ACS Sustainable Chemistry & Engineering

pubs.acs.org/journal/ascecg

Research Article

Alternative Processing Sequence for Process Simplification, Cost Reduction, and Enhanced Light Olefin Recovery from Shale Gas

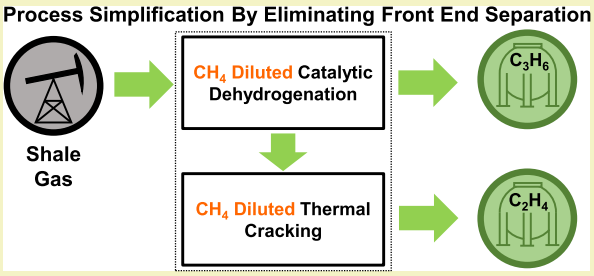
Zewei Chen and Rakesh Agrawal*

Cite This: *ACS Sustainable Chem. Eng.* 2021, 9, 13893−13901

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Natural gas liquids (NGLs) in shale gas are the predominant feedstock for light olefin production. Conventionally, NGLs are separated from CH_4 and then fractionated into individual components before these components go through either steam cracking or catalytic dehydrogenation. In this work, we introduce an alternative processing sequence to intensify and simplify the conventional process. In the resulting processes, some of the front-end separations are delayed toward the end, which eliminates several repeated separations and associated equipment. Light hydrocarbons, such as CH_4, serve as diluents to enhance the performance of steam cracker and catalytic dehydrogenation reactors. Modeling results for a 100 million standard cubic feet per day shale gas feed from the Bakken field show that the alternative processing sequence not only eliminates duplication of some process steps, leading to several process simplifications, reduced cost, and energy demand, but also increased olefin yield from the shale gas NGLs. The proposed concepts could be applied to many other reaction-separation networks, resulting in a more enriched flowsheet search space for investigation.



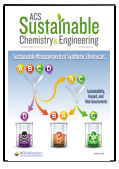
KEYWORDS: *process intensification, shale gas, dehydrogenation*

INTRODUCTION

The shale gas boom in the United States provides abundant natural gas liquids (NGLs) as feedstocks to produce olefins such as ethylene, propylene, and butene,[1] which are crucial building blocks to manufacture plastic, fiber, rubber, and so forth.[2,3] Figure 1 depicts the conventional process scheme to produce light olefins from shale gas.[4] This scheme consists of three sections: front-end separation, NGL activation, and postreaction separation. In the front-end separation section, dry and sweet shale gas first passes through an NGL recovery unit, typically a cryogenic demethanizer[5] to separate natural gas liquids from CH_4. The recovered natural gas liquids are further fractionated into individual component streams, including ethane, propane, butane, and C_{5+} through a sequence of distillation columns.[6] In the NGL activation section, the NGL component streams are dehydrogenated into olefins through either steam cracking or catalytic dehydrogenation processes. Steam cracking of NGLs produces mainly ethylene,[7−9] while catalytic dehydrogenation of C_3H_8 and C_4H_{10} produces C_3H_6 and C_4H_8, respectively.[10−14] It is worth noting that while propane and butane are also feedstocks for steam cracking to produce ethylene, there is no commercial catalytic ethane dehydrogenation process, due to the limitation of equilibrium conversion.[15] Some of the side products from the steam cracker are H_2 and CH_4, and from the C_3H_8 and C_4H_{10} catalytic dehydrogenation units are H_2, CH_4, and C_2 hydrocarbons. Therefore, in the postreaction separation step, the effluent streams from steam cracker and catalytic dehydrogenation reactor units pass through a series of separation steps including H_2 removal, C_1/C_2 separation, dehydration, and so forth to purify the olefin products.

Over the past few decades, natural gas venting and flaring in remote shale gas basins has become a serious issue, contributing toward significant wastage of shale resources and increased greenhouse gas emissions.[16] Remote shale gas basins lack processing, gathering, and distribution infrastructures for large-scale processing plants at central locations, hence medium- to small-scale plants near the shale gas wellhead provide a promising option. However, smaller-scale installation also faces several challenges such as limited capital expenditure, variations in the feed flow and its composition, etc., necessitating simpler and more intensified process design. The conventional scheme contains several well-known capital and energy intensive units, hence is unlikely to be economically attractive at a small to medium size. Both steam cracking and catalytic dehydrogenation require high temperatures (850 °C for stream cracking and 500−650 °C for catalytic dehydrogenation of propane and butane) and low partial pressure of NGLs to achieve a high conversions per pass.[7−9] Steam is introduced

Received: July 27, 2021
Revised: September 20, 2021
Published: October 4, 2021



https://doi.org/10.1021/acssuschemeng.1c05091
ACS Sustainable Chem. Eng. 2021, 9, 13893−13901

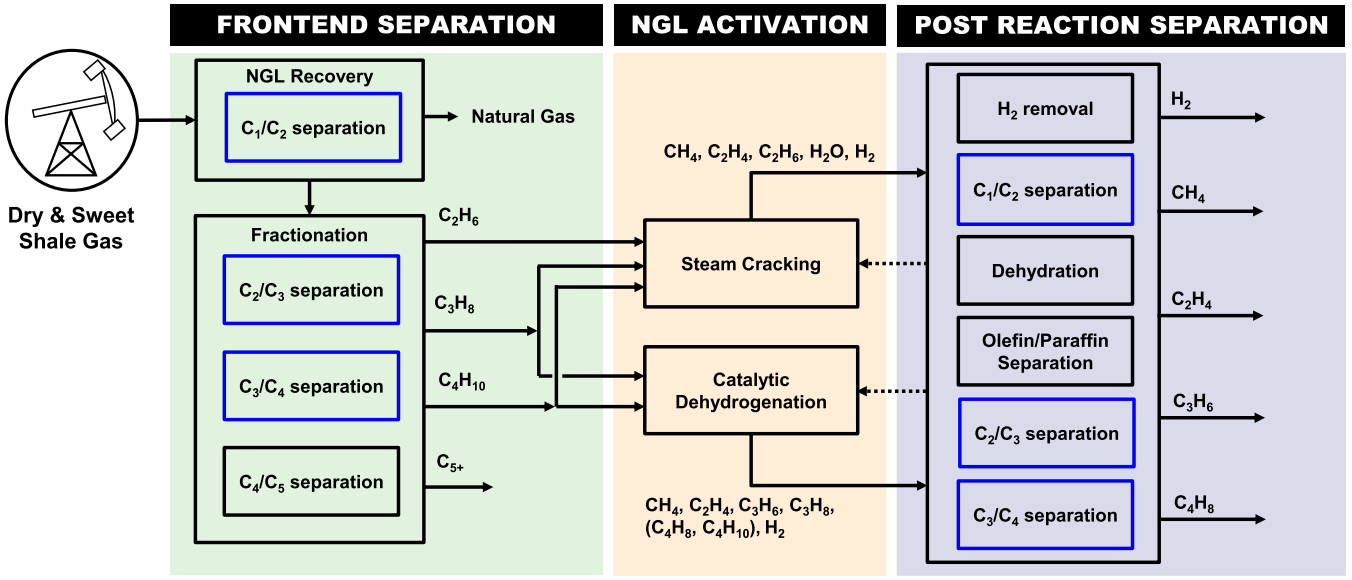


Figure 1. Processing sequence of the conventional process.

