

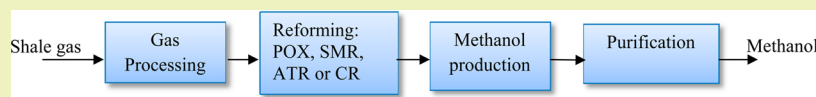
Techno-Economic Assessment and Environmental Impact of Shale Gas Alternatives to Methanol

Laura M. Julián-Durán,[†] Andrea P. Ortiz-Espinoza,[†] Mahmoud M. El-Halwagi,^{‡,§} and Arturo Jiménez-Gutiérrez^{*,†}

[†]Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Celaya, Gto 38010, Mexico

[‡]Chemical Engineering Department, Texas A&M University, College Station, Texas 77843, United States

[§]Chemical and Materials Engineering Department, King Abdulaziz University, Jeddah, Saudi Arabia 21589



ABSTRACT: Recent discoveries of shale gas reserves have promoted a renewed interest in gas-to-liquid technologies for the production of fuels and chemicals. One option of particular interest for the chemical industry is the production of methanol. In this work, an economic and environmental analysis for the production of methanol from shale gas is presented. Four reforming technologies, partial oxidation, steam methane reforming, autothermal reforming, and a combined reforming, are considered for the production of the syngas to be fed to the methanol plant. Process simulations are used to assess the performance of each resulting flowsheet. The results identify partial oxidation and autothermal reforming as the most suitable options for methanol production from an economic viewpoint, but the use of the combined reforming turned out to be the best sustainable alternative from an environmental viewpoint.

KEYWORDS: Shale gas, Gas reforming alternatives, Methanol process, Techno-economic analysis, CO₂ emissions, Antrim Shale

INTRODUCTION

The development of technologies for natural gas extraction has been motivated by the search for energy alternatives. Over the past half century, the consumption of natural gas has grown from 23 trillion cubic feet (Tcf) in 1965 to 113 Tcf in 2010 and is projected to reach 185 Tcf in 2040.¹ Conventional reservoirs of natural gas are wells produced from sands and carbonates with pore spaces, whose permeability allows the flow through the wellbore, while unconventional reservoirs are wells that produce natural gas from low permeability formations such as tight gas, coal bed methane, and shale gas.²

The renovated interest in the natural gas industry has been promoted by the recent discoveries of shale gas reserves. Shale gas is a natural gas found in fine-grained sedimentary rocks. In the United States, shale gas production at the end of 2013 was approximately 24.6 Bcf/d, which amounts to 40% of the dry gas production;³ the most active shales are the Marcellus, Haynesville, Barnett, Fayetteville, Eagleford, Woodford, and Antrim.⁴ Shale gas is extracted with methods that use a combination of horizontal drilling and hydraulic fracturing.^{2,5}

The main component of shale gas is methane, but heavier hydrocarbons, such as ethane and propane, and other inorganic gases, such as carbon dioxide and nitrogen, are also present. The shale gas composition depends on the well from which it is extracted. Large contents of components such as nitrogen require specific gas processing techniques.⁶

Several chemicals can be produced from shale gas. In order to accomplish such transformation, the first step needed to purify the shale gas to yield a composition similar to that of natural gas. Available reforming technologies can then be used to transform

natural gas into a synthesis gas that can be converted into a wide variety of chemical products.^{7,8} One such chemical is methanol, which in addition to its use as a fuel or fuel additive is an intermediate for the production of other major chemical products such as acetic acid, formaldehyde, dimethyl terephthalate, and methyl *tert*-butyl ether, among others.⁹ Some studies have been reported on the economics of methanol production from natural gas. Lange¹⁰ compared the use of a once-through reactor series to the use of a conventional methanol reactor with several reforming alternatives. Later, Lange¹¹ compared the production of methanol with a recycle reactor to the use of a reactor series using steam methane and partial oxidation reformers. Environmental considerations have been addressed mainly for methanol production from biomass.^{12–14}

On the potential use of shale gas to produce methanol, a recent study by Ehlinger et al.⁶ carried out a sensitivity analysis to assess the impact of the methanol selling price and established targets for energy integration. The analysis was based on the use of partial oxidation (POX) as the reforming technique to provide the syngas needed for the methanol production. Because there are other viable reforming techniques, there are opportunities and complexities associated with the selection and integration of the type of reformers for the methanol plants.

This work is aimed at developing a technical, economic, and environmental assessment of methanol production from shale gas. The work introduces the following new aspects: (1)

Received: May 21, 2014

Revised: September 1, 2014

Published: September 3, 2014

Consideration and assessment of the impact of different gas reforming technologies on the production of methanol are evaluated. In addition to the POX alternative, steam methane reforming (SMR), autothermal reforming (ATR), and a combined reforming (CR) are considered in this analysis. (2) Evaluation of energy and environmental considerations and integration with technical and economic objectives are considered.

