1

Shale Gas as an Option for the Production of Chemicals and Challenges for Process Intensification

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1.1 Introduction

Shale gas is unconventional natural gas trapped or adsorbed in shale rock formations. As opposed to conventional natural gas, shale gas is difficult to extract because of the low porosity of the rock formations in which it is confined. This particular characteristic implied a high cost for the extraction of this gas, so that its production remained unfeasible until the development of more suitable extraction technologies, such as hydraulic fracturing and horizontal drilling [1]. Hydraulic fracturing is a stimulation technique used to increase the flow rate of gas and oil in low permeability reservoirs. This method consists in injecting high-pressurized fluids into the well to create fractures and maintain them opened to allow the flux of gas and oil [1, 2]. Hydraulic fracturing is generally combined with horizontal drilling to increase the area covered with a lower number of wells. These two technologies have led to an increase in the net production of natural gas in the United States (US) for more than a decade, which has been referred to as the shale gas revolution [1, 3].

The aim of this chapter is to give an overview of shale gas and its potential to produce value-added chemicals. This chapter addresses the following aspects: shale gas composition and places where deposits are located, effect of shale gas discoveries on natural gas prices, alternatives to produce chemicals from shale gas, and opportunities for process intensification.

1.2 Where Is It Found?

Although shale gas has been known for a while, the first shale gas well was drilled in 1821 in Chautauqua, NY, its exploitation was possible only until the development of hydraulic fracturing and horizontal drilling technologies. After the oil crises of the 1970s, the US government and some oil and gas companies, separately, initiated the investment in research projects to evaluate and make shale gas extraction possible. From the beginning of the 2000s, technical

Table 1.1 Major shale gas plays in the United States.

Shale play	State(s)	Percentage of dry shale gas production in 2018
Marcellus	PA, WV, OH, and NY	32.7
Permian	TX and NM	12.3
Utica	OH, PA, and WV	11.3
Haynesville	LA and TX	11.0
Eagle Ford	TX	7.1
Woodford	OK	5.0
Barnett	TX	4.4
Mississippian	OK	3.8
Niobrara–Codell	CO and WY	3.4
Bakken	ND and MT	2.7
Fayetteville	AR	2.3
Rest of the United States "shale"		4.0

Source: Adapted from EIA 2018 [4].

and economic factors promoted the idea to produce natural gas from shale formations. The Barnett shale play was the first basin to be exploited in a large scale, with the hydraulic fracturing technology being tested there. Following the success to extract natural gas from the Barnett shale play, shale gas extraction began in other locations. Table 1.1 gives basic information about the major shale gas plays in the United States.

Apart from US reserves, recoverable shale gas resources around the world have been found in countries such as China, Argentina, Algeria, Canada, Mexico, Australia, South Africa, and Russia [3, 5]. Despite these discoveries, several factors such as geological aspects and the lack of the necessary infrastructure have curbed the development of the shale gas industry in those other countries [6, 7].

Table 1.2 Recent shale gas reserves and production in for the six countries with more shale gas reserves.

Country	Unproved recoverable reserves by 2013 (Tcf)	Production in 2018 (Bcf/yr)	References
China	1115.20	353.15	[8]
Argentina	801.50	365.00	[9]
Algeria	706.90	No production	[10]
United States	662.50 (by 2015)	7079.62	[4]
Canada	572.90	182.80	[11]
Mexico	545.20	No production	[12]

Source: From EIA 2015 [13].

Table 1.2 shows the production rates in 2018 for the six countries with more unproved technically recoverable shale gas resources.

1.3 Shale Gas Composition

One particular characteristic of shale gas is its varying composition. Shale gas composition depends heavily on the location of the sources, and it may variate even within wells in the same play. The primary component of shale gas is methane, but it also contains considerable quantities of natural gas liquids (NGLs) such as ethane and propane. Apart from these components, shale gas also contains acid gases such as CO_2, H_2S, and inorganic components such as nitrogen [5, 14]. The separation of NGLs from methane has induced industries to look for alternatives to transform them into more valuable products, but at the same time the varying composition of shale gas represents a challenge for the treatment plants, which have to be robustly designed to handle such variations in the gas composition.

