

VOL. 61, 2017



DOI: 10.3303/CET1761258

#### Guest Editors: Petar S Varbanov, Rongxin Su, Hon Loong Lam, Xia Liu, Jiří J Klemeš Copyright © 2017, AIDIC Servizi S.r.I. **ISBN** 978-88-95608-51-8; **ISSN** 2283-9216

# Process Design and Analysis of Ethylene and Propylene Manufacturing from Shale Gas

## Minbo Yang<sup>a</sup>, Fengqi You<sup>b,\*</sup>

<sup>a</sup>Northwestern University, Evanston, Illinois, 60208, USA <sup>b</sup>Cornell University, Ithaca, New York 14853, USA fengqi.you@cornell.edu

In this paper, we develop two novel process designs for manufacturing ethylene and propylene from shale gas. In the first process design, raw shale gas is processed to produce the mixture of ethane-propane, which is then stream co-cracked to produce ethylene and propylene. In the second process design, ethane and propane are produced from shale gas separately; then, ethylene is mainly produced via the steam cracking of ethane, and propylene is mostly manufactured via the dehydrogenation of propane. We also consider a conventional naphtha cracking design, in order to compare the economic and environmental performance of manufacturing ethylene and propylene from shale gas with from naphtha. All process designs are modeled and simulated in Aspen HYSYS to obtain the mass and energy balances. On this basis, we conduct a comparative techno-economic and environmental analysis. The economic analysis indicates that the two proposed designs results in much lower production costs for ethylene and propylene than the conventional naphtha cracking design. However, in terms of life cycle GHG emissions, manufacturing ethylene and propylene and propylene is more attractive.

#### 1. Introduction

Ethylene and propylene are important building blocks for the manufacturing of various chemicals. In the U.S., steam cracking of hydrocarbons is the leading technology applied for producing ethylene, and nearly half of propylene is produced as a byproduct from steam crackers. In recent years, advances in drilling and fracturing technologies leads to a boom of shale gas production in the U.S. (Gao et al., 2017). With extra supply of natural gas liquids (NGLs) derived from shale gas, the production of ethylene and propylene from shale gasbased feedstocks, instead of from naphtha, is of particular interest (Jenkins, 2014). There are some recent publications addressing the process design and synthesis for manufacturing olefins from shale gas via ethane steam cracking (He et al., 2014) and methane oxidative coupling (He et al., 2015). Besides, an intensified process design for manufacturing olefins from shale gas was recently presented (Gong et al., 2017). However, these contributions only focus on the production of ethylene from shale gas and do not explore the economics of manufacturing propylene from shale gas. Environmental impacts of manufacturing olefins from shale gas are of particular interest. Greenhouse gas (GHG) emissions is a big concern for the shale gas life cycle (Gao et al., 2015a), although upstream shale gas processing and downstream shale gas processing are typically controlled by different stakeholders (Gao et al., 2017). In addition, considerable consumption of heat and refrigeration for downstream shale gas processing (He et al., 2016) and olefins manufacturing (Arvidsson et al. 2015) also leads to significant amounts of GHG emissions. With different feedstocks, there are concerns on which one is more attractive regarding economics and environmental impacts. Thus, systematic comparisons of producing ethylene and propylene from shale gas and naphtha under the same conditions are necessary. We propose two novel process designs for manufacturing ethylene and propylene from shale gas, based on the steam co-cracking of ethane-propane technology, respectively. We also consider a conventional process design in which ethylene and propylene are produced by the steam cracking of naphtha. We perform detailed process simulation and a comparative techno-economic and environmental analysis for the three designs. Finally, production costs and life cycle GHG emissions of ethylene and propylene are explored and compared.

1561

### 2. Process description

In this work, shale gas from Marcellus region in the U.S. is analysed for the production of ethylene and propylene, as olefins projects in this region are drawing particular interest. The composition of raw shale gas is given in Table 1. A co-cracking design and a technology integrated design for making ethylene and propylene from shale gas are developed. Each design includes shale gas processing and olefins manufacturing stages.

Table 1: Compositions of key process streams of shale gas processing (Laurenzi and Jersey, 2013).

Composition (mol%)	Raw shale gas	Pipelines gas	NGLs	Ethane	Propane
CH <sub>4</sub>	79.4	90.2	0.37	0.54	0
C <sub>2</sub> H <sub>6</sub>	16.1	9.0	68.61	99.41	2.17
C <sub>3</sub> H <sub>8</sub>	4.0	0.3	31.01	0.05	97.83
N <sub>2</sub>	0.4	0.5	0	0	0
CO <sub>2</sub>	0.1	0.01	0	0	0



Figure 1: Process flowsheets of shale gas processing stage.