The objectives of this work are (a) to carry out an analysis to determine the appropriate processing gas for a selected type of shale gas, (b) to develop a technical analysis of each reforming technology, (c) to perform an energy and economic analysis of each alternative, and (d) to develop an initial environmental assessment for the process based on each reforming technology. A case study for the production of 10,000 tpd of methanol from shale gas is used to demonstrate the approach and to draw useful observations from the results.

■ PROCESS DESCRIPTION

Antrim shale, located in the northern part of the state of Michigan, is considered as a basis for the methanol process. This type of shale is predominantly biogenic, in which the consumption of organic material produces methane as a byproduct.¹⁵ Compositions of various wells from Antrim Shale are shown in Table 1. The average of Antrim shale gas composition is used in this work.

Table 1. Antrim Shale Gas Composition¹⁵

well	C ₁	C ₂	C ₃	CO ₂	N ₂
1	27.5	3.5	1.0	3.0	65.0
2	57.3	4.9	1.9	0.0	35.9
3	77.5	4.0	0.9	3.3	14.3
4	85.6	4.3	0.4	9.0	00.7
average	61.97	4.17	1.05	3.83	28.97

The steps for methanol production from shale gas are shown in Figure 1. Shale gas must be processed before it is sent to the

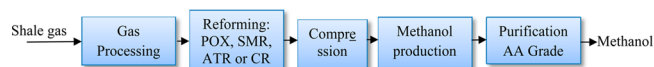


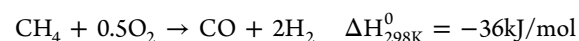
Figure 1. Main steps for methanol synthesis from shale gas.

methanol plant. The reported information for the gas processing stage by Ehlinger et al.⁶ was used in this work. The reforming step is analyzed assuming a desired yield for the H₂:CO ratio of 2. Compression of the syngas is needed for its use as a feed to the methanol reactor. The final purification step for the methanol product using distillation completes the overall process.

Gas Processing. In the gas processing step, shale gas is purified for its use as a process feedstock. The shale gas is treated for acid and nitrogen removal, after which the gas is fed to a cooler and finally sent to a series of cryogenic columns in order to recover natural gas (Figure 2). Membranes are commonly used to separate nitrogen. The series of cryogenic columns consist of two columns. The first column is a demethanizer; the gas extracted is compressed and heated to reach the conditions given in Table 2. The second column is a de-ethanizer, where ethane is separated from heavier hydrocarbons.

Reforming. Four reforming alternatives are considered. The description of each option is given below.

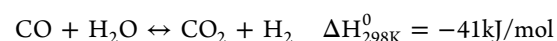
Partial Oxidation (POX). This reformer is mainly used to produce syngas from heavy hydrocarbons. Oxygen is provided from an air separation unit.¹⁶ The oxidation reaction in the POX reactor is



The temperature of the POX reactor is between 1200 and 1500 °C.⁸ The reaction is exothermic, and the outlet stream has low amounts of carbon dioxide, which has to be removed before the methanol synthesis step.

Figure 3 shows the diagram for a methanol flowsheet using POX. A ratio of shale gas to oxygen of 1.5 is taken as a basis in this work. The feed is preheated to 300 °C, and the POX reactor operates at 30 bar. The stream from the POX reactor exits at about 1350 °C.

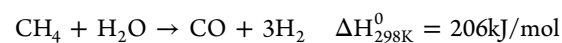
Partial oxidation leads to a H₂:CO ratio of about 1.8. In order to adjust the desired ratio of 2.0, a water gas shift (WGS) reactor is added. The WGS reactor operates at 250 °C and 30 bar, and the following reaction takes place



The syngas produced is cooled, and water is separated with a flash unit at 45 °C and 30 bar. The gas stream is sent to a separator where 99.8% of CO₂ is removed. Finally, the syngas is compressed to 83 bar.

The ASPEN Plus RGibbs model, based on a minimization of the Gibbs free energy, was used to simulate the adiabatic POX reactor, while the WGS reactor was simulated with the ASPEN Plus Rstoic model.

Steam Methane Reforming (SMR). This technology is widely used for the production of synthesis gas. The SMR reaction is endothermic, catalyzed by nickel. In the SMR reactor, which is generally a multitubular reactor, the main reaction is as follows:



In addition, a water gas shift reaction is needed. The molar ratio of steam to shale gas in the feed stream is 3.^{17,18} The reactor temperature is commonly 850 °C. The catalyst is damaged at higher temperatures, and coke formation is observed at lower temperatures. In this case, a significant production of hydrogen is achieved, although the process is energy intensive because of the endothermic reaction.

Figure 4 shows the methanol flowsheet for this process. Shale gas and steam are mixed and sent to a prereformer to convert higher hydrocarbons into hydrogen and carbon oxides to avoid coking formation at high temperatures. The exit stream is preheated to 400 °C and sent to the SMR reactor, which operates at 1200 °C and 20 bar. Then, syngas is separated into vapor and liquid phases. The liquid stream is mainly wastewater, while the vapor phase is sent to a separator to remove 98% of CO₂. The H₂:CO ratio from the SMR reactor is usually around 3. In order to adjust the H₂:CO ratio, the CO₂ stream is recycled, and the excess of H₂ is extracted. The syngas stream is finally compressed from 20 to 83 bar.