1.4 Shale Gas Effect on Natural Gas Prices

The high availability of natural gas, generated as a result of the increasing production of shale gas, has caused a noticeable drop of its price in the United States. Moreover, the ability to extract natural gas from deposits that are not associated to crude oil reservoirs has uncoupled natural gas and crude oil prices [1]. These facts have contributed to what has been defined as the new era of cheap natural gas, in which it has been priced consistently under US$5 per million Btu for almost a decade in the United States [15]. In particular, natural gas prices in 2019 have shown a decrease from 3.18 at the beginning of the year to US$2.07 per million Btu in September [16]. Even more, in an extreme situation, producers at the Waha hub in the Permian basin in West Texas had to pay the pipeline to take the excess of gas, showing a negative US$9 in April, which contributed to an average price of only 73 cents per million Btu for the first eight months of 2019, compared with an average market price of US$2.10 in 2018 (which is also lower than the five year average from 2014 to 2018 of US$2.80) [17]. These trends create an opportunity for the development of technologies to transform shale/natural gas into value-added chemicals. One additional point to consider is the increasing amount of liquefied natural gas that is being exported from the United States [18]. As this quantity grows, international natural gas prices may also get affected.

The main consumers of natural gas are the electricity generation industry, the residential sector, the industrial sector, and the chemical industry. Low natural gas prices have incentivized the electric power plants to switch from coal to natural gas, with an impact not only on the economy of these systems but also on the environment by reducing the total greenhouse gas emissions [1].

Another sector that has shown interest in switching from oil-based feedstocks, such as naphtha or crude oil, to natural gas is the chemical industry. The availability of inexpensive natural gas and NGLs has boosted the chemical industry to create new plants for the production of value-added chemicals using methane and NGLs as feedstock [5, 19].

1.5 Alternatives to Produce Chemicals from Shale Gas

Due to the increasing availability of low-cost natural gas, the chemical industry has started to invest in the research and development of chemical routes that can transform methane into value-added chemicals. Some of the chemical compounds that have received special attention are methanol, ethylene, propylene, and liquid fuels obtained from syngas. Some of the processes to produce the aforementioned chemicals are discussed next.

1.6 Synthesis Gas

Synthesis gas is a mixture of carbon monoxide and hydrogen typically needed for the production of chemicals such as a methanol, ammonia, or gas-to-liquid (GTL) products. The production process for synthesis gas varies depending on the oxidizing agent selected for the reforming of the natural gas. The main reforming processes are steam reforming (SR), partial oxidation (POX), and dry reforming (DR) [20]. The characteristics of these processes are listed in Table 1.3.

Although these processes may be used separately, combinations of two or more of the main reforming options have been proposed to enhance the overall performance of the reforming task. One such process is the autothermal reforming (ATR) in which the exothermic nature of the POX reforming is combined with the endothermic SR [21].

In all of these reforming alternatives, energy and water usage and generation are key points to consider when selecting the appropriate technology. Studies regarding heat and mass integration potential for the SR, POX, and ATR options can be consulted in the work of Martínez et al. [21] and Gabriel et al. [22].

**Table 1.3** Reforming options and their characteristics.

Reforming option	Oxidizing agent	Conditions	Chemistry	Type
Steam reforming	H_2O	Endothermic	$CH_4 + H_2O \rightarrow CO + 3H_2$	Catalytic
Partial oxidation	O_2	Exothermic	$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	Catalytic/non catalytic
Dry reforming	CO_2	Endothermic	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	Catalytic

Source: Adapted from Noureldin et al. 2014 [20].

1.7   Methanol

Typically, methanol is used as an intermediate to produce other chemicals such as acetic acid, formaldehyde, and MTBE, among others [23]. The production process for methanol consists of three stages, reforming, synthesis, and purification. In the first stage, the main goal is to transform methane into syngas. For this purpose a reforming process is selected. One important factor to consider when selecting the reforming process is that the ratio of H_2 to CO to feed the methanol synthesis reactor has to be equal to 2.