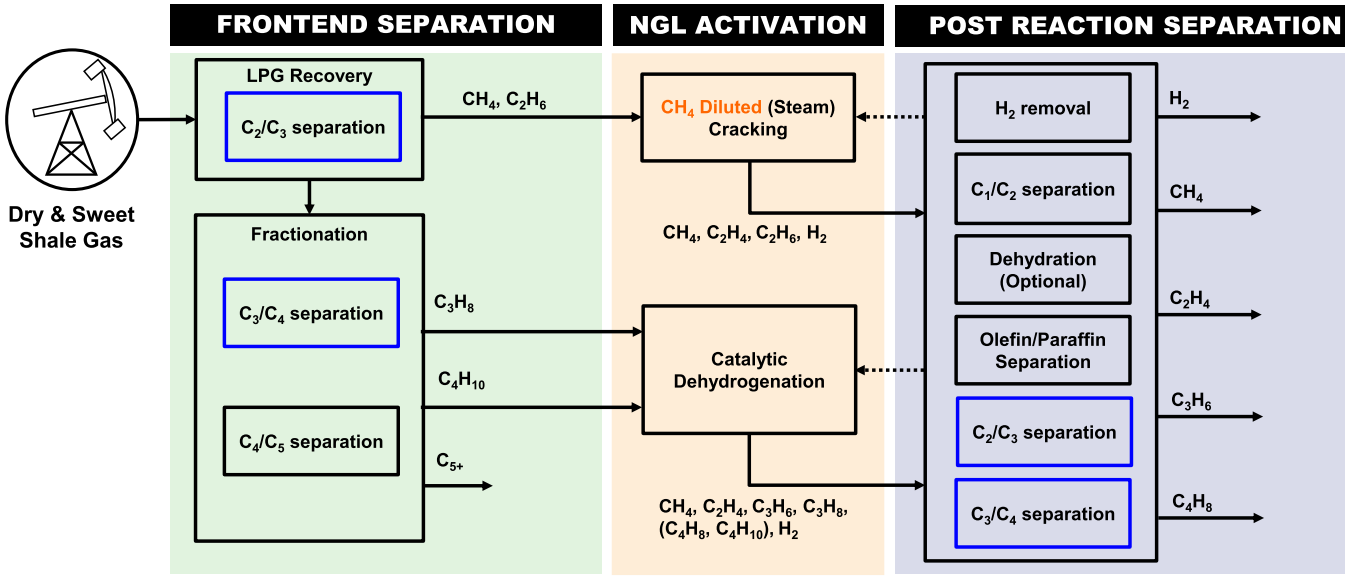


Figure 2. Processing sequence with a CH_4-diluted cracker.

to the steam cracker to decrease the partial pressure of hydrocarbons;[7,9] diluents such as CH_4, N_2, H_2, or steam are also sometimes introduced to catalytic dehydrogenation reactors.[17−20] Consequently, additional separation steps are needed to remove these diluents, which are then recycled and remixed with the reactor feed, contributing significantly to the process complexities and the costs associated with the process. Moreover, several postreaction separations including C_1/C_2 separation, C_2/C_3 separation, and C_3/C_4 separation (as outlined with blue boxes in Figure 1) are repeated separations as they are also performed in the front-end separation step. Due to this duplication of separation steps, more equipment is employed contributing to increased capital expenditure. Systematic process intensification and simplification are needed toward an economical yet efficient process at a small to medium scale.

In this article, we propose an alternative processing sequence, which simultaneously eliminates repeated separation units and enhances conversions in the reactors, resulting in much simpler and intensified processes. The evolution of the process framework is shown through step by step illustrations of block diagrams. Benefits of the new processing sequence are illustrated through Aspen Plus simulations with a 100 million standard cubic feet per day (MMSCFD) feed rate from the Bakken shale gas basin. This size is representative of a shale gas-processing plant, which receives multiple feeds from various shale gas-gathering stations.[21] In a previous publication, we employed a similar change for a small size plant with a 10 MMSCFD feed rate[22] to produce liquid hydrocarbons. In that work, the entire feed is sent to a thermal dehydrogenation unit and then converted into a liquid fuel, with the emphasis on cost and process simplification. However, the concept has the potential to be a generalized process-intensification strategy, hence should not be limited to only one specific feed condition and product. In this work, we extend, explore, and show the benefits of the concept for larger-size shale gas

https://doi.org/10.1021/acssuschemeng.1c05091
ACS Sustainable Chem. Eng. 2021, 9, 13893−13901

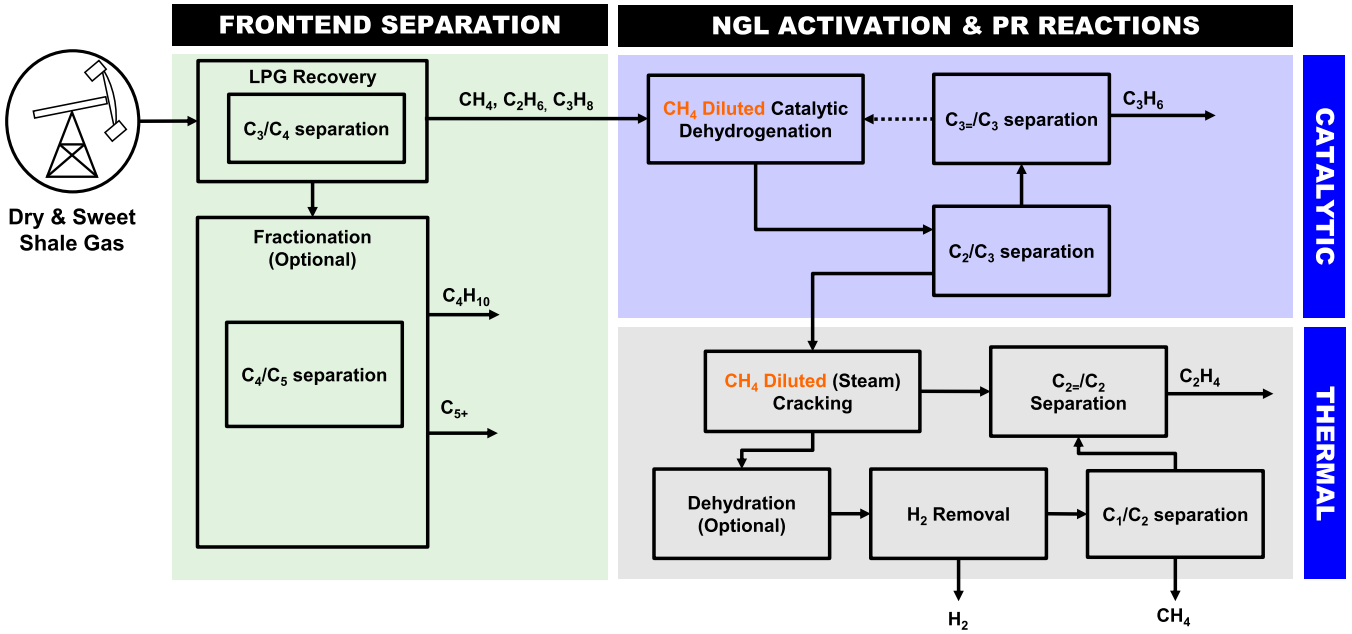


Figure 3. Processing sequence with a CH_4-diluted catalytic dehydrogenation reactor and cracker.

plants to produce individual olefins. These olefins can then be upgraded to diverse fuels and chemicals, which provides greater flexibility and wider application for our processes.

