gas stream **S4** from the top of the absorption column, which mainly contains CH_4, H_2, and N_2, is sent to the H_2 membrane unit (unit **31**). The liquid stream **S5** from the bottom of the absorption column is flashed to ambient pressure through a valve. Then, the stream is heated against a portion of the product stream **S6** and the oligomerization outlet stream **S3** to a temperature specified for the storage of liquid hydrocarbon product. Stream **S8** is a two-phase stream at ambient pressure and it is separated into a gas stream **S7**, which is compressed and recycled to the entrance of the dehydrogenation reactor and a liquid product stream in the flash drum (unit **24** in Figure 2A and unit **26** in Figure 2B). A portion (94%) of the liquid product stream **S6** from the flash drum is cooled and sent to the top tray of the absorption column as the absorbent and the rest of the product is collected as the final liquid hydrocarbon product. Key stream information in the process is summarized in Tables S2 and S3.

Back in the 1970s, NGL recovery from natural gas was historically achieved through an absorption process wherein NGL is absorbed into a liquid phase by contacting the shale gas with a refrigerated lean oil (average mol wt 100–150).[40,41] Although our processes use a similar absorption process to achieve CH_4/C_{2+} separation, there are 3 major new features of our process when compared to the conventional lean oil absorption process, providing its great economic and operability benefits. First, our process uses part of the liquid hydrocarbon product as absorbent. Conventional lean oil absorption process is very difficult to operate, as the lean oil deteriorates with time and it is difficult to predict the efficiency at removing liquids from the gas. The deterioration of the absorbent is no longer an issue in our process, as a portion of the absorbent is constantly replaced by the new liquid product. Second, the process allows part of the CH_4 to be absorbed into the liquid phase to enhance the recovery of C_2H_6 and C_2H_4. The conventional lean oil absorption process can only achieve 40% recovery of $C_2\ H_6$ to avoid significant absorption of CH_4 into the liquid phase.[42] In our process, absorbing a portion of CH_4 into the liquid phase is no longer a hurdle because the absorbed CH_4, along with other absorbed light hydrocarbons, is recycled back to the entrance of the dehydrogenation reactor. In other words, rather than pursuing a CH_4/C_{2+} separation, a much easier $CH_4/(CH_4,C_{2+})$ separation is achieved for the purpose of our process. Third, the process does not need a distillation column to regenerate the liquid product. In the conventional lean oil absorption process, a distillation column is needed to vaporize all of the absorbed NGL and regenerate lean oil, which makes the process energy intensive and leads to significant deterioration of the absorbent. However, in our process, the liquid from the absorption column passes through a valve and a heat exchanger to condition the liquid product for ambient storage; then, a simple flash drum is sufficient to regenerate the absorbent.

The gaseous stream **S4** from the top of the absorption column is mainly a mixture of CH_4 and H_2. This stream cannot be transported through natural gas pipelines as it has a low volumetric heating value due to the presence of H_2. Hence, a membrane unit is needed to remove H_2. In processes I and II, the membrane unit separates the feed into a CH_4-rich stream containing only 1% H_2 and another H_2-rich stream containing ~70% H_2. This H_2-rich stream, which cannot be transported as a by-product due to limited pipeline facilities, is directly used as the fuel to the dehydrogenation furnace. A detailed description of this membrane model may be found in the Supplemental experimental procedures.

Benefits over the benchmark process

To establish a fair comparison, a benchmark process is simulated and analyzed using the same models and assumptions as our new processes. This benchmark