For the synthesis of methanol, compression of the syngas obtained from the reforming stage is needed. Then, the compressed syngas is fed to a catalytic reactor in which the following reactions take place:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

$$CO + 2H_2 \rightarrow CH_3OH$$
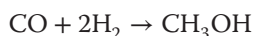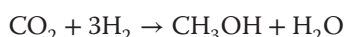
The synthesis reactor operates at 83 bar and 260 °C. The outlet of the reactor is cooled and sent to a flash unit to separate the unreacted syngas and recirculate it. Additionally, a fraction of the recycled syngas is purged, with a potential use as fuel. The crude methanol obtained from the flash unit is purified using one or two distillation columns [23].

This process has been analyzed to assess its environmental impact and its safety characteristics [23, 24]. The main drawbacks of the process are the high pressure required for the operation of the synthesis reactor and the wasted fraction of non-recycled syngas. Ortiz-Espinoza et al. [24] studied the effect of different operating pressures for the methanol synthesis reactor on the safety, environmental, and economic characteristics of the methanol production process using POX reforming. The high operating pressure is related to the profitability of the process, but safety properties may be hindered by such operating conditions. Greenhouse emissions are an additional item of relevance for consideration. Figure 1.1 shows the results of the analysis conducted by Ortiz-Espinoza et al. [24], in which values of three metrics used for profitability, inherent safety, and sustainability are reported for different reactor pressures and recycling fractions for the unreacted syngas. Such metrics were the return on investment (ROI) for economic performance, process route index (PRI) for inherent safety, and total emissions of CO_2 equivalents for process sustainability. One can observe the gradual trend of the three metrics that reflect their conflicting behavior. In summary, the economic potential of the process is better at high pressures and high recycling fractions, but if safety is of primary concern, a lower pressure would favor the process characteristics.

It should also be noticed that the methanol synthesis reaction is exothermic; therefore, heat integration options may be considered to further enhance the environmental and economic performance of the process.
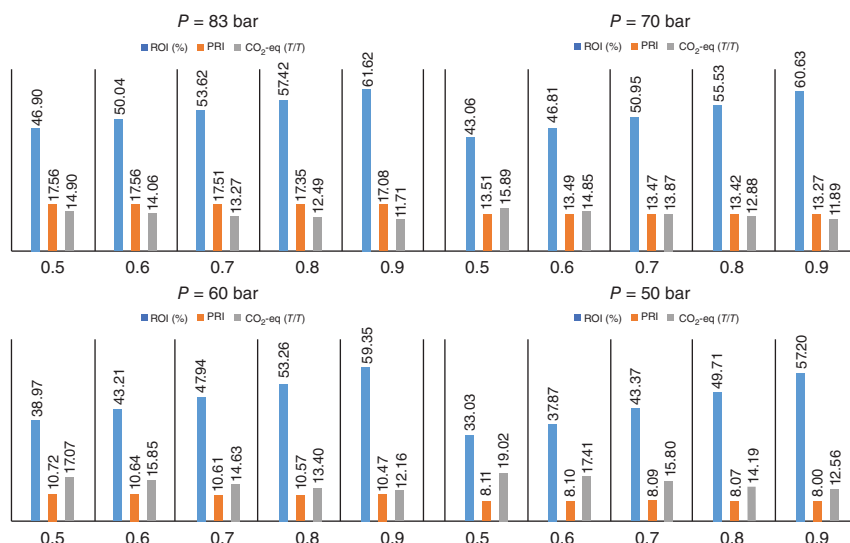
Figure 1.1 Safety, sustainability, and economic indicator for different pressures and recycling fractions in the methanol production process.

1.8 Ethylene

Ethylene is a major building block used in the chemical industry to produce a wide variety of important chemicals. The increasing availability of shale gas has boosted the ethylene industry as several ethylene production plants have been planned to be built in the United States [5]. The alternatives to produce ethylene include processes that use NGLs as feedstock, such as ethane cracking or propane dehydrogenation [25], and processes that transform methane to ethylene [26, 27]. Among the processes that convert methane to ethylene, two important options are the oxidative coupling of methane (OCM) and the methanol to olefins (MTO) technology. OCM is a direct process in which methane and oxygen are fed to a catalytic reactor, with the products of the reaction being separated in a purification stage that consists of the removal of water and CO_2 and a cryogenic distillation train [26]. Although this process is known for the low yield achieved in the reactor, which render a process option with low profitability, the development of new catalyst structures has made possible the construction of demonstration facilities for this technology that offer better economic perspectives [28].