EVOLUTION OF THE PROCESS FRAMEWORK

In this section, the alternative processing sequence is illustrated with a step-by-step evolution of the process framework. The core idea is to delay the front-end separation to the back end, which enables the utilization of CH_4 as a diluent in the cracking and catalytic dehydrogenation reactors and avoids the recycle of any additional diluent to these reactors. The first evolution step is shown in Figure 2. The dry and sweet shale gas feed passes through a C_2/C_3 separation, wherein it is separated into a stream containing CH_4 and C_2H_6, and another stream containing C_{3+} (C_{n+} is used to signify C_n and heavier hydrocarbons). The CH_4 and C_2H_6 mixture stream then passes through a thermal cracker, wherein C_2H_6 is cracked into C_2H_4. CH_4 serves as a diluent in the reactor to decrease the partial pressure of ethane, leading to a high- equilibrium conversion per pass toward C_2H_4. It is worth noting that the introduction of steam could be eliminated if coke formation in the reactor is demonstrated to be either negligible or acceptable without steam. Equipment associated with steam generation, steam preheating, and dehydration would then be eliminated, resulting in a much simpler reactor design. The effluent stream from the cracker passes through a series of purification steps including H_2 removal, C_1/C_2 separations, C_2H_6/C_2H_4 separation, etc.

On the other hand, C_{3+} stream from the C_2/C_3 separation is further fractionated into C_3H_8, C_4H_{10}, and C_{5+}, whereas C_3H_8 and C_4H_{10} are dehydrogenated in catalytic dehydrogenation units individually. The outlet streams of dehydrogenation units are then separated into H_2, olefin product streams, and unconverted paraffin streams, whereas the paraffin streams are recycled back to the dehydrogenation reactors. In both catalytic dehydrogenation reactors, hydrocarbons lighter than the reactive paraffin in the feed are generated as byproducts through cracking. These byproducts have to be separated from olefin products through a series of separation steps, which are often duplications of separations in the front-end. In our new process framework depicted in Figure 2, the front-end C_1/C_2 separation of Figure 1 is delayed to the postreaction step and the duplicated C_1/C_2 separation in Figure 1 is now eliminated. In a previous work reported by He and You,[4] the duplicated C_1/C_2 separation equipment at the backend of Figure 1 is eliminated by recycling the effluent stream from steam cracking to the front-end C_1/C_2 separation. However, such a recycle stream nearly doubles the C_2 concentration in the feed to the demethanizer and requires reseparation of the recycled ethane and ethylene from C_{3+}. This contributes to increased energy demand for separation. Furthermore, the alternative processing sequence provides additional benefit of using CH_4 as the diluent in the cracker to enhance the conversion and selectivity.

In the second evolution step shown in Figure 3, using the same strategy, CH_4 is additionally used as a diluent in the catalytic dehydrogenation reactor. In the process framework of Figure 3, the dry and sweet shale gas first passes through a C_3/C_4 separation, wherein it is separated into a stream containing CH_4, C_2H_6, and C_3H_8, and another stream containing C_{4+}. The CH_4, C_2H_6, and C_3H_8 mixture stream is sent to a catalytic dehydrogenation reactor, wherein CH_4 is a diluent in the reactor to increase the conversion. Additionally, CH_4 also provides a thermal mass to sustain the reactor temperature. Different from steam cracking, where the reactor is operated isothermally in a furnace, catalytic dehydrogenation is performed in a sequence of adiabatic reactor beds with intermediate heating. CH_4 increases the heat capacity of the feed stream and somewhat mitigates the temperature decrease. The effluent stream from the catalytic dehydrogenation reactor is then sent to a C_2/C_3 separation unit and then a C_3H_6/C_3H_8 separation unit (denoted as $C_{3=}/C_3$ separation in Figure 3). Propylene from C_3H_6/C_3H_8 separation is collected as the product, while propane is recycled back to the catalytic dehydrogenation unit. The second stream containing H_2, CH_4, and C_2H_6 from the C_2/C_3 separation unit passes through the CH_4-diluted cracking unit. Optionally, a hydrogen-permeable membrane unit may be used to separate some H_2 from this

https://doi.org/10.1021/acssuschemeng.1c05091
ACS Sustainable Chem. Eng. 2021, 9, 13893−13901

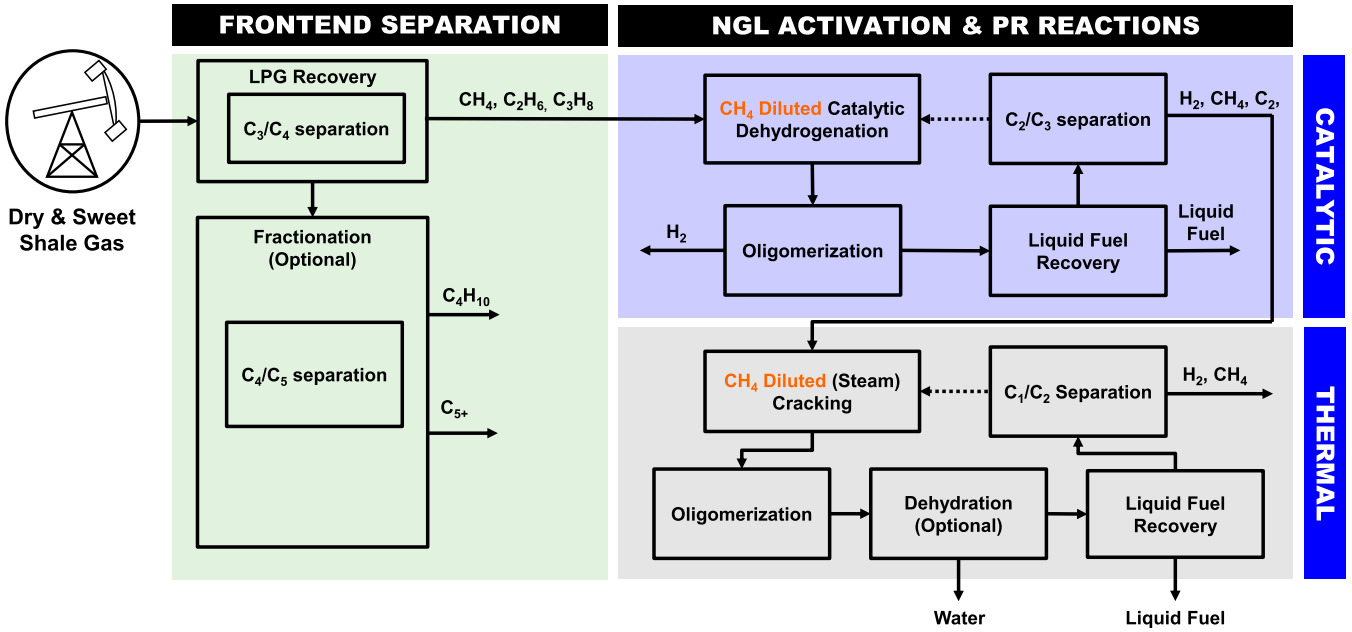


Figure 4. Further extension of the processing sequence in Figure 3 to include downstream upgrading steps.