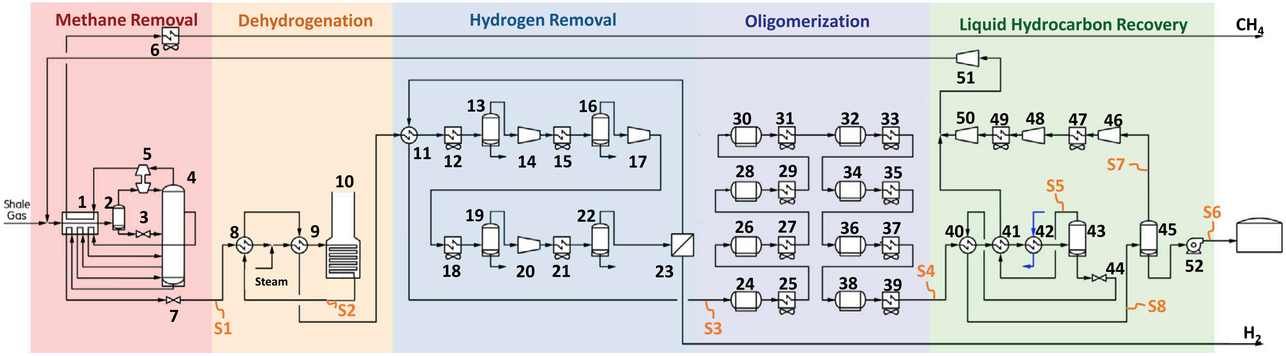

Figure 3. Benchmark process III

The benchmark process consists of methane removal, dehydrogenation, hydrogen removal, oligomerization, and liquid hydrocarbon recovery. It follows the conventional process hierarchy.

process is adapted from the work by Ridha et al.[8] (see Note S3 for a detailed synthesis procedure). The benchmark process follows a conventional hierarchy of front-end separation, NGL activation, NGL upgrading (see Figure 3). This process consists of five sequential processing blocks: methane removal, dehydrogenation, hydrogen removal, oligomerization, and liquid hydrocarbon recovery, and it is called process III for reference. Similar to most of the conventional processes, shale gas first passes through a cryogenic demethanzier, in which CH_4 is removed from C_{2+} NGL. NGL from the demethanzier is then sent to a steam cracker operated at 2 bar. The steam:hydrocarbon mass ratio is 1:3. The same kinetic model as our new processes is used in the simulation of the steam cracker. The outlet stream of the dehydrogenation reactor is then compressed and sent to a membrane separation unit to separate H_2. The permeate stream of the membrane unit is collected as a H_2-rich by-product and used as the fuel to the steam cracker. The retentate side stream, which contains dehydrogenated olefin products and unconverted NGLs, is sent to the oligomerization reactor in which part of olefins is converted into liquid hydrocarbons. This oligomerization reactor uses the same RGibbs model in Aspen Plus as our proposed processes. The outlet stream of this oligomerization reactor is then sent to the liquid hydrocarbon recovery unit in which the unconverted gas stream is separated from the liquid hydrocarbon product and recycled back to the front-end demethanzier. The stream information of this process can be found in Table S4.

The performance of these three processes is summarized in Table 2. The definitions of performance metrics are described in the Supplemental experimental procedures. The benchmark process III produces 4,659 kg/h liquid fuel, while our processes I and II produce 4,999 kg/h and 5,268 kg/h liquid fuel, which are 7.3% and 13.1% higher than process III, respectively. The average molecular weights of the final products are 147.7, 148.4, and 149.7 for processes I, II, and III, respectively, which lie between the molecular weights of gasoline (~ 95) and diesel (~200). Either gasoline or diesel may be targeted with specific catalysts and operating conditions. Process III has a significantly higher pipeline natural gas production rate (7,300 kg/h) than processes I and II (6,618 kg/h and 6,336 kg/h, respectively), mainly due to the fact that the conventional demethanzier only has 90%–95% recovery of NGL, leaving the remaining 5%–10% NGL in the natural gas stream. The higher heat values (HHVs) of the natural gas stream produced in processes I, II, and III are 957, 955, and 993, respectively, which are higher than the minimum HHV requirement of pipeline natural gas.

Table 2. Performance summary of processes I, II, and III

Flowsheet	Units	Process I	Process II	Process III
Feed and product				
Feed flowrate	kg/h	12,370	12,370	12,370
Liquid fuel flowrate	kg/h	4,999	5,268	4,659
Liquid fuel average molecular weight	g/mol	147.7	148.4	149.7
Pipeline natural gas flowrate	kg/h	6,618	6,336	7,300
Natural gas higher heat value	BTU/SCF	957	955	993
Dehydrogenation				
Yield toward olefins per pass	%	58	61	57
CH_4:H_2 production ratio	–	1.09	0.77	0.96
Oligomerization				
Conversion	%	89.1	89.1	89.9
Number of reactor stages	–	5	5	8
Liquid hydrocarbon recovery				
C_{2+} losses to gaseous streams	%	4.3	4.3	14.8
Overall C_{2+} losses	%	29.0	25.2	33.9

Important performance metrics of the flowsheets, including feed and product flowrates, liquid fuel average molecular weight, natural gas higher heating value, yield toward olefins per pass and CH_4:H_2 ratio in dehydrogenation, conversion, and number of reactor stages in oligomerization, C_{2+} losses to gaseous streams and overall C_{2+} losses are listed. SCF, standard cubic feet.