Autothermal Reforming (ATR). This alternative is a combination of steam methane reformer and partial oxidation, where the energy required is low due to the combination of the reactions of each process. As a result, the temperature control is improved, and the deactivation catalyst by carbon decomposition is avoided. Additionally, the H₂:CO ratio is adjusted by feeding oxygen. The ATR reactor consists of a burner and a fixed bed catalyst, where the outlet gas composition is very close to

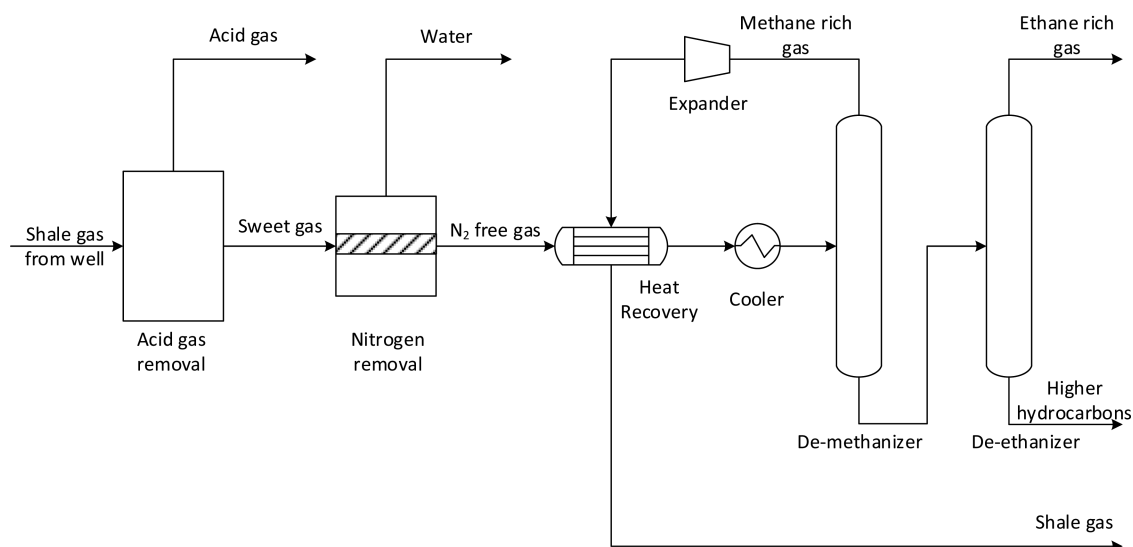
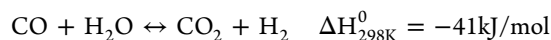
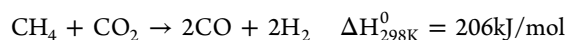
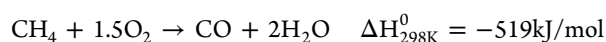


Figure 2. Pretreatment stage for Antrim shale gas.

Table 2. Composition and Conditions of Shale Gas Stream after Gas Processing

component	composition (mol %)
methane	95.4
ethane	3.89
propane	0.04
carbon dioxide	0.59
nitrogen	0.08
stream conditions	
temperature (°C)	26
pressure (Bar)	26

thermodynamic equilibrium of an adiabatic reactor in a large-scale process.^{19–21} The reactions in the ATR reformer are



For this case, shale gas and steam are mixed and preheated at 350 °C. The gas stream is sent to an adiabatic prereformer to convert higher hydrocarbons into syngas. The outlet stream and oxygen are fed to an ATR reactor, which operates at 25 bar. The gas mixture from the ATR reactor exits at 1290 °C. Syngas at 25 bar is separated at 40 °C into a liquid phase, which is basically

water and a vapor stream that goes for 99.8% CO₂ removal. The syngas reaches a pressure of 83 bar in the compressor. Figure 5 shows the methanol flowsheet with the ATR alternative.

For the process simulations, an ASPEN Plus RGibbs model was used for both the prereformer and the ATR reactor.

Combined Reforming (CR). The combined reforming consists of a combination of steam methane reforming and autothermal reforming.^{8,22} A better energy utilization can be obtained with respect to the individual use of SMR or ATR.²³ Figure 6 shows the process flowsheet.

In this case, shale gas and steam are mixed and sent to an SMR reactor, which operates at 20 bar and 850 °C. The outlet stream and shale gas are mixed and fed to the ATR reactor, which operates adiabatically at 30 bar. As in the ATR case, the H₂:CO ratio is adjusted with an oxygen stream for the desired ratio of 2.

The syngas stream is cooled to 40 °C to separate water, while the gas stream is sent to a unit in which 98% of CO₂ is separated and recirculated to the SMR reactor in order to lower the amount of oxygen needed to adjust the H₂:CO ratio. Syngas is compressed to 83 bar and sent to the methanol synthesis loop.