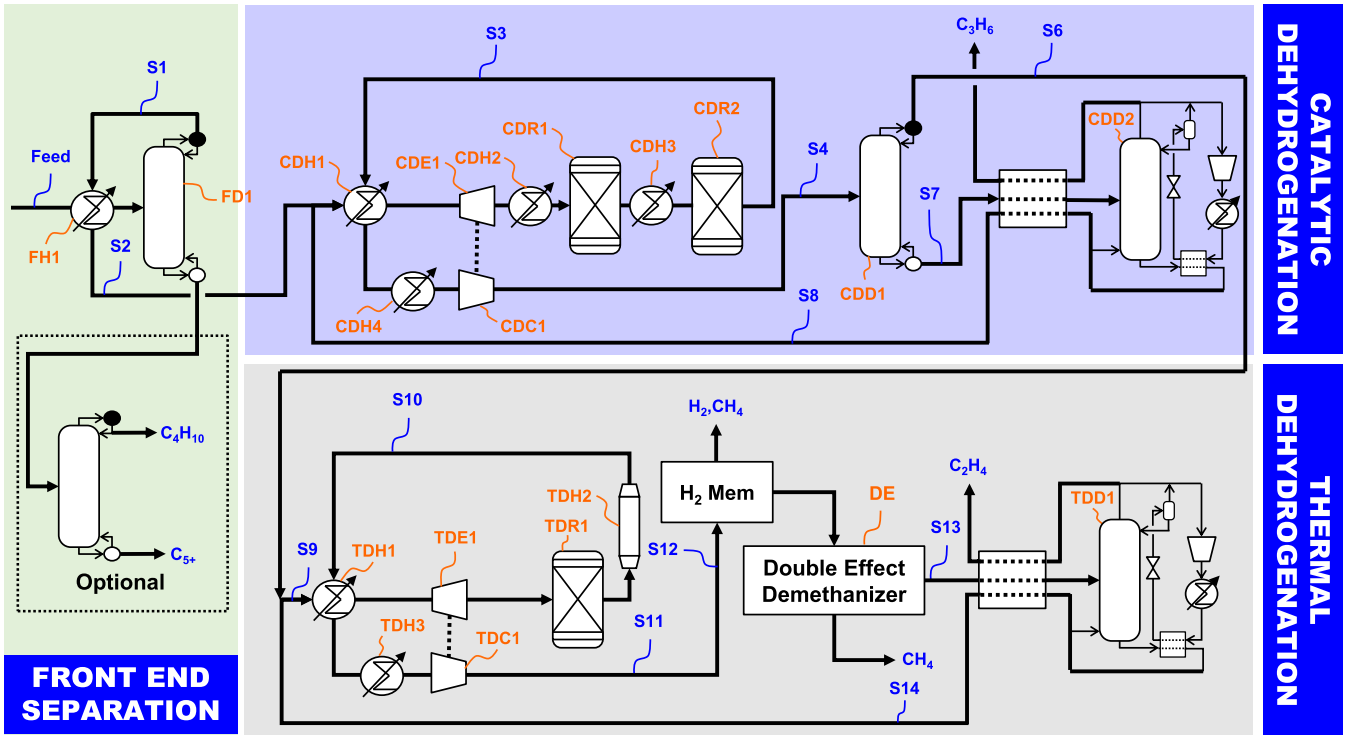


Figure 5. Detailed flowsheet of the process framework in Figure 3.

stream prior to feeding it to the cracking unit. The effluent stream from this cracker then passes through a series of separation steps including dehydration, C_1/C_2 separation, and $C_{2=}/C_2$ separation. This process framework has no repeated separations steps. Meanwhile, conversions in both catalytic dehydrogenation and thermal cracker are enhanced by CH_4 dilution.

The process framework could be further extended to include downstream valorization steps such as oligomerization, alkylation, polymerization, aromatization, etc. In such cases, some or all of the separations at the backend could be eliminated or delayed after the valorization step. Figure 4 shows an exemplary process belonging to this category. An oligomerization unit is used to upgrade olefins into a liquid fuel. In the process depicted in Figure 4, the effluent stream from the catalytic and thermal dehydrogenation reactors is fed to a C_3H_6 oligomerization and a C_2H_4 oligomerization reactor, respectively, without any prior purification step. This is under the notion that an oligomerization catalyst can be paraffin and H_2 tolerant.[23] Paraffin/olefin separations are now eliminated from the system and liquid fuel recovery systems need to be designed instead. Separating the liquid fuel from light olefins

https://doi.org/10.1021/acssuschemeng.1c05091
ACS Sustainable Chem. Eng. 2021, 9, 13893−13901

would be much easier than separating paraffins from their corresponding olefins. Apparently, other downstream process options, including polymerization, alkylation, aromatization, etc., could also be included in the system. Depending on whether paraffins and H_2 are inert in those reactors, the separation of paraffins and H_2 from olefin products may or may not be delayed to the end of the process. Nevertheless, the proposed processing sequence creates a whole new slate of processes, which are worthy of further investigation.

Besides the benefits described above, the proposed processing sequence also opens up an unprecedented opportunity to revisit conventional process-intensification strategies. Most literature studies to intensify this process have focused on the development of alternative technologies and the integration of adjacent unit operations.[6,24−32] For example, Halvorsen et al. studied a dividing wall column configuration for the front-end NGL fractionation. Collins et al.[33] studied the use of a membrane reactor for catalytic dehydrogenation with a pure C_3H_8 feed. However, all these strategies are developed for a conventional processing sequence. Our introduction of alternative processing sequence provides opportunities to revisit and re-examine the benefits of those intensification strategies within the new process flowsheets.