Chemkin simulations show that processes I, II, and III have 58%, 61%, and 57% yield toward olefins in dehydrogenation reactor, respectively (Table 2). The CH_4:H_2 production ratio, which is an indicator for the selectivity of the reactor, is 1.09, 0.77, and 0.96 for processes I, II, and III, respectively (see Supplemental experimental procedures for the definition of the CH_4:H_2 production ratio). A higher CH_4:H_2 production ratio indicates a lower selectivity. Since there is a trade-off between the selectivity and conversion as residence time varies, the dehydrogenation reactors are operated at such residence times that the yields of olefins per pass are maximized. It is worth noting that the yield of olefins in process II, which has a low partial pressure of C_{2+}, is 5% higher than the benchmark process and that the CH_4:H_2 production ratio of this process is also much lower, leading to reduced C_{2+} losses.

Resulting PI

PI is a design concept that offers innovative solutions for making a substantial improvement in terms of cost, energy efficiency, emission, environmental footprint, processing volume, and safety of a chemical process.[22] In this section, we discuss the PI resulting from the alternative process hierarchy and how it reduces the number of pieces of equipment and enhances operability of the process, and consequently, lower process cost. Different from most of the PI studies in the literature, which focus on developing new technologies or combining adjacent unit operations into one piece of equipment, PI in our work is achieved by eliminating unnecessary or repeated unit operations. This simplification strategy minimizes the number of pieces of equipment, and consequently reduces capital costs and enhances the operability, which is especially beneficial for a small-scale installation with limited capital expenditure.

Table 3 summarizes several key unit operations in the conventional process, and their corresponding PI strategy in our new processes. In the front-end separation step, the energy- and capital-intensive cryogenic demethanzier is eliminated (a typical demethanizer configuration can be found in Figure 3). This elimination not only simplifies the process by reducing the number of unit operations but it also increases the operability of the process, as the process becomes insensitive

Table 3. Unit operations in the conventional process scheme and their corresponding PI in the alternative processes (Figure 2)

Unit operations	PI
Front-end separation	
Cryogenic demethanizer	eliminated
NGL activation	
Water conditioning and generation	eliminated
Steam cracker	simpler thermal dehydrogenation
Furnace	convection section eliminated
Post-reaction demethanizer	eliminated
Post-reaction dehydration	eliminated
NGL upgrading	
Oligomerization reactor	temperature increase is mitigated
Liquid hydrocarbon recovery	
Lean oil absorption	use of product liquid

PI includes both the elimination and simplification of some unit operations. PI, process intensification.

to the relative quantities of various hydrocarbons in the C_{2+} fraction of the shale gas feed. In the NGL activation step, a thermal dehydrogenation reactor with CH_4 as diluent is used to activate NGLs into olefins. Steam, which is the diluent in the conventional steam cracker, is no longer needed to reduce the partial pressure of C_{2+} in the thermal dehydrogenation reactor. This means that all of the equipment associated with water conditioning and steam generation, as well as post-reaction dehydration, is eliminated. The convection section of the furnace is also eliminated to further reduce the capital cost. In the NGL upgrading step, the operability of the oligomerization reactor is enhanced due to the presence of CH_4 and H_2 as thermal mass that can mitigate the adiabatic temperature increase. The oligomerization reactors in processes I and II have 5 stages, while the oligomerization reactor in process III without H_2 and CH_4 needs 8 stages to maintain the same temperature range using adiabatic packed bed reactors. The proposed process hierarchy not only eliminates any prior separation but it also facilitates heat management around the reactors. In the liquid fuel recovery step, an absorption column with a portion of the product as absorbent is used to recover C_{2+} from the effluent stream of the oligomerization reactor. When compared with the conventional cryogenic demethanizer, the capital cost is dramatically decreased (see Figure 4 and Tables S6–S8 for capital costs). When compared with lean oil absorption, not only is the equipment count reduced by eliminating the external absorbent and the regeneration tower but also the operability of the process is enhanced as constant replenishment of the absorbent with the new liquid product resolves issues associated with the deterioration of an absorbent in a closed loop.