The steam methane reforming and autothermal reforming were simulated with the ASPEN Plus RGibbs model.

Methanol Synthesis. The chemical reactions for the methanol synthesis from synthesis gas are

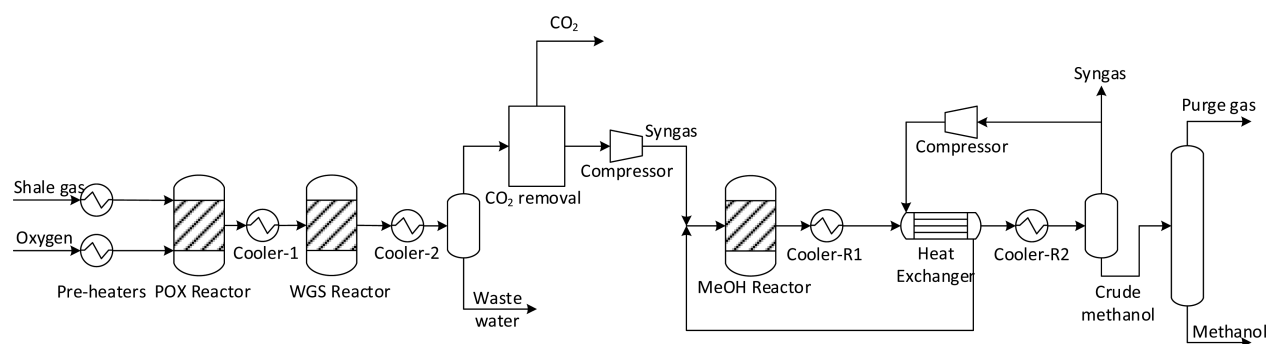


Figure 3. Methanol flowsheet using POX.

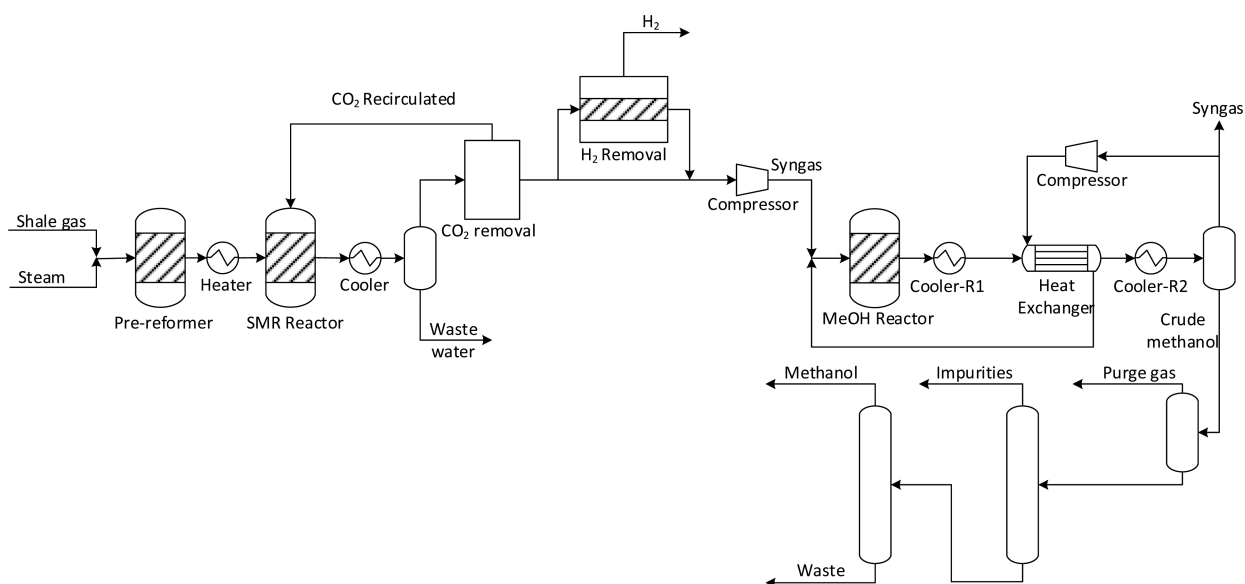


Figure 4. Methanol flowsheet using SMR.