Figure 1 shows the process flowsheets for the processing of Marcellus shale gas, which consists of five sections: acid gas removal, dehydration, NGLs recovery, compression, and NGLs fractionation. Figure 1(a) shows a monoethanolamine (MEA)-based absorption unit to remove acid gas. Raw shale gas is fed into the bottom of an absorber (T-101) and contacts with a lean MEA solution from the top of the absorber to remove acid gas. The rich MEA solution from the bottom of the absorber T-101 is fed into a stripper (T-102) for regeneration. After removing acid gas, the sweet gas is water-saturated. Water must be removed to prevent hydrate formation in the cryogenic separation process. Figure 1(b) shows a triethylene glycol (TEG)-based process for water removal. The sweet gas enters an absorber (T-201) from the bottom and contacts with a lean TEG stream. The rich TEG stream from the absorber T-201 is introduced into a distillation tower (T-202) for TEG regeneration. The lean TEG stream from the bottom of tower T-202 is sent to a stripper (T-203) to further reduce the water content. Most of the dried gas is introduced into an NGLs recovery section, as shown in Figure 1(c). In the NGLs recovery section, the dry gas is first cooled in a cold box. The gas product from the separator V-301 flows through an expander (EX-301) to further lower its temperature, and then it enters another separator V-302. Liquid products from separators V-301 and V-302 are introduced into a demethanizer (T-301). Gas products from the separator V-302 and the demethanizer T-301 are methane-rich. These two streams are merged and then sent to the compression section, as shown in Figure 1(d). The NGLs product from the demethanizer T-301 is then introduced into an NGLs fractionation unit as shown in Figure 1(e), where it is separated into ethane and propane (see Table 1). Note that in the co-cracking design, since ethylene and propylene are produced via the steam cracking of ethane-propane mixture, the NGLs fractionation section is excluded at the shale gas processing stage.

1562





Figure 2: Process flowsheet of olefins manufacturing stage in the co-cracking design.

The process flowsheets of olefins manufacturing stage in the co-cracking design are shown in Figure 2. The mixture of ethane and propane sourced from shale gas is steam co-cracked in cracking furnaces. The reaction scheme for the steam co-cracking of ethane-propane mixture is taken from existing literature (Sundaram and Froment, 1977), and a mass-based hydrocarbons-to-steam ratio of 1:0.4 is considered. The cracking gas is first cooled in heat exchangers E-501 and E-502 and then cooled to 40 °C in a quench tower. Next, the cracking gas is pressurized to 3.7 MPa via a five-stage compressor. During compression, the temperature of cracking gas is controlled below 100 °C by intermediate coolers to prevent olefin polymerization. Acid components in the cracking gas are removed in the caustic tower, and water content is reduced in a molecular sieve dryer that is modelled as a component splitter in the simulation. Sequentially, the cracking gas is further cooled and pre-separated in a series of cold boxes. Liquid products from separators V-501~V-504 are fed into a demethanizer (T-503), where methane and hydrogen in the liquid phase are removed. The bottom product of the demethanizer T-503 is nearly methane-free and is introduced into a deethanizer (T-504). After being mixed with some hydrogen-rich gas, the gas product from the deethanizer T-504 is introduced into a hydrogenator (R-501), where acetylene is reacted with hydrogen and converted into ethylene or ethane. The gas product from hydrogenator R-501 is fed into a C<sub>2</sub> splitter (T-509) with 120 trays. The ethylene product with a purity of 99.9% is drawn from the 9<sup>th</sup> tray of C<sub>2</sub> splitter. The gas product from the top of C<sub>2</sub> splitter is ethylene-rich and is further cooled to reduce the amount of gas recycled to be recompressed. The liquid product from the separator V-506 is routed to the 1<sup>st</sup> tray of C<sub>2</sub> splitter. Ethane from the bottom of C<sub>2</sub> splitter is recycled as a feed of cracking furnaces. The liquid product from the bottom of the deethanizer T-504 is fed to a depropanizer (T-505). The overhead product of the depropanizer T-505 is sent to a  $C_3$  splitter (comprising columns T-506 and T-507). Polymer-grade propylene is obtained from the top of column T-506. Propane from the bottom of column T-507 is fed into cracking furnaces. Last, a debutanizer (T-508) is used to separate the bottom product from the depropanizer T-505 into C<sub>4</sub> mixture and C<sub>5+</sub>.