Economic analysis

For capital costs estimation, equipment sizes are prepared following the sizing basis listed in Table S5. We caution readers that capital costs estimation in Aspen Plus is only preliminary and should be followed with a detailed analysis before the execution of a project. Hence, it is unfair to compare the cost estimation in this article with the cost data of any licensed processes. However, the use of capital costs estimation in Aspen Plus provides us a consistent basis to compare alternate processes as well as assess the potential of a new process.

Figure 4 shows the cost breakdown of process I, process II, and process III. The total capital expenditure (CAPEX) of process I and process II are \$24 million and \$25 million,

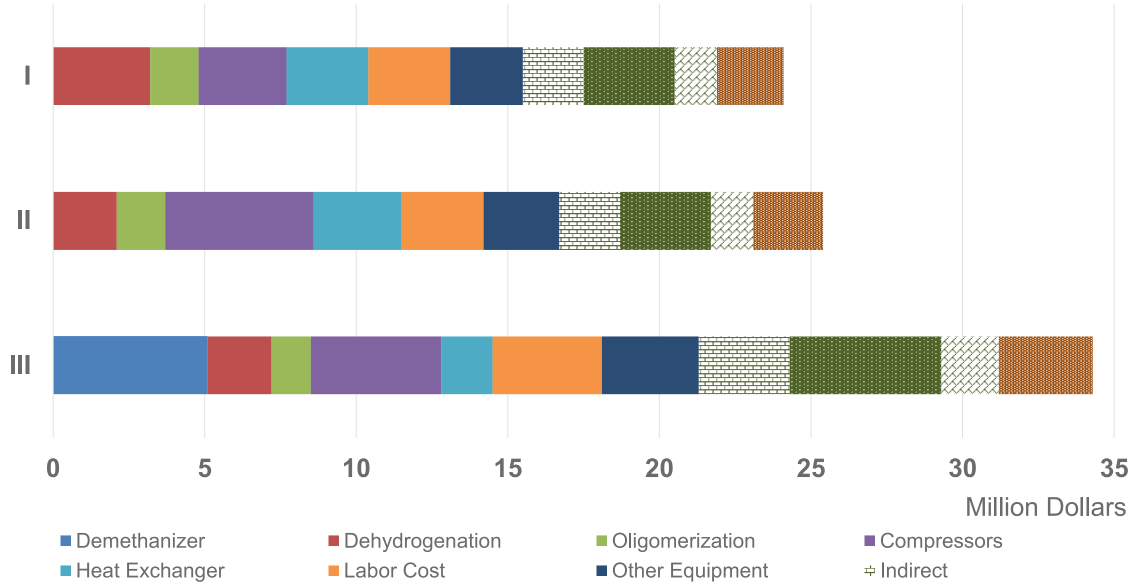

Figure 4. Cost breakdown of process I, process II, and process III shows that processes I and II have lower costs than process III
The blocks with solid colors represent the equipment purchase cost for different pieces of equipment, including demethanizer, thermal dehydrogenation reactor (dehydrogenation), oligomerization reactor (oligomerization), compressors, heat exchangers, and other equipment. The blocks with patterns represent the installation cost, engineering cost, indirect cost, other project cost, and contingency.

respectively. As a comparison, the CAPEX of process III is $35 million. Process I and process II have 31% and 29% cost savings, respectively, over the benchmark process. From the cost breakdown of individual pieces of equipment in Figure 4, the savings of process I and process II are mainly from the elimination of the front-end demethanizer. The proposed process hierarchy not only increases the conversion per pass in the dehydrogenation reactor, which decreases the recycle flow rate, but also delays the separation to the end of the process, which results in a highly intensified and low-cost separation system. The equipment cost is summarized in Tables S6–S8.