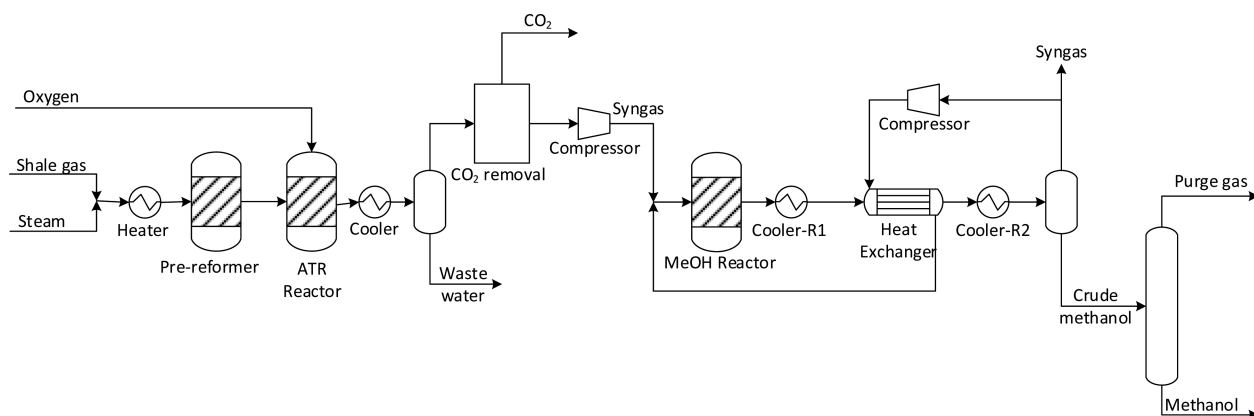


Figure 5. Methanol flowsheet using ATR.

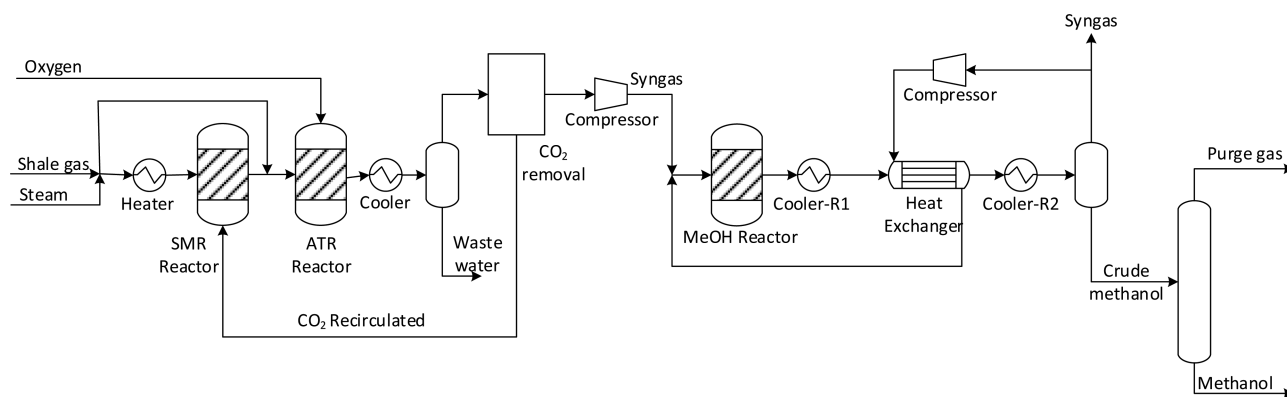
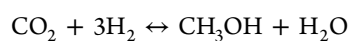
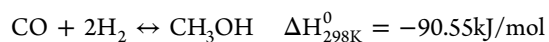


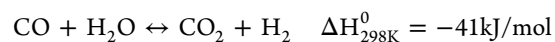
Figure 6. Methanol flowsheet using CR.



$$\Delta H_{298\text{K}}^0 = -49.43\text{kJ/mol}$$



The water gas shift reaction is



Research has gradually improved the operating conditions of the methanol reactor. Early last century, BASF developed a high pressure process over $\text{ZnO}/\text{Cr}_2\text{O}_3$ catalyst, which was operated at up to 250–350 bar and 320–450 °C. In the 1960s, Imperial Chemical Industries (ICI, now Syntex) developed the low-pressure process that operated at 35–55 bar and 200–300 °C.²³

The reactions in the low-pressure process take place over Cu/ZnO/Al₂O₃ catalysts.²⁴

The synthesis reactions are highly exothermic. The methanol reactor, which was modeled using the Aspen Plus RPlug model, operates at 83 bar and has a constant reactor temperature of 260 °C. The packed tubular reactor has 30,000 tubes of 12 m and a diameter of 0.04 m. The catalyst has 2000 kg/m³, and the reactor void volume is 0.5. The kinetics from Vanden Bussche and Froment²⁴ was used to simulate the reactor. The outlet steam of the reactor is cooled to 45 °C, and the methanol crude is separated.

During the methanol synthesis loop, the syngas is recirculated to improve the conversion in the reactor. The recycle compressor changes the pressure from 75 to 83 bar, and half of the syngas is extracted during the recycle, with a potential use as fuel.

Purification. Methanol can be purified to grades C, A, or AA. Methanol with grade C is for wood alcohol used in denaturing. Methanol with grade A is used as a solvent. Grade AA, also called B, refers to the purest methanol (99.85% of purity) and is used for chemical applications where high purity is required.⁶ Methanol purification is carried out by distillation, for which one or two columns are used. The first column, or topping column, is for light ends removal and acts as a refluxed stripper. A second column, or refinery column, is sometimes necessary to purify the methanol product.⁹

In this work, the methanol is considered to be purified to AA grade. In the POX alternative, only the topping column is required to reach the AA grade. A column is used with 12 theoretical stages, operating with a 1.5 reflux ratio and at 1.5 bar. In the SMR alternative, the crude methanol is sent to a flash unit

operating at 0 °C and 10 bar. Next, the liquid phase is sent to a topping column; the outlet bottom stream is fed to a refinery column with 20 theoretical stages, 1.5 reflux ratio, and pressure of 1.5 bar. Finally, methanol is obtained at the top of the refining column. In the ATR case, the methanol AA grade is obtained from the bottom of the topping column.