PROCESS SIMULATIONS

Figure 5 depicts a detailed flowsheet resulting from the framework in Figure 3. The flowsheet is simulated in Aspen Plus with general simulation assumptions summarized in Table 1. The feed is assumed to be a 100 MMSCFD dry and sweet shale gas from the Bakken field with its composition, temperature, and pressure listed in Table S1.[4,21]

Table 1. General Assumptions for the Simulations

items	values
equation of state	Peng Robinson
pressure drop across each unit operation	0.21 bar
model for distillation columns	RadFrac
purity and recovery from distillation	99%
efficiency of compressors	72%
temperature approach in cryogenic heat exchangers	3 °C
temperature approach in other heat exchangers	10 °C

Front-End Separation. The sweet and dry shale gas feed, which is at 30 bar and ambient temperature, first passes through a C_3/C_4 separation unit **FD1** in which C_{4+} components are recovered from the bottom of the debutanizer distillation column. C_{4+} components could be directly sold as LPG or, as indicated in Figure 5, be further separated into butane and C_{5+}. The C_{4+} components, if passed through the catalytic dehydrogenation reactor, would be cracked into light hydrocarbons including CH_4, which has a low value as a chemical. The C_{4+} components would also deteriorate performance of the dehydrogenation catalyst and accelerate coke formation in the reactor. Therefore, C_{4+} needs to be separated at the front-end. This debutanizer column requires cooling to about −10 °C in the condenser. Due to the presence of CH_4 in the feed, its condenser temperature is much lower than that in a conventional debutanizer. Nevertheless, this is the only separation step at the front-end of our new process, which is much simpler than the conventional process, wherein a sequence of distillation columns is needed.

CH_4- and C_2H_6-Diluted Catalytic Dehydrogenation. In the catalytic dehydrogenation block, stream **S2** is preheated against the effluent gas **S3** to 600 °C in the heat exchanger **CDH1** and then expanded to 5 bar, before being sent to the dehydrogenation reactors **CDR1** and **CDR2**. After the reaction, the effluent stream is compressed back to 15 bar, to perform the backend C2/C3 separation. Notice that the compression is operated at near ambient temperature, while the expansion is operated at a much higher temperature (around 600 °C), which suffices the expansion to provide work for the compression. The expander and compressor could be a compander running on a common shaft.

To achieve a high conversion and selectivity, the conventional catalytic dehydrogenation is generally operated at a low C_3H_6 partial pressure. The dehydrogenation reactor in the Catofin™ process is operated under vacuum to achieve a low partial pressure,[34] but maintaining safety operation of hydrocarbons under vacuum results in additional cost. Using a diluent has also been proposed by other practitioners, but they all add diluents to the reactor on purpose, resulting in additional equipment cost. For example, a patent application from UOP disclosed a process, whereby diluent methane is added to a pure light paraffin such as propane, butane, or pentane in a molar ratio of diluent to hydrocarbon in a range of 0.1:1 to 3.0:1.[17] The mixture is then sent to the catalytic dehydrogenation unit of the Olefex™ process. However, methane is generally recovered from a demethanizer in the front-end shale gas-processing plant and after the reaction, it needs to be separated again in another demethanizer, which is a duplication of the demethanizer in the front-end shale gas-processing step. In our new process, on the other hand, utilizing CH_4 and C_2H_6 in the shale gas as the diluent avoids the duplication of the demethanizer.

The feed to the catalytic dehydrogenation reactor in our new process is a mixture of CH_4, C_2H_6, and C_3H_8, wherein for the Bakken field feed, the mole fraction of CH_4 and C_2H_6 together is around 80%. Consequently, the partial pressure of C_3H_8 is around 1 bar, similar to the partial pressure in a conventional propane dehydrogenation reactor. The catalytic dehydrogenation reactor is simulated using a kinetic model adapted from Lobera et al.'s work,[35] as shown in Table 2. This kinetic model considers both dehydrogenation and cracking reactions for C_3H_8. While in Lobera et al.'s original model, C_2H_4 hydrogenation is also considered as a side reaction, this reaction is unlikely to take place in our reactor due to the presence of a large amount of C_2H_6. Hence both CH_4 and C_2H_6 are inert in this catalytic dehydrogenation reactor. We

Table 2. Kinetics of Propane Dehydrogenation

propane dehydrogenation	
$C_3H_8 \leftrightarrow C_3H_6 + H_2$	$-r_1 = \frac{k_1(P_{C_3H_8} - (P_{C_3H_6}P_{H_2}/K_{eq}))}{1 + (P_{C_3H_6}/K_{C_3H_6})}$
	$k_1 = k_{01}e^{[-E_{a1}/R(\frac{1}{T}-\frac{1}{T_0})]}$, $K_{C_3H_6} = K_0e^{[-\Delta H/R(\frac{1}{T}-\frac{1}{T_0})]}$
propane cracking	
$C_3H_8 \rightarrow C_2H_4 + CH_4$	$-r_2 = k_2P_{C_3H_8}$
	$k_2 = k_{02}e^{[-E_{a2}/R(\frac{1}{T}-\frac{1}{T_0})]}$

https://doi.org/10.1021/acssuschemeng.1c05091
ACS Sustainable Chem. Eng. 2021, 9, 13893−13901

also assume the coke formation and catalyst deactivation are negligible. The parameter values of this model are listed in Table S2.

The outlet stream **S3** of the catalytic dehydrogenation, which mainly consists of H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, and C_3H_6, is cooled to near ambient temperature in the heat exchangers **CDH1** and **CDH4** and then compressed to 15 bar. The compressed stream **S4** is sent to a distillation column **CDD1** to separate C_3H_8 and C_3H_6 from other light components. Stream **S7** containing C_3H_8 and C_3H_6 then passes through a heat pump-assisted C_3H_6/C_3H_8 splitter **CDD2**. Propylene from this splitter is collected as the product and propane is recycled back to the catalytic dehydrogenation reactor. It is worth noting that the catalytic dehydrogenation and its post reaction separations are subject to further process intensification using conventional strategies. For example, a membrane reactor could be used for catalytic dehydrogenation to further increase the conversion; dividing wall columns and membrane cascade could be used for C_3H_6/C_3H_8 and C_2H_6/C_3H_8 separations.[36,37]

Thermal Dehydrogenation. In the thermal dehydrogenation block, similarly, stream **S9** is first preheated to 600 °C then expanded to 3 bar in the expander. The expanded stream is then sent to a thermal dehydrogenation unit operating at 850 °C. The thermal dehydrogenation reactor is simulated using the C_2H_6 pyrolysis kinetics proposed by Sundaram and Froment.[38] Again CH_4 is a diluent in the reactor, which increases the conversion and selectivity of the reactor. The effluent stream of the reactor is quenched to 600 °C in a transferline heat exchanger **TDH2** to avoid side reactions.

The cooled and compressed stream **S11** then passes through a series of separation steps consisting of a H_2 membrane unit, a double effect demethanizer, and a C_2H_6/C_2H_4 splitter for product purification. A H_2-rich stream is collected from the permeate side of the membrane unit and used as a fuel gas for the catalytic dehydrogenation and thermal cracker. The H_2 membrane is operated at such a stage that 99% H_2 recovery is achieved. Although the single-membrane unit cannot simultaneously achieve high recovery and purity, allowing a portion of CH_4 permeating through the membrane is acceptable. This portion of CH_4 will be used as a fuel gas together with H_2. On the contrary, in the conventional process, whereas the feed to the H_2 removal unit only contains H_2 and C_{2+}, a portion of C_2H_6 has to permeate, to achieve a high recovery of H_2, resulting in the loss of olefin products.