The costs of production for process I, process II, and process III are listed in Table 4. The pricing basis for the raw material (dry sweet shale gas) is $0.11/lb. Fuel gas is valued as fuel, which is $4/MMBTU (metric million British thermal units). The catalysts used in all of the processes are $10/lb and have a 1-year lifetime.[43] The total costs of production for process I, process II, and process III are $1.31, $1.35, and $1.40/gal liquid fuel, respectively. Compared to the benchmark process, process I and process II have a 4% and 7% operating cost reduction, respectively. The internal rate of return of the processes increases from 14% to 26% for process I and 24% for process II. The savings of operating costs mainly come from the increase in liquid fuel production.

DISCUSSION

An alternative process hierarchy is applied to a natural gas liquid to liquid fuel process for small-scale plants. While a conventional shale gas process follows a front-end separation, NGL activation, NGL upgrading hierarchy, our process follows a different hierarchy of NGL activation, NGL upgrading, back-end separation. To illustrate the benefit of this different process hierarchy, an exemplary process via dehydrogenation followed by oligomerization is analyzed.

In our process, the feed shale gas is fed to the dehydrogenation reactor without any front-end separation of methane. CH_4 in the shale gas decreases the partial pressure

Table 4. Cost of production ($/gal liquid fuel) and cash flow analysis of process I, process II, and process III

	Price	Process I	Process II	Process III
Shale gas	$0.11/lb	(1.72)	(1.68)	(1.85)
Catalyst	$10/lb, 1-y lifetime	(0.01)	(0.01)	(0.01)
Electricity	$0.05/kWh	(0.09)	(0.11)	(0.10)
Natural gas	$4/MMBTU	0.66	0.59	0.78
Fixed costs		(0.14)	(0.14)	(0.21)
Total costs		(1.31)	(1.35)	(1.40)
Liquid fuel		1.89	1.89	1.89
Capital cost		$24 MM	$25 MM	$35 MM
IRR, %		26	24	14

The costs of production include shale gas raw material cost, catalyst cost, electricity cost, and fixed cost. The membrane cost is small compared to other costs; therefore, they are not listed here. The numbers in parentheses indicate debit terms, while the numbers without parentheses indicate credit terms. IRR, internal rate of return.

of NGL in the dehydrogenation reactor and results in a high conversion per pass. The outlet stream from the dehydrogenation reactor is directly sent to the oligomerization reactor sequence. Again, CH_4 and H_2 pass through the reactor without any prior separation. These light components serve as thermal mass to somewhat mitigate the temperature increase in the reactor. The alternative process hierarchy delays all of the separation to the end of the process; hence, a highly intensified and simplified separation system is designed. In this separation system, a portion of the final product is used as the absorbent to separate C_{2+} from CH_4 and H_2 in an absorption column. Two configurations, process I and process II, with a high-pressure dehydrogenation reactor and a low-pressure dehydrogenation reactor, are simulated. A benchmark process III with conventional hierarchy is also simulated. Through an economic analysis of all three processes, process I and process II configurations show a, respectively, 86% and 71% greater internal rate of return than process III.

Although this article focuses on a specific process route via dehydrogenation followed by oligomerization, the NGL activation, NGL upgrading, and back-end separation hierarchy has the potential to be applied to many other gas-to-liquid processes and set up a general guideline for small-scale gas-to-liquid plants (several potential application scenarios are listed in Note S4).

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Rakesh Agrawal (agrawalr@purdue.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

Data reported in this article will be shared by the lead contact upon request. This article does not report original code.

Simulation procedures

The processes presented in this work are simulated rigorously with dehydrogenation reactors simulated in Chemkin, membrane unit simulated in MATLAB, and the rest of the process simulated in Aspen Plus. An interface script is written in MATLAB to transfer inputs and outputs between Aspen Plus and Chemkin. The capital cost estimate is done in Icarus Capital Cost Estimator (ACCE) version 8.8, 1Q14 cost basis. The program is used with no cost adjustments or index changes, other than that area dimensions are set so that Aspen will estimate them. No scope other than the equipment is entered; all bulks and material items are estimated by ACCE (see Table S5 for modeling assumptions).