The columns for the ATR and the CR processes were modeled similarly as for the POX alternative.

RESULTS AND DISCUSSION

The basis for the analysis is a methanol production of 10,000 ton per day (tpd). The reactions and conditions established in each case determine the amount of raw material required. The use of CR requires lower amounts of shale gas and oxygen than the other reforming options, although it is not self-sufficient in water consumption. SMR shows the lowest water needs but the highest shale gas consumption. For the POX technology, the amount of shale gas and oxygen fed to the syngas production stage are slightly lower than for the ATR based process.

Economic Evaluation. The methanol plant economics was estimated assuming 350 operating days per year, a tax rate of 25%, and a 10 year linear depreciation scheme to calculate the annualized fixed cost.^{25,26} The selling price of methanol was taken as \$600/ton.⁶ The total capital investment (TCI) was estimated with the six-tenths rule based on reported data for methanol plants with similar syngas production stages.^{6,27} The fixed capital investment (FCI) was assumed as 85% of the total investment. The return on investment (ROI) was calculated for each process using the following formula²⁵

$$\text{ROI} = \frac{(\text{Annual Sales} - \text{Annual Fixed Cost} - \text{Annual Operating Cost})(1 - \text{Tax Rate}) + \text{Annual Fixed Cost}}{\text{TCI}}$$

The heating utilities conditions are high-pressure steam at 100 kPa and low-temperature heating oil at 344 C and 3.5 bar, and their respective costs were taken as \$4 and 7/MM Btu,²⁵ respectively. The costs of shale gas and oxygen were assumed to be respectively \$4.71/MM Btu and \$0.05/lb,⁶ respectively.

Table 3 shows the operating costs for the process for each reforming case. The values for TCI, FCI, and ROI for each case

Table 3. Operating Cost for the Methanol Plant for Different Reformer Options

	POX	SMR	ATR	CR
utilities (MM\$/yr)	259.78	683.41	528.39	867.37
raw material (MM\$/yr)	652.12	648.75	675.25	547.53
labor (MM\$/yr)	10.69	6.52	5.70	5.46
total (MM\$/yr)	922.59	1,338.68	1,209.34	1,420.36

are reported in Table 4. The POX alternative requires the highest capital investment, while the CR alternative is the one with the lowest capital investment. On the other hand, POX requires the

Table 4. Profitability for the Methanol Plant with Each Reforming Option

	POX	SMR	ATR	CR
TCI (MM\$)	1,970.52	1,644.22	1,711.08	1,533.78
FCI (MM\$)	1,674.94	1,397.59	1,454.42	1,303.71
ROI (%)	46.9	36.9	41.2	35.4

lowest operating cost, while CR requires the highest operating cost. ROI calculations indicate that technologies based on POX and ATR offer the higher ROI, while CR and SMR reformers provide rather similar profitability.

The use of shale gas as a raw material for the methanol process requires a preprocessing step due to impurities that need to be removed in order to provide it with pipeline quality for the plant.

Environmental Assessment. The environmental assessment conducted here is based on the amount of CO₂ emissions, which can have several sources. CO₂ emissions can be generated directly from burning fuels. Other sources include shale gas preprocessing to meet pipeline and process requirements. Additionally, there are streams exiting the process while containing CO₂. The calculations carried out for each option were based on emissions generated from burning fuels, effects of electricity consumption, and estimation of CO₂ equivalent units for outlet streams and gas preprocessing. Natural gas was assumed to be used for heaters.

In order to estimate the CO₂ emissions from burning fuels, the fuel analysis approach from EPA²⁸ was used, which involves the determination of carbon content of fuel combusted and its application to the amount of fuel burned. The steps of the approach are as follows:

Step 1. Determination of the amount of fuel combusted.

Step 2. Conversion of the amount of fuel combusted into energy units. The approach uses carbon content factors based on energy units, which are less variable than those based on physical

units (mass or volume). The heating value was used for this purpose.

Step 3. Estimation of carbon content of fuels combusted. To estimate the carbon content, energy content was multiplied by carbon content coefficients.

Step 4. Estimation of carbon emissions. When the fuel is burned most of the carbon is converted into CO₂ and sent into the atmosphere. To estimate the total carbon emissions, the carbon content was multiplied by the fraction of carbon oxidized. The fraction of carbon oxidized was assumed to be 1 for this case.

Step 5. Conversion to CO₂ emissions. To obtain the total amount of CO₂ emissions, the carbon emissions were multiplied by the molecular weight ratio of CO₂ to Carbon.