The olefins manufacturing stage in the technology integrated design is shown in Figure 3. Ethane is sent to the ethane steam cracking section that is similar to the steam cracking section depicted in Figure 2. The reaction scheme used for ethane steam cracking is taken from existing literature (Sundaram and Froment, 1977). Propane is fed into propane dehydrogenation reactors (R601~R604) after being heated (Gu et al., 2016). Hydrogen is injected into the propane feed to reduce the coke formation with a mole-based hydrogen-

to-hydrocarbons ratio of 0.6:1. The kinetic model for propane dehydrogenation is taken from a literature source (Chin et al., 2011). After being cooled, compressed, and dried, the reactor effluent is introduced into a deethanizer (T-601). The ethane-rich gas from the overhead of deethanizer T-601 is taken as a feed of cracking furnaces. The bottom product of the deethanizer T-601 is introduced into a depropanizer. Note that the rest of the separation unit is similar to that described in Figure 2 excluding a debutanizer. After being purified by pressure swing adsorption, part of hydrogen is injected into the propane feed as aforementioned.



Figure 3: Process flowsheet of olefins manufacturing stage in the technology integrated design.

In addition to the two novel process designs for manufacturing ethylene and propylene from shale gas, we also consider a conventional process design for manufacturing ethylene and propylene from naphtha. The reaction scheme used for naphtha cracking is taken from (Kumar and Kunzru, 1985), where naphtha is represented as a pseudo-pure compound. A steam-to-naphtha ratio of 0.5:1 is applied. The naphtha cracking section is similar to that shown in (Burn, 2011), and the olefins separation section is similar to that descried in Figure 2. Thus, the process flowsheet of the naphtha cracking design is not depicted in this paper.

#### 3. Results and discussion

In this work, we consider a production scale of 1 Mt/y ethylene (8,000 h/y). The three introduced process designs are modelled and simulated in Aspen HYSYS 7.2. The chosen thermodynamic methods for acid gas removal, dehydration, and other sections are Amine Pkg-KE, Glycol package, and Peng-Robinson, respectively. The mass and energy balances of the three designs are obtained as given in Table 2. As can been seen from Table 2, the co-cracking design, technology integrated design, and naphtha cracking design result in propylene-to-ethylene ratios of 0.23, 0.70, and 0.41, respectively. It means that there exists a propylene gap if shifting feedstocks from naphtha to ethane-propane mixture for steam crackers. However, the propylene gap can be addressed by the integration of ethane steam cracking and propane dehydrogenation. Note that the co-cracking design and the technology integrated design require external fuel, which is considered as the methane-rich gas produced at shale gas processing stages in the following analysis.

We next evaluate the production costs of manufacturing ethylene and propylene from wet shale gas. The total production cost can be estimated as the sum of direct manufacturing costs, plant overhead, fixed costs, and general expenses (Seider et al, 2009). Aspen Process Economic Analyzer 7.2 is employed to evaluate the total production cost. The annual production costs of shale gas processing stages associated with the co-cracking design and the technology integrated design are estimated as \$1,210.2 M, and \$1,546.7 M, respectively. As multiple products are produced at the stage of shale gas processing, cost allocation is employed based on economic values. The production cost for ethane-propane mixture is estimated as \$221.8 /t, and production costs for ethane and propane are estimated as \$145.8 /t and \$337.3 /t, respectively.

annual production costs of olefins manufacturing stages in the co-cracking design, the technology integrated design, and the naphtha cracking design are estimated as \$510.0 M, \$701.4 M, and \$1,489.1 M, respectively. On this basis, production costs of ethylene and propylene are evaluated and compared in Figure 4. It can be seen that the technology integrated design results in the lowest production costs and the naphtha cracking design does the highest.

	Co-cracking design	Technology integrated design	Naphtha cracking design
Shale gas processing stage			
Input			
Shale gas, kmol/h	47,790	61,860	-
Solvent (MEA, TEG), kg/h	52.2	67.0	-
Makeup water kt/h	1.2	1.8	-
Output			
Pipeline gas, kmol/h	40,851	52,083	-
Ethane, t/h	197.3	150.9	-
Propane, t/h		101.8	-
Direct CO <sub>2</sub> emissions, t/h	78.0	111.8	-
Olefins manufacturing stage			
Input			
Hydrocarbon feed, t/h	197.3	252.7	368.0
External fuel demand, GJ/h	1643	3397	-351
Makeup water, kt/h	1.1	2.5	1.8
Output			
Ethylene, t/h	125.0	125.0	125.0
Propylene, t/h	28.4	87.1	51.3
C₄s, t/h	8.4	13.1	7.2
C₅+, t/h	1.6	0	134.2
Hydrogen, t/h	10.8	17.7	8.3
Direct CO <sub>2</sub> emissions, t/h	148.3	169.8	164.0

Table 2: Mass and energy balances for manufacturing ethylene and propylene from shale gas and naphtha.



Figure 4: Production costs and life cycle GHG emissions of ethylene and propylene via the three designs.