The dehydrogenation reactor is simulated in Chemkin using a combination of the kinetic model developed by Sundaram and Froment,[34] and the kinetic model developed by Keipi et al.[44] The former described a radical reaction scheme for the cracking of ethane, propane, normal and isobutane, ethylene, and propylene, while the latter described a kinetic scheme for methane pyrolysis. The combined kinetic model covers all major components in the feed stream **S1** to the dehydrogenation reactors (see Tables S2 and S3 for stream compositions). The oligomerization reactor is simulated in Aspen Plus using the RGibbs reactor model with all of the linear α-olefins up to 20 carbons as allowable products (see Note S2 and Figures S2–S4 for details). The catalyst loading is 4.0×10^{-6} gmol C_{2+} feed/(g catalyst · s), which is based on the extrapolation of Figure 3 in the study by Toch et al.[45] It is worth noting that the actual product distribution highly depends on the catalyst and corresponding kinetics, rather than the thermodynamic limit predicted by the RGibbs model. In this work, the RGibbs model is used only to demonstrate the feasibility of our current process design, rather than predicting the actual product distribution. Ten percent of the C_2H_4 in the feed is assumed to be inert, to account for inefficiencies of the reactor design. Both process I and process II achieve >89% conversion in the oligomerization reactor. The liquid product is valued as if it is regular gasoline.

Economic analysis

In the annual cash flow analysis, the process is assumed to have a project life of 15 years of continuous operation. Although the lifetime of a shale gas well is generally 3–5 years, our small-scale plant is assumed to be mobile and can move from one gas gathering station to another. There is no cost or interruption assumptions associated with moving the facility to different active gas collection areas. All of the capital is spent the year before startup and the facility operates at 95% capacity annually every year thereafter. The modified accelerated cost recovery system (MACRS) depreciation is applied with a 21% tax rate. The terminal value is 5 times the annual operating income. Working capital includes 30 days accounts receivable, accounts payable, and 2 days of inventory.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.xcrp.2021.100581.

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AUTHOR CONTRIBUTIONS

Conceptualization, Z.C., Y.L., and R.A.; methodology, Z.C., Y.L., E.A.R.G., and R.A.; software, Z.C., Y.L., W.P.O., E.A.R.G., and G.S.; validation, Z.C., Y.L., E.A.R.G., and G.S.; formal analysis, Z.C., Y.L., E.A.R.G., G.S., and R.A.; investigation, Z.C., Y.L., E.A.R.G., G.S., and R.A.; resources, Z.C., Y.L., E.A.R.G., G.S., and R.A.; data

curation, Z.C., Y.L., W.P.O., E.A.R.G., and G.S.; writing, Z.C., Y.L., and R.A.; visualization, Z.C. and E.A.R.G.; supervision, R.A.; project administration, R.A.; funding acquisition, R.A. All of the authors have read and agreed to the published version of the manuscript.

DECLARATION OF INTERESTS

The authors' employer Purdue University has filed for a US process patent.