The following equation gives the estimation of CO₂ emissions,

$$\text{CO}_2 \text{ emissions (kg/day)} \\ = (F)(\text{HC}_{\text{Fuel}})(C_{\text{Fuel}})\left(\frac{44 \text{ kgCO}_2}{12 \text{ kgC}}\right)$$

where F is the amount of fuel used for combustion (scf/day), HC_{Fuel} is the fuel heat content, and C_{Fuel} is the carbon content coefficient of the fuel. For natural gas, the heat content is 1029 BTU/scf and the carbon content coefficient is 14.47 kg carbon/MMBtu. For the electricity consumption emissions, a factor of 0.782 MT of CO₂/MWh was used.²⁹

To obtain the total amount of CO₂ emitted, emissions from preprocessing and outlet streams were accounted for. Table 5

Table 5. Daily CO₂ Emissions for Combined Gas Processing and Methanol Plant (kg/day)

	total
POX	145,323,190
SMR	198,007,785
ATR	146,603,745
CR	124,590,857

shows the CO₂ emissions for the process for each reforming option. The results show that the process based on combined reforming gives the best sustainable option from environmental considerations, while the use of SMR gives the option with the highest carbon footprint.

CONCLUSIONS

A technical, economic, and environmental analysis for methanol production from shale gas has been presented. After a shale gas processing step, four reforming technologies, partial oxidation (POX), steam methane reforming (SMR), autothermal reforming (ATR), and combined reforming (CR), were considered for the supply of syngas for the methanol plant. Computer-aided simulations were used to assess the performance of each option. The results show that the use of POX or ATR provides the alternative with the best profitability potential for methanol production. From an environmental viewpoint, however, the process based on CR turns out to be the option with the lowest carbon footprint. The results provide the incentive for the development of multiobjective optimization models taking into account the economic and environmental aspects considered here. The results can also be used as the modeling and optimization bases for processes that employ hybrid feedstocks^{30,31} (e.g., shale gas, biomass, etc.) and for regional or national supply chain analysis and optimization of shale gas networks.^{32,33}

AUTHOR INFORMATION

Corresponding Author

*Tel.: +52-461-611-7575, ext. 5577. E-mail: arturo@iqcelaya.itc.mx.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Support from Mexico's Consejo Nacional de Ciencia y Tecnología (CONACyT) through Project 207798 is gratefully acknowledged.

REFERENCES

- (1) *International Energy Outlook 2013*; U.S. DOE/EIA-0484(2013); U.S. Energy Information Administration: Washington, DC, July 2013.
- (2) *Modern Shale Gas Development in the United States: A Primer*. Report DE-FG26-04NT15455; Office of Fossil Energy and National Energy Technology Laboratory, U.S. Department of Energy: Washington, DC, April 2009.
- (3) *Monthly Shale Production Report*; Report Number 354; LCI Energy Insight: El Paso, TX, January 2014.
- (4) *World Shale Gas and Shale Oil Resource Assessment*; U.S. Energy Information Administration and Department of Energy: Washington, DC, June 2013.
- (5) Arthur, J. D.; Bohm, B. P. J.; Coughlin, B. J.; Layne, M. *Evaluating the Environmental Implications of Hydraulic Fracturing in Shale Gas Reservoirs*; ALL Consulting: Tulsa, Oklahoma, 2008.
- (6) Ehlinger, V. M.; Gabriel, K. J.; Noureldin, M. M. B.; El-Halwagi, M. M. Process design and integration of shale gas to methanol. *ACS Sustainable Chem. Eng.* **2014**, *2* (1), 30–37.
- (7) Martínez, D. Y.; Jiménez-Gutiérrez, A.; Linke, P.; Gabriel, K. J.; Noureldin, M. M. B.; El-Halwagi, M. M. Water and energy issues in gas-to-liquid processes: Assessment and integration of different gas-reforming alternatives. *ACS Sustainable Chem. Eng.* **2014**, *2* (2), 216–225.
- (8) Noureldin, M. M. B.; Elbasher, N. O.; El-Halwagi, M. M. Optimization and selection of reforming approaches for syngas generation from natural/shale gas. *Ind. Eng. Chem. Res.* **2014**, *53* (5), 1841–55.
- (9) Cheng, W. H., Kung, H. H., Eds.; *Methanol Production and Use*; Marcel Dekker: New York, 1994.
- (10) Lange, J. P. Perspectives for manufacturing methanol at fuel value. *Ind. Eng. Chem. Res.* **1997**, *36* (10), 4282–90.
- (11) Lange, J. P. Methanol synthesis: A short review of technology improvements. *Catalysis Today*. **2001**, *64* (1–2), 3–8.
- (12) Kumabe, K.; Fujimoto, S.; Yanagida, T.; Ogata, M.; Fukuda, T.; Yabe, A.; Minowa, T. Environmental and economic analysis of methanol production process via biomass gasification. *Fuel* **2008**, *87* (7), 1422–27.
- (13) Demirbas, A. Political, economic and environmental impacts of biofuels: A review. *Appl. Energy*. **2009**, *86* (1), S108–S117.
- (14) Renó, M. L. G.; Lora, E. E. S.; Palacio, J. C. E.; Venturini, O. J.; Buchgeister, J.; Almazan, O. A LCA (life cycle assessment) of the methanol production from sugarcane bagasse. *Energy* **2011**, *36* (6), 3716–3726.
- (15) Bullin, K. A.; Krouskop, P. E. Expanding the shale gas infrastructure. *Chem. Eng. Prog.* **2012**, *108* (8), 49–52.
- (16) P. E. York, A.; Xiao, T.; L.H. Green, M. Brief overview of the partial oxidation of methane to synthesis gas. *Top. Catal.* **2003**, *22* (3–4), 345–358.
- (17) Lucredio, A. F.; Assaf, E. M. Cobalt catalysts prepared from hydrotalcite precursors and tested in methane steam reforming. *J. Power Sources* **2006**, *159* (1), 667–672.
- (18) Andrade, M. L.; Almeida, L.; do Carmo Rangel, M.; Pompeo, F.; Nichio, N. Ni-Catalysts supported on Gd-doped ceria for solid oxide fuel cells in methane steam reforming. *Chem. Eng. Technol.* **2014**, *37* (2), 343–48.