The other alternative for ethylene production is MTO, which is a more complex process as it involves several stages. First, the reforming of natural gas and the production of methanol take place. After the methanol synthesis, the crude methanol is sent to a catalytic reactor where low-weight olefins are produced. In the reactor a variety of components are produced, such as ethylene and propylene, butylene, C_5s, hydrogen, low-weight hydrocarbons, water, and CO_2. The effluent of the reactor is then sent to separation and purification units, which start with CO_2 removal and dehydration units. Then, the remaining stream is sent to a distillation train consisting of demethanizer, deethanizer, and depropanizer columns, as well as C_2 and C_3 splitters. A column to separate C_4s and C_5s is also

needed. The overall process is very energy intensive, as it involves a reforming stage and a large distillation train.

Even when the MTO technology has been reported to be more profitable than the OCM option [26], the latter technology is less complex and avoids the need to transform the natural gas to intermediate products such as syngas. That provides an incentive to develop improvements to this technology in order to enhance its overall performance and profitability. Proposed ideas to achieve such improvements include the use of membranes in the CO_2 separation system and modifications to the ethylene fractionation column to reduce heating and condenser duties [29, 30].

1.9   Benzene

Benzene is an important starting molecule in the petrochemical industry. The production of benzene from shale gas was considered in Pérez-Uresti et al. [31], and a process based on the direct methane aromatization (DMA) route was designed. In this process, methane is fed to a DMA reactor operating at 800 °C and atmospheric pressure. The main products of the reaction are benzene and hydrogen. The effluent from the DMA reactor is sent to a membrane unit to separate the hydrogen. Then, the remaining stream is cooled and compressed to be separated in a flash tank. The gas stream obtained from the flash separator is methane-rich and is recycled to the DMA reactor. The liquid stream is fed to a distillation column where benzene is obtained as a top product. Although the DMA process competes with the traditional production routes based on catalytic reforming or steam cracking of liquid petroleum feedstocks, it represents an attractive alternative given the low prices of natural gas.

1.10   Propylene

Propylene has typically been produced as a byproduct either from the steam cracking of naphtha to produce ethylene or from the fluid catalytic cracking to produce gasoline. With the shale gas boom and the excess of NGLs such as ethane, the production of ethylene has switched the feedstock from naphtha to ethane. This action has eliminated the production of propylene as a byproduct, opening an opportunity for the development of on-purpose propylene production processes. The alternatives to produce propylene from shale gas include two options via methanol and one using the propane obtained from the purification of shale gas [32, 33]. The processes to produce propylene via methanol are the MTO route and the methanol to propylene (MTP) process [33]. The MTO process is described earlier in the ethylene section. MTP follows a similar path. First, natural gas is transformed into syngas gas using a reforming alternative, and then the syngas is transformed into methanol. As opposed to the MTO process, where crude methanol is sent to the MTO reactor, methanol has to be purified for its use as feedstock for the MTP process. Therefore, the crude methanol obtained from

the methanol synthesis reactor is sent to a flash unit and purified using a distillation column. The purified methanol is then fed to a reactor, where it is converted to dimethyl ether and water. Then, the outlet stream of the reactor is sent to a fixed bed catalytic reactor to produce propylene. The effluent from the fixed bed reactor contains propylene, gasoline, and LPG, as well as water. It is sent to a flash unit to remove water and the remaining stream is purified using distillation columns.

Another alternative for the production of on-purpose propylene is the propane dehydrogenation process, in which a depropanizer column is used to separate C^{4+} compounds that may be present in the fresh material. The purified propane enters a cold box to refrigerate the effluent from the propylene production reactor. Then, the propane stream is mixed with hydrogen and sent to a fired-heater before being fed to a fluidized catalyst bed reactor. The reaction is highly endothermic. The outlet stream of the reactor contains propylene, propane, light gases, ethane and ethylene, and some heavier hydrocarbons. The reactor effluent is cooled, compressed, and sent to a cool box where hydrogen is separated from the hydrocarbons. The liquid stream from the cold box is sent to a selective hydrogenation process (SHP) to further improve the production of propylene. The effluent from the SHP is fed to a deethanizer column to remove light gases. Finally, the remaining stream is fed to a C_3-splitter column to produce the propylene. The propane obtained at the bottom of the splitter column is recycled to the depropanizer column [32].