The rejected (high-pressure) stream from the membrane unit mainly consists of CH_4, C_2H_6, and C_2H_4, and it is sent to a demethanizer consisting of double effect distillation columns (See Figure 6). In this double effect configuration, the feed is first cooled to −69 °C in the main heat exchanger by transferring heat from the feed to the product streams. The cooled stream is sent to the bottom of a high-pressure distillation column (HP) operated at 30 bar. A portion of the vapor from the top of the column is recovered as HP CH_4 and the remaining vapor is condensed by boiling the C_{2+} liquid at the bottom of a low-pressure distillation column (LP) operating at 1.5 bar. A portion of the condensed CH_4 stream is returned as reflux to the HP column and the remaining portion is subcooled in a heat exchanger, reduced in pressure across a Joule-Thompson valve and fed as the top reflux to the LP column. Similarly, the bottom liquid from the HP column is fed at an intermediate location of the LP column. Due to the low pressure in the LP column, its bottom temperature is lower

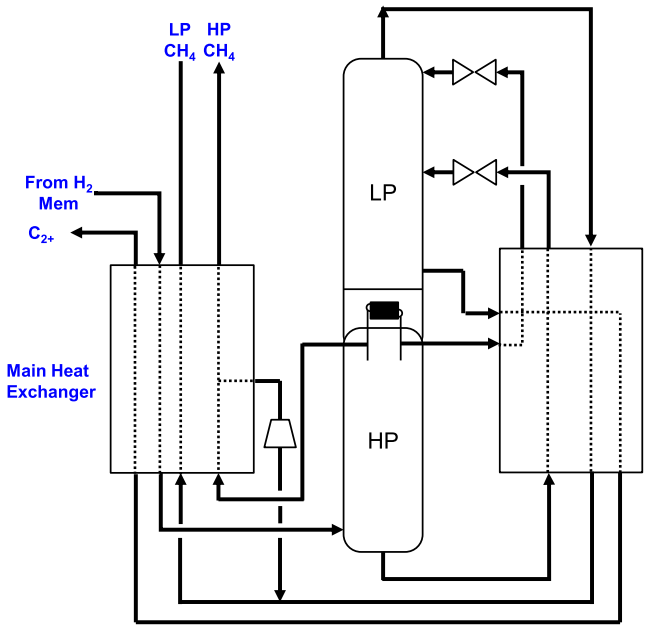


Figure 6. Double effect demethanizer configuration.

than the condenser temperature of the high-pressure column, hence its reboiler is heat integratable with the high-pressure condenser. The double effect column configuration is a very efficient and widely used configuration for air separation,[39] however, its application in shale gas separation is rare. This is because the difference in the boiling points between the light component N_2 and heavy component O_2 in the air separation is much lower compared to the corresponding difference between the boiling points of the lightest and heaviest components in the shale gas, hence it is hard to use the pressure difference to achieve the thermal integration. In our novel process design, C_{3+} is separated in advance, so that the temperature difference between the light and heavy components is narrowed down. The double effect column can achieve 99% purity and recovery of C_2H_6 and C_2H_4 from CH_4, while the conventional scheme only achieves 90% ∼ 95% C_{2+} recovery. As the convetional process utilizes a turboexpander to provide the reflux to the cryogenic distillation column, the recovery is limited by the maximum liquid fraction allowable in the turboexpander.[40]

RESULTS AND DISCUSSION

The simulation results of our new process depicted in the previous section (Figure 5) and the conventional process (Figure S1) are summarized in Table 3. The conventional process follows the processing sequence depicted in Figure 1. A brief description of this conventional process is provided in the Appendix. For the same 100 MMSCFD feed, our new process produces 407.2 kg/min ethylene and 315.8 kg/min propylene, which are 9.8 and 10.5% higher than the conventional process. In addition to a much higher olefin yield, the new process has a 75.9 million dollars total capital cost, which is 6.8% lower than the conventional process. Consequently, the capital cost per unit olefin products of our new process is 21.9% lower than the conventional configuration. Besides the cost reduction, our new process also shows significant advantages in terms of energy consumption. The fuel consumption per unit product of our new process, which is mainly due to the heat requirement of catalytic and thermal

https://doi.org/10.1021/acssuschemeng.1c05091
ACS Sustainable Chem. Eng. 2021, 9, 13893−13901

Table 3. Summary of Our New Process and the Conventional Process

flowsheets	our new process	conventional process
feed flowrate	100 MMSCFD	100 MMSCFD
ethylene product flowrate	407.2 kg/min	370.9 kg/min
propylene product flowrate	315.8 kg/min	285.7 kg/min
capital cost (unit product)	0.105 MM/(kg/min)	0.128 MM/(kg/min)
fuel consumption (unit product)	6.11 KBTU/kg	6.61 KBTU/kg
electricity (unit product)	0.74 MJ/kg	1.09 MJ/kg
refrigerants (unit product)	−10 °C, 0.50 MJ/kg	7 °C, 0.61 MJ/kg
	−71 °C, 0.60 MJ/kg	−56 °C, 0.37 MJ/kg

dehydrogenation reactors, is 8% lower than the conventional process. The electricity per unit product, which is mainly used for compressors and pumps, is 47% lower than the conventional process, due to the fact that the dehydrogenation reactors of our new process are operated at much higher pressures than the ones in the conventional process. The only metric, which is higher for the new process is the refrigerant requirements, which are needed for C2/C3 separation and C3/C4 separations. Especially for the backend C2/C3 separation, our new process has a cooling duty of 0.60 MJ/kg at −71 °C, which is at a lower temperature and a higher duty than its counterpart for the conventional process. Nevertheless, it is a reasonable trade-off considering the dramatic simplification and cost reduction of the entire process.

Figure 7 shows the capital cost distribution of different blocks for the new process and the conventional process. The major cost saving comes from the front-end block. In the conventional process, the feed shale gas is separated into a natural gas stream, a C_2H_6 stream, a C_3H_8 stream, and a C_{4+} stream using a demethanizer, a de-ethanizer, and a depropanizer in the front-end block. However, in the new process, only one depropanzier is needed to separate C_{4+} from the rest of the components, while the front-end demethanizer and de-ethanizer are eliminated, leading to a $ 13 MM cost saving. The costs of individual unit operations are shown in Tables S3 and S4.

From the simulations and cost analysis results above, we can conclude several general principles for process synthesis and intensification: when a feed mixture contains inert components and has constituents that are also created in downstream processing, which must be separated downstream, then one should carefully evaluate the merit of (1) avoiding upstream separation of the constituents from the feed mixture, and (2) arranging the processing sequence so the duplication of separation between any two components is avoided. Furthermore, potential advantages of the inert in the feed for the downstream endothermic reactions, which are unfavored according to the Le Chatelier's principle, should be carefully explored against the increase in the cost due to an increase in the equipment size. Clearly, our shale gas processing is one such example. An example of where the suggested sequence is not applicable is coal gasification with O_2. This is an exothermic reaction, and N_2 from air should be separated to decrease the equipment size, compression cost, etc (and N_2 is not a byproduct of coal gasification). However, if NH_3 is to be produced via this process, one may not perform upstream air separation.