(19) Gabriel, K. J.; Linke, P.; Jiménez-Gutiérrez, A.; Martínez, D. Y.; Noureldin, M. M. B.; El-Halwagi, M. M. Targeting of the water-energy nexus in gas-to-liquid processes: A comparison of syngas technologies. *Ind. Eng. Chem. Res.* **2014**, *53* (17), 7087–7102.

(20) Gabriel, K. J.; Noureldin, M. M.; El-Halwagi, M. M.; Linke, P.; Jiménez-Gutiérrez, A.; Martínez, D. Y. Gas-to-liquid (GTL) technology: Targets for process design and water-energy nexus. *Curr. Opin. Chem. Eng.* **2014**, *5*, 49–54.

(21) Lu, J.; Zhuang, H.; Yang, Q.; Wang, X.; Zheng, J.; Chen, J.; Sun, Y. Controller design and experiment for autothermal reforming of methanol in miniature reactor. *ISA Trans.* **2014**, DOI: 10.1016/j.isatra.2013.12.015.

(22) Vosloo, A. C. Fischer–Tropsch: A futuristic view. *Fuel Process. Technol.* **2001**, *71* (1–3), 149–55.

(23) Tijm, P. J. A.; Waller, F. J.; Brown, D. M. Methanol technology developments for the new millennium. *Appl. Catal., A* **2001**, *221* (1–2), 275–282.

(24) Bussche, K. M. V.; Froment, G. F. A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃ catalyst. *J. Catal.* **1996**, *161* (1), 1–10.

(25) El-Hawagi, M. M. *Sustainable Design through Process Integration: Fundamentals and Applications to Industrial Pollution Prevention, Resource Conservation, and Profitability Enhancement*; Butterworth-Heinemann: Oxford, 2012.

(26) Peters, M. S.; Timmerhaus, K. D.; West, R. E. *Plant Design and Economics for Chemical Engineers*, 5th ed.; Mc-Graw-Hill: New York, 2003.

(27) Sider, A. Louisiana Group Plants to Build Largest Methanol Plant in North America. *Hydrocarbon Processing*, March 1, 2013.

(28) *Direct Emissions from Stationary Combustion Sources*; EPA430-K-08-003; U.S. Environmental Protection Agency: Washington, DC, May 2008.

(29) Electricity Emission Factors, Voluntary Reporting of Greenhouse Gases Program. U.S. Energy Information Administration. http://www.eia.gov/survey/form/eia_1605/emission_factors.html (accessed September 5, 2014).

(30) Baliban, R. C.; Elia, J. A.; Weekman, V.; Floudas, C. A. Process synthesis of hybrid coal, biomass, and natural gas to liquids via Fischer–Tropsch synthesis, ZSM-5 catalytic conversion, methanol synthesis, methanol-to-gasoline, and methanol-to-olefins/distillate technologies. *Comput. Chem. Eng.* **2012**, *47*, 29–56.

(31) Noureldin, M. M. B.; Bao, B.; Elbashir, N. O.; El-Halwagi, M. M. Benchmarking, insights, and potential for improvement of Fischer–Tropsch-based biomass-to-liquid technology. *Clean Technol. Environ. Policy* **2014**, *16*, 37–44.

(32) Cafaro, D. C.; Grossmann, I. E. Strategic planning, design, and development of the shale gas supply chain network. *AIChE J.* **2014**, *60* (6), 2122–2142.

(33) Elia, J. A.; Baliban, R. C.; Floudas, C. A. Nationwide energy supply chain analysis for hybrid feedstock processes with significant CO₂ emissions reductions. *AIChE J.* **2012**, *58* (7), 2142–2154.