These processes represent an excellent opportunity for the independent production of propylene instead of obtaining it as a byproduct of other processes.

1.11 Process Intensification Opportunities

The incentive for shale gas monetization can also be viewed as an opportunity to develop intensified processes for shale gas transformation technologies. Recent efforts to design intensified processes have been observed. Process intensification is understood here as a search for more competitive process alternatives via the development of more compact flowsheets (i.e. with fewer pieces of equipment or smaller sizes of the same number of equipment units) and/or with a reduction on the consumption of basic resources (raw materials, energy) through more efficient designs.

The first efforts to develop formal design methodologies for intensified processes were due to the work by Gani and his research group [34–36]. Such initial methodologies make use of the concepts of tasks and phenomena, giving rise to the concepts of phenomena building blocks (PBBs), which represent the tasks involved in a process unit such as reaction, heating, cooling, mass transfer, and so forth; the combination of PBBs provides simultaneous phenomena building blocks (SPBBs), which are used to model the operations involved in a process. For instance, in a distillation column, the following SPBBs can be observed. Each tray shows a mixture with two phases, with contact, transfer, and separation between the two phases (vapor and liquid), while the condenser adds cooling and the reboiler adds heating to the previous SPBBs, as shown in Figure 1.2 for a column with five trays.
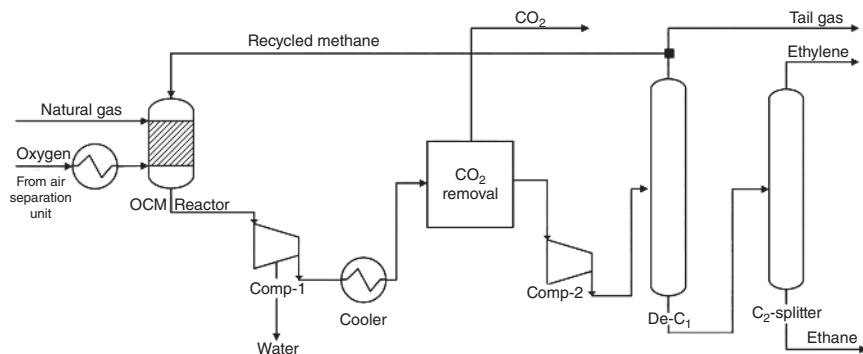
M = C = 2phM = PC(VL) = PT(VL) = PS(VL)

Distillate

M = 2phM = PC(VL) = PT(VL) = PS(VL)

M = 2phM = PC(VL) = PT(VL) = PS(VL)

Feed

M = 2phM = PC(VL) = PT(VL) = PS(VL)

M = 2phM = PC(VL) = PT(VL) = PS(VL)

M = 2phM = PC(VL) = PT(VL) = PS(VL)

M = H = 2phM = PC(VL) = PT(VL) = PS(VL)

Bottom

Figure 1.2 Simultaneous phenomena building blocks in a conventional distillation column.

Using these concepts, Lutze et al. [36] developed a methodology for process design of intensified processes, consisting of three stages. In the first one, a basic process flowsheet is synthesized. In the second stage, SPBBs are developed and a superstructure that contains all the possible tasks of the system is formulated. The problem is then solved as a mixed-integer nonlinear programming (MINLP) model to obtain the intensified structure that minimizes a given objective function such as the total annual cost of the system. Babi et al. [34] applied an extended formulation of that model that included sustainability metrics to a case study dealing with the production of dimethyl carbonate. In the work by Castillo-Landero et al. [37], such a methodology was taken as a basis, but instead of formulating an MINLP model to search for the optimal intensified configuration, a sequential approach with gradual intensification of the process was conducted until a final structure with a minimum number of equipment units was obtained. One advantage of this procedure is that one can assess individual levels of process intensification so that a structure that favors a given metric of interest can be selected.