CONCLUSIONS AND OUTLOOK

An alternative processing sequence is applied to the natural gas liquid to light olefin process. The alternative processing sequence creates a new slate of processes, which are much simpler and more intensified than the conventional process. Various resulting process-intensification concepts for our new process are summarized in Table 4. In the front-end separation section, both cryogenic demethanizer and C_2/C_3 separations, which are duplication of back end separations, are eliminated. In the NGL activation section, because CH_4 is used as a diluent in the catalytic dehydrogenation and a thermal cracker, the performance of the reactors is enhanced. Moreover, steam injection could be eliminated, resulting in the elimination of its associated equipment including water conditioning and generation, etc. In the postreaction section, dehydration could be eliminated due to the elimination of the steam injection. For H_2 separation, a simpler membrane unit is used, which can achieve 99% H_2 purity without much loss of C_{2+}. For demethanization, a more efficient double effect distillation column configuration is designed.

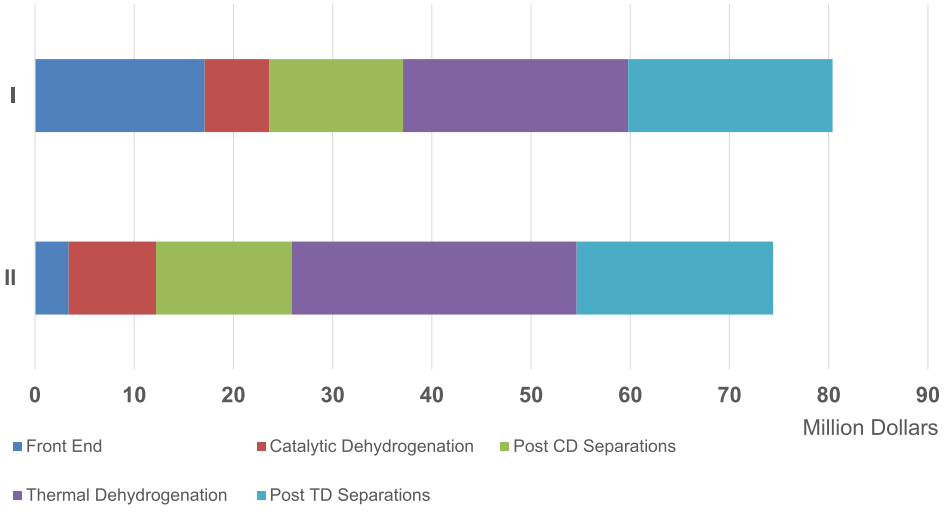


Figure 7. Cost breakdown of the conventional process (I) and the new process with the proposed processing sequence (II).

https://doi.org/10.1021/acssuschemeng.1c05091
ACS Sustainable Chem. Eng. 2021, 9, 13893−13901

Table 4. Unit Operations in Conventional Processes and Their Corresponding Process Intensification in the New Process

unit operations	process intensification
front-end separation	
cryogenic demethanizer	eliminated
C_2/C_3 Separation	eliminated
NGL activation	
water conditioning and generation	optional
steam cracker	simpler thermal dehydrogenation
catalytic dehydrogenation	CH_4-diluted catalytic dehydrogenation
postreaction separation	
dehydration	optional
H_2 removal	membrane
demethanizer	double effect configuration

Our process simulations for the new 100 MMSCFD shale gas NGLs to olefin plant show that as compared to a plant based on a conventional processing sequence in addition to the process intensification and simplification, the new process has the potential to provide a higher olefin yield (9.8% increase for ethylene and 10.5 for propylene), consumes less fuel (by 8%), demands a lower power (by 47%), and requires a lower capital. The capital cost reduction per unit of olefin products is estimated to be ∼ 22% lower than the conventional process.

It is worth noting that this work not only creates novel shale gas process flowsheets, but the resulting underlying general principles discussed above also have the potential to provide an important process-intensification concept, which expands the flowsheet search space for process engineers to investigate. In our future work, we plan to extend this concept to other reaction separation networks, where novel processes can be generated through the new processing sequence of the various separation and reaction steps. The proposed shale gas process and the known processes could also be represented as a superstructure. We do plan to perform a superstructure-based optimization framework to systematically determine the optimal process design for shale gas application.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c05091.

Representative Bakken field shale gas process parameters; parameter values for the kinetic equation in Table 2; detailed flowsheet of the conventional process scheme; equipment list of our new process in Figure 5; and equipment list of the conventional process in Figure S1 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Rakesh Agrawal − *Davidson School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47906, United States;* orcid.org/0000-0002-6746-9829; Phone: +1 765 586 7259; Email: agrawalr@purdue.edu

Author

Zewei Chen − *Davidson School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47906, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.1c05091

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the National Science Foundation under Cooperative agreement no. EEC-1647722 for funding.

■ REFERENCES

(1) Chaudhuri, U. R. *Fundamentals of Petroleum and Petrochemical Engineering*; CRC Press, 2016, pp 101−102.

(2) Siirola, J. J. The impact of shale gas in the chemical industry. *AIChE J.* **2014**, *60*, 810−819.

(3) Chen, Q.; Dunn, J. B.; Allen, D. T. Aggregation and allocation of greenhouse gas emissions in oil and gas production: Implications for life-cycle greenhouse gas burdens. *ACS Sustainable Chem. Eng.* **2019**, *7*, 17065−17073.

(4) He, C.; You, F. Shale gas processing integrated with ethylene production: novel process designs, exergy analysis, and techno-economic analysis. *Ind. Eng. Chem. Res.* **2014**, *53*, 11442−11459.

(5) Getu, M.; Mahadzir, S.; Long, N. V. D.; Lee, M. Techno-economic analysis of potential natural gas liquid (NGL) recovery processes under variations of feed compositions. *Chem. Eng. Res. Des.* **2013**, *91*, 1272−1283.

(6) Halvorsen, I. J.; Dejanović, I.; Maråk, K. A.; Olujić, Ž.; Skogestad, S. Dividing-Wall Column for Fractionation of Natural Gas Liquids in Floating Liquefied Natural Gas Plants. *Chem. Eng. Technol.* **2016**, *39*, 2348−2354.

(7) Sabbe, M. K.; Van Geem, K. M.; Reyniers, M.-F.; Marin, G. B. First principle-based simulation of ethane steam cracking. *AIChE J.* **2011**, *57*, 482−496.

(8) Grace Chan, K. Y.; Inal, F.; Senkan, S. Suppression of coke formation in the steam cracking of alkanes: ethane and propane. *Ind. Eng. Chem. Res.* **1998**, *37*, 901−907.