We also perform a cradle-to-gate life cycle assessment (LCA) to evaluate GHG emissions for the production of ethylene and propylene associated with the three designs. We do not consider water footprint in this case, because most water consumption in shale gas life cycle is at the hydraulic fracturing process (Gao et al., 2015b). This LCA encompasses the environmental impact during the acquisition of feedstocks, shale gas processing, and olefins manufacturing. The life cycle inventory is calculated based on the mass and energy balances obtained by process simulation. Data used to model GHG emissions during feedstocks acquisition are collected from existing literature (Laurenzi and Jersey, 2013) and the Ecoinvent database. Note that since shale gas processing and olefins manufacturing stages produce multiple products, co-product allocation is employed based on economic values. The life cycle GHG emissions of ethylene and propylene manufactured

via the three designs are assessed and compared in Figure 4. Such results show that manufacturing ethylene and propylene from naphtha is more attractive in terms of GHG emissions.

#### 4. Conclusion

In this work, we proposed two novel process designs for manufacturing ethylene and propylene from wet shale gas, depending on the steam co-cracking of ethane-propane and the integration of ethane steam cracking and propane dehydrogenation, respectively. To compare the production costs and life cycle GHG emissions for manufacturing ethylene and propylene from shale gas and naphtha, we also considered a conventional process design in which ethylene and propylene are produced via the steam cracking of naphtha. We modelled and simulated all process designs in Aspen HYSYS to obtain the mass and energy balances, which were then used to conduct a comparative techno-economic and environmental analysis. The obtained results indicated that ethylene and propylene manufactured via the proposed designs required lower production costs but led to higher life cycle GHG emissions than those manufactured via the conventional naphtha cracking design.

#### References

- Arvidsson M., Johansson E., Morandin M., Harvey S., 2015. Integration of biomass gasification-based olefins production in a steam cracker plant-global GHG emission balances. Chemical Engineering Transactions, 45, 787-792.
- Chin S., Radzi S., Maharon I., Shafawi M., 2011. Kinetic model and simulation analysis for propane dehydrogenation in an industrial moving bed reactor. International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering, 5(4), 260-266.
- Froment G.F.; Van De Steene, B.O., Vanden Berghe, P.J., Goossens A., 1977. Thermal cracking of light hydrocarbons and their mixtures. AIChE Journal, 23(1), 93-106.
- Gao J., You F., 2015a. Shale Gas Supply Chain Design and Operations toward Better Economic and Life Cycle Environmental Performance: MINLP Model and Global Optimization Algorithm. ACS Sustainable Chemistry & Engineering, 3, 1282-1291.
- Gao J., You F., 2015b. Optimal design and operations of supply chain networks for water management in shale gas production: MILFP model and algorithms for the water-energy nexus. AIChE J., 61, 1184-1208.
- Gao J., You F., 2017a. Design and Optimization of Shale Gas Energy Systems: Overview, Research Challenges, and Future Directions. Computers & Chemical Engineering, DOI: 10.1016/j.compchemeng.2017.01.032
- Gao J., You F., 2017b. Game Theory Approach to Optimal Design of Shale Gas Supply Chains with Consideration of Economics and Life Cycle Greenhouse Gas Emissions. AIChE Journal, DOI: 10.1002/aic.15605
- Gong J., Yang M., You F., 2017. A systematic simulation-based process intensification method for shale gas processing and NGLs recovery process systems under uncertain feedstock compositions. Computers & Chemical Engineering, DOI: 10.1016/j.compchemeng.2016.11.010
- Gu Y., Remigy J.C., Favier I., Gómez M., Noble R.D., Lahitte J.F., 2016. Membrane reactor based on hybrid nanomaterials for process intensification of catalytic hydrogenation reaction. Chemical Engineering Transactions, 47, 367-372.
- He C., You F., 2014. Shale gas processing integrating with ethylene production: Novel process designs, exergy analysis, and techno-economic analysis. Industrial & Engineering Chemistry Research, 53, 11442-11459.
- He C., You F., 2015. Towards more cost-effective and greener chemicals production from shale gas by integrating with bioethanol dehydration: Novel process design and simulation-based optimization. AIChE Journal, 61, 1209-1232.
- He C., You F., 2016. Deciphering the true life cycle environmental impacts and costs of the mega-scale shale gas-to-olefins projects in the United States. Energy & Environmental Science, 9, 820-840.
- Jenkins S., 2014. Propane production via propane dehydrogenation. Chemical Engineering, 121(1), 27-28.
- Kumar P., Kunzru D., 1985. Modeling of naphtha pyrolysis. Industrial & Engineering Chemistry Process Design and Development, 24(3), 774-782.
- Laurenzi I.J., Jersey G.R., 2013. Life cycle greenhouse gas emissions and freshwater consumption of Marcellus shale gas. Environmental Science & Technology, 2013, 47(9), 4896-4903.
- Seider W.D., Seader J.D., Lewin D.R., 2009, Annual Costs, Earnings, and Profitability Analysis, Product and process design principles: Synthesis, analysis and evaluation, John Wiley & Sons, New York, USA

1566