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REFERENCES

1. US Department of Energy (2019). Natural Gas Flaring and Venting: State and Federal Regulatory Overview, Trends, and Impacts. https://www.energy.gov/sites/prod/files/2019/08/f65/Natural%20Gas%20Flaring%20and%20Venting%20Report.pdf.
2. US Energy Information Administration (2021). About U.S. Natural Gas Pipelines. https://www.eia.gov/energyexplained/natural-gas/natural-gas-pipelines.php.
3. Fisher, D., and Wooster, M.J. (2019). Multi-decade global gas flaring change inventoried using the ATSR-1, ATSR-2, AATSR and SLSTR data records. Remote Sens. Environ. *232*, 111298.
4. Roehner, R., Panja, P., and Deo, M. (2016). Reducing gas flaring in oil production from shales. Energy Fuels *30*, 7524–7531.
5. Elvidge, C.D., Bazilian, M.D., Zhizhin, M., Ghosh, T., Baugh, K., and Hsu, F.-C. (2018). The potential role of natural gas flaring in meeting greenhouse gas mitigation targets. Energy Strategy Rev. *20*, 156–162.
6. US Energy Information Administration (2021). Natural gas. https://www.eia.gov/dnav/ng/hist/rngwhhdm.htm.
7. US Energy Information Administration (2021). Hydrocarbon gas liquids explained. https://www.eia.gov/energyexplained/hydrocarbon-gas-liquids/prices-forhydrocarbon- gas-liquids.php.
8. Ridha, T., Li, Y., Gençer, E., Siirola, J.J., Miller, J.T., Ribeiro, F.H., and Agrawal, R. (2018). Valorization of shale gas condensate to liquid hydrocarbons through catalytic dehydrogenation and oligomerization. Processes (Basel) *6*, 139.
9. Gong, J., and You, F. (2018). A new superstructure optimization paradigm for process synthesis with product distribution optimization: application to an integrated shale gas processing and chemical manufacturing process. AIChE J. *64*, 123–143.
10. Gong, J., Yang, M., and You, F. (2017). A systematic simulation-based process intensification method for shale gas processing and NGLs recovery process systems under uncertain feedstock compositions. Comput. Chem. Eng. *105*, 259–275.
11. He, C., and You, F. (2014). Shale gas processing integrated with ethylene production: novel process designs, exergy analysis, and techno-economic analysis. Ind. Eng. Chem. Res. *53*, 11442–11459.
12. Bahadori, A. (2014). Natural Gas Processing: Technology and Engineering Design (Gulf Professional Publishing).
13. Getu, M., Mahadzir, S., Long, N.V.D., and Lee, M. (2013). Techno-economic analysis of potential natural gas liquid (NGL) recovery processes under variations of feed compositions. Chem. Eng. Res. Des. *91*, 1272–1283.
14. Myers, D.N., Myers, D.N., and Zimmermann, J.E. (2015). Propane dehydrogenation process utilizing fluidized catalyst system. US Patent US8927799B2, filed November 1, 2010, and published January 6, 2015.
15. Ren, T., Patel, M., and Blok, K. (2006). Olefins from conventional and heavy feedstocks: energy use in steam cracking and alternative processes. Energy *31*, 425–451.
16. Jiang, Z., Chen, Z., Huff, J., Shenvi, A.A., Tawarmalani, M., and Agrawal, R. (2019). Global minimization of total exergy loss of multicomponent distillation configurations. AIChE J. *65*, e16737.
17. Halvorsen, I.J., Dejanović, I., Maråk, K.A., Olujić, Ž., and Skogestad, S. (2016). Dividing-Wall Column for Fractionation of Natural Gas Liquids in Floating Liquefied Natural Gas Plants. Chem. Eng. Technol. *39*, 2348–2354.
18. Gobina, E., and Hughes, R. (1994). Ethane dehydrogenation using a high-temperature catalytic membrane reactor. J. Membr. Sci. *90*, 11–19.
19. Champagnie, A.M., Tsotsis, T.T., Minet, R.G., and Wagner, E. (1992). The study of ethane dehydrogenation in a catalytic membrane reactor. J. Catal. *134*, 713–730.
20. Demirel, S.E., Li, J., and Hasan, M.F. (2017). Systematic process intensification using building blocks. Comput. Chem. Eng. *105*, 2–38.
21. Demirel, S.E., Li, J., and Hasan, M.F. (2019). Systematic process intensification. Curr. Opin. Chem. Eng. *25*, 108–113.
22. Demirel, S.E., Li, J., El-Halwagi, M., and Hasan, M.F. (2020). Sustainable Process Intensification Using Building Blocks. ACS Sustain. Chem. Eng. *8*, 17664–17679.
23. Lutze, P., Gani, R., and Woodley, J.M. (2011). Phenomena-based process synthesis and design to achieve process intensification. Comput. Aided Chem. Eng. *29*, 221–225.
24. Lutze, P., Babi, D.K., Woodley, J.M., and Gani, R. (2013). Phenomena based methodology for process synthesis incorporating process intensification. Ind. Eng. Chem. Res. *52*, 7127–7144.
25. Tula, A.K., Babi, D.K., Bottlaender, J., Eden, M.R., and Gani, R. (2017). A computer-aided software-tool for sustainable process synthesis-intensification. Comput. Chem. Eng. *105*, 74–95.
26. Gvakharia, A., Kort, E.A., Brandt, A., Peischl, J., Ryerson, T.B., Schwarz, J.P., Smith, M.L., and Sweeney, C. (2017). Methane, black carbon, and ethane emissions from natural gas flares in the Bakken Shale, North Dakota. Environ. Sci. Technol. *51*, 5317–5325.
27. Bhasin, M., McCain, J., Vora, B., Imai, T., and Pujado, P. (2001). Dehydrogenation and oxydehydrogenation of paraffins to olefins. Appl. Catal. A Gen. *221*, 397–419.
28. Sundaram, K., and Fernandez-Baujin, J. (1988). Effect of methane and hydrogen during thermal cracking of light hydrocarbons. AIChE J. *34*, 321–325.
29. Leesemann, C.J. (1949). Process for dehydrogenation of hydrocarbons in the presence of a gaseous diluent. Filed April 10, 1946, published February 8, 1949. US Patent US2461331A *2*.
30. Gami, A.C. (2014). Use of hydrocarbon diluents to enhance conversion in a dehydrogenation process at low steam/oil ratios. US Patent 14/052,949, filed October 14, 2013, and published April 24, 2014.
31. Leonard, L.E., Bozzano, A.G., and Towler, G.P. (2013). Hydrocarbon dehydrogenation with inert diluent. US Patent US20130158327A1, filed December 16, 2011, and published June 20, 2013.
32. Sundaram, K., and Froment, G. (1977). Modeling of thermal cracking kinetics I:

thermal cracking of ethane, propane and their mixtures. Chem. Eng. Sci. *32*, 601–608.

33. Sundaram, K., and Froment, G. (1977). Modeling of thermal cracking kinetics—II: cracking of isobutane, of n-butane and of mixtures ethane—propane—n-butane. Chem. Eng. Sci. *32*, 609–617.
34. Sundaram, K.M., and Froment, G.F. (1978). Modeling of thermal cracking kinetics. 3. Radical mechanisms for the pyrolysis of simple paraffins, olefins, and their mixtures. Ind. Eng. Chem. Fundam. *17*, 174–182.
35. Karimzadeh, R., Godini, H.R., and Ghashghaee, M. (2009). Flowsheeting of steam cracking furnaces. Chem. Eng. Res. Des. *87*, 36–46.
36. Yuan, B., Zhang, Y., Du, W., Wang, M., and Qian, F. (2019). Assessment of energy saving potential of an industrial ethylene cracking furnace using advanced exergy analysis. Appl. Energy *254*, 113583.
37. Small, B., and Kreischer, B. (2011). Olefin oligomerization. US Patent US7994376B2, filed June 8, 2009, and published August 9, 2011.
38. Harandi, M.N., and Owen, H. (1991). Reactor and recovery system for upgrading lower olefins. US Patent 5,059,744, filed September 29, 1989, and published October 22, 1991.
39. Jeffrey, M., and Guanghui, Z. (2019). Ni Catalysts for High-temperature Oligomerization. US Patent 2018-MILL-68123, filed March 22, 2019, and published August 10, 2021.
40. Mak, J. (2008). Configuration and process for NGL recovery using a subcooled absorption reflux process. US Patent 7,377,127, filed May 8, 2002, and published May 27, 2008.
41. Rincón, M.D., Jiménez-Junca, C., and Duarte, C.R. (2016). A novel absorption process for smallscale natural gas dew point control and dehydration. J. Nat. Gas Sci. Eng. *29*, 264–274.
42. Wall, J. (1979). Gas processing handbook. Hydrocarbon Process. *58*.
43. US Department of Energy (DOE) Bioenergy Technologies Office (BETO) (2019). Catalyst Cost Model Development (CatCost).. https://www.energy.gov/sites/prod/files/2019/03/f61/Catalyst%20Cost%20Model%20Development%20%28CatCost%29_NL0030154.pdf.
44. Keipi, T., Li, T., Løvås, T., Tolvanen, H., and Konttinen, J. (2017). Methane thermal decomposition in regenerative heat exchanger reactor: Experimental and modeling study. Energy *135*, 823–832.
45. Toch, K., Thybaut, J., Arribas, M., Martinez, A., and Marin, G. (2017). Steering linear 1-alkene, propene or gasoline yields in ethene oligomerization via the interplay between nickel and acid sites. Chem. Eng. Sci. *173*, 49–59.