(9) van Goethem, M. W. M.; Barendregt, S.; Grievink, J.; Verheijen, P. J. T.; Dente, M.; Ranzi, E. A kinetic modelling study of ethane cracking for optimal ethylene yield. *Chem. Eng. Res. Des.* **2013**, *91*, 1106−1110.

(10) Weckhuysen, B. M.; Schoonheydt, R. A. Alkane dehydrogenation over supported chromium oxide catalysts. *Catal. Today* **1999**, *51*, 223−232.

(11) Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. Catalytic dehydrogenation of light alkanes on metals and metal oxides. *Chem. Rev.* **2014**, *114*, 10613−10653.

(12) Biloen, P.; Dautzenberg, F.; Sachtler, W. Catalytic dehydrogenation of propane to propene over platinum and platinum-gold alloys. *J. Catal.* **1977**, *50*, 77−86.

(13) Hu, B.; Schweitzer, N.M.; et al. Selective propane dehydrogenation with single-site CoII on SiO2 by a non-redox mechanism. *J. Catal.* **2015**, *322*, 24−37.

(14) Sahebdelfar, S.; Ravanchi, M. T.; Tahriri Zangeneh, F.; Mehrazma, S.; Rajabi, S. Kinetic study of propane dehydrogenation and side reactions over Pt−Sn/Al2O3 catalyst. *Chem. Eng. Res. Des.* **2012**, *90*, 1090−1097.

(15) Frey, F. E.; Huppke, W. F. Equilibrium dehydrogenation of ethane, propane, and the butanes. *Ind. Eng. Chem.* **1933**, *25*, 54−59.

(16) Elvidge, C.; Ziskin, D.; Baugh, K.; Tuttle, B.; Ghosh, T.; Pack, D.; Erwin, E.; Zhizhin, M. A fifteen year record of global natural gas flaring derived from satellite data. *Energies* **2009**, *2*, 595−622.

(17) Leonard, L. E.; Bozzano, A. G.; Towler, G. P. Hydrocarbon dehydrogenation with inert diluent. US Patent 13/328,931, 2013.

(18) Sundaram, K. M.; Fernandez-Baujin, J. M. Effect of methane and hydrogen during thermal cracking of light hydrocarbons. *AIChE J.* **1988**, *34*, 321−325.

(19) Leesemann, C. J. Process for dehydrogenation of hydrocarbons in the presence of a gaseous diluent. US Patent 2,461,331, 1949.

(20) Gami, A. C. Use of hydrocarbon diluents to enhance conversion in a dehydrogenation process at low steam/oil ratios. US Patent 14,052,949, 2014.
(21) We acknowledge guidance from Professor David Allen of University of Texas, Austin for our choice of plant size.
(22) Chen, Z.; Li, Y.; Oladipupo, W. P.; Rodriguez Gil, E. A.; Sawyer, G.; Agrawal, R. Alternative ordering of process hierarchy for more efficient and cost-effective valorization of shale resources. *Cell Rep. Phys. Sci.* **2021**, 100581.
(23) Miller, J. T.; Zhang, G. Phosphate-promoted nickel catalyst for high temperature oligomerization. US Patent No. 11,084,023. August 10, 2019.
(24) Semenova, S. I. Polymer membranes for hydrocarbon separation and removal. *J. Membr. Sci.* **2004**, *231*, 189−207.
(25) Dong, J.; Lin, Y. S.; Liu, W. Multicomponent hydrogen/hydrocarbon separation by MFI-type zeolite membranes. *AIChE J.* **2000**, *46*, 1957−1966.
(26) Lokhandwala, K. A.; Baker, R. W. Hydrogen/hydrocarbon separation process, including PSA and membranes. 6,592,749 B1, 2003.
(27) Arruebo, M.; Coronas, J.; Menéndez, M.; Santamaría, J. Separation of hydrocarbons from natural gas using silicalite membranes. *Sep. Purif. Technol.* **2001**, *25*, 275−286.
(28) Cavani, F.; Ballarini, N.; Cericola, A. Oxidative dehydrogenation of ethane and propane: How far from commercial implementation? *Catal. Today* **2007**, *127*, 113−131.
(29) Kung, H. H. *Advances in Catalysis*; Elsevier, 1994; Vol. *40*, pp 1−38. DOI: 10.1016/S0360-0564(08)60655-0.
(30) Mamedov, E. A.; Cortés Corberán, V. Oxidative dehydrogenation of lower alkanes on vanadium oxide-based catalysts. The present state of the art and outlooks. *Appl. Catal., A* **1995**, *127*, 1−40.
(31) Gong, J.; You, F. Resilient design and operations of process systems: Nonlinear adaptive robust optimization model and algorithm for resilience analysis and enhancement. *Comput. Chem. Eng.* **2018**, *116*, 231−252.
(32) Jiang, Z.; Chen, Z.; Huff, J.; Shenvi, A. A.; Tawarmalani, M.; Agrawal, R. Global minimization of total exergy loss of multicomponent distillation configurations. *AIChE J.* **2019**, *65*, No. e16737.
(33) Collins, J. P.; Schwartz, R. W.; Sehgal, R.; Ward, T. L.; Brinker, C. J.; Hagen, G. P.; Udovich, C. A. Catalytic dehydrogenation of propane in hydrogen permselective membrane reactors. *Ind. Eng. Chem. Res.* **1996**, *35*, 4398−4405.
(34) Seo, S.-T.; Won, W.; Lee, K. S.; Jung, C.; Lee, S. Repetitive control of CATOFIN process. *Korean J. Chem. Eng.* **2007**, *24*, 921−926.
(35) Lobera, M. P.; Téllez, C.; Herguido, J.; Menéndez, M. Transient kinetic modelling of propane dehydrogenation over a Pt−Sn−K/Al2O3 catalyst. *Appl. Catal., A* **2008**, *349*, 156−164.
(36) Chen, Z.; Agrawal, R. Classification and comparison of dividing walls for distillation columns. *Processes* **2020**, *8*, 699.
(37) Chavez Velasco, J. A.; Tumbalam Gooty, R.; Tawarmalani, M.; Agrawal, R. Optimal design of membrane cascades for gaseous and liquid mixtures via MINLP. *J. Membr. Sci.* **2021**, *636*, 119514.
(38) Sundaram, K. M.; Froment, G. F. Modeling of thermal cracking kinetics—I: Thermal cracking of ethane, propane and their mixtures. *Chem. Eng. Sci.* **1977**, *32*, 601−608.
(39) Agrawal, R.; Thorogood, R. M. Production of medium pressure nitrogen by cryogenic air separation. *Gas Sep. Purif.* **1991**, *5*, 203−209.
(40) Ridha, T.; Li, Y.; Gençer, E.; Siirola, J.; Miller, J.; Ribeiro, F.; Agrawal, R. Valorization of shale gas condensate to liquid hydrocarbons through catalytic dehydrogenation and oligomerization. *Processes* **2018**, *6*, 139.

https://doi.org/10.1021/acssuschemeng.1c05091
ACS Sustainable Chem. Eng. 2021, 9, 13893−13901