Interesting challenges arise when shale gas processes are considered for process intensification. Let us take, for instance, the basic flowsheet for the production of ethylene from shale gas, or natural gas, shown in Figure 1.3. As discussed earlier, this process shows a fairly simple structure but an adverse profitability, which poses a particular incentive to explore potential benefits that an effective process intensification task could provide. Nonetheless, noticeable challenges exist for its transformation into an intensified process that combines

Figure 1.3 Basic flowsheet for ethylene production from shale/natural gas.

the process tasks, namely, reaction and several separation tasks. First of all, the reactor performs a catalytic, gas-phase reaction task, which consists of a complex reaction mechanism. Secondly, the separation tasks consist of a combination of compression for water condensation and absorption for CO_2 removal (typically carried out with an amine such as MEA). Combination of absorption and membrane could possibly be considered. The distillation train, finally, is highly energy intensive. Given the tasks identified for this process, and the aim to intensify it, the use of membrane units would be of special consideration. Membrane units could conceptually be designed first to carry out the individual tasks. Then, combinations of reaction and separation tasks based on such membrane units could be considered. The resulting structure would include innovative gas-phase membrane-reactive-separation units. The design of effective membranes that, among other things, could separate the gas mixture that requires cryogenic distillation systems could provide a significant impact on the process economics. It should be mentioned that some efforts to combine reactive distillation with membrane separation have been reported (e.g. [38]). However, the reaction for which the intensification with membrane units has been considered has been typically implemented for liquid-phase reactions. In such cases, membranes aid in improving the effectiveness of the process, for instance, by releasing one of the products of the reversible reaction to improve its yield. The problem posed by shale gas processes is the gas-phase reaction that requires special membrane materials for its effective application. The aspects outlined here taking the OCM transformation technology as an example provide a clear incentive toward the design of more competitive alternatives based on more compact, innovative shale gas-intensified technologies.

1.12 Potential Benefits and Tradeoffs Associated with Process Intensification

Although intensification opportunities for shale gas technologies remain to be explored, it is worthy of mention its potential benefits and possible tradeoffs based on the results from research and applications of intensification methodologies. First, it could be mentioned that a direct economic impact that would

favor investment and operating costs could be observed. A notable example is the intensified process design developed by Eastman Chemicals for the production of 400 kT/yr of methyl acetate that transformed a flowsheet with 10 units (one reactor and nine separation columns) into a single reactive-distillation piece of equipment. The resulting intensified process had 1/5 of capital investment and 1/5 of energy costs with respect to the original process [39]. One could also expect improvements in other factors such as carbon footprint and global warming metrics [37]. However, tradeoffs with other aspects such as process inherent safety and process controllability remain to be assessed. In an initial work to account for process inherent safety for a case study dealing with the intensification of an isoamyl acetate process, it was found that a partially intensified process could provide a better alternative in terms of inherent safety expectations with respect to a fully intensified process [40]. On the other hand, the effect of losing degrees of freedom for process control that arises from intensifying an original process and how it affects the process operability and controllability is an item that remains to be addressed.

1.13 Conclusions

An analysis of shale gas availability and its potential implications to support a shale gas industry that expands its use as an energy source to include transformation processes into value-added chemical products has been presented. Designs for shale gas transformation into valuable chemicals such as methanol and ethylene are examples of current efforts to produce higher value-added molecules particularly valuable as precursors of important end products. The development of extraction technologies has provided the basis for the development of shale gas monetization strategies. It has been shown how the profitability of shale gas processes may be in conflict with other important considerations such as the process safety, which sets the incentive for the development of multi-objective optimization formulations to obtain designs that offer the best compromises between such conflicting metrics. Another interesting challenge, in addition to the development of efficient and profitable shale gas flowsheets, lies in the design of intensified processes for flowsheets originally based on conventional reaction and separation units. Current intensification methodologies could be taken as a basis, with the challenge of its application for cases based on gas-phase reactions that involve complex reaction mechanisms and different types of separation processes. The development of membrane-based processes seems like a promising alternative in the search for innovative shale gas intensified processes.

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