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Impact of Natural Gas and Natural Gas Liquids on Chemical Manufacturing in the United States

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Impact of Natural Gas and Natural Gas Liquids on Chemical Manufacturing in the United States

by

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Dedication

To my family for their constant support and for always inspiring creativity.

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Impact of Natural Gas and Natural Gas Liquids on Chemical Manufacturing in the United States

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The University of Texas at Austin, 2016

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Natural gas and natural gas liquids production in the United States has increased dramatically since 2005, due primarily to recent advancements in horizontal drilling and hydraulic fracturing. As raw materials for chemical production, the increased availability, at low cost, of these materials has the potential to change the structure of the United States chemical manufacturing industry. Industry-wide modeling, coupled with region-specific analysis, was used to map potential changes in chemical manufacturing as natural gas liquids continue to expand their influence in the chemical manufacturing industry. A network model was used to analyze technology development and to evaluate trends in the industry based on material flows throughout supply chains. Agent-based modeling and simulation was used for analysis of individual chemical markets and to determine the viability of emerging markets.

The network model was used to quantify how downstream chemical supply chains respond to changes in natural gas and natural gas liquid prices. The model was also used to identify new reaction pathways that may become viable as the industry evolves and how those new pathways will impact costs and utility consumption in the system of chemical manufacturing technologies. Using the Four Corners region as a case study, an analytic process was developed and implemented to evaluate greenfield

manufacturing based on regional feedstock availability and global chemical markets. Conceptual development of a comprehensive model of the natural gas liquids industry was also completed to map the challenges in developing chemical manufacturing system models that will include the impacts of exports, midstream infrastructure, supply, and new chemical demand.

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Chapter 1: Introduction

Natural gas and crude oil production in the United States has increased dramatically since 2005,[1,2] due primarily to recent advancements in horizontal drilling and hydraulic fracturing. With this change in oil and gas development, natural gas liquids (NGLs) have also experienced a surge in production.[3] Natural gas liquids include ethane, propane, normal butane, isobutane, and natural gasoline (pentanes and heavier alkanes). These chemicals can be extracted from a wet (liquids-rich) natural gas stream at a natural gas processing plant (called natural gas plant liquids, NGPLs) or from refinery streams (called paraffinic liquefied refinery gases, LRGs). A description of each NGL component and its uses is provided in Table 1-1. Natural gas liquids are valuable commodities and are used in many different sectors of the economy. In 2014, the United States produced 2,964 thousand barrels/day (MBbl/d) of NGPLs primarily for use as chemical feedstocks, home heating fuel, and transportation fuel. A variety of other applications are also available.[4]

Table 1-1: Natural gas liquids attribute summary.[5]

Name	Chemical Formula	Abbreviation	Applications
Ethane	C_2H_6	C2	petrochemical feedstock
Propane	C_3H_8	C3	heating, cooking fuel, petrochemical feedstock
n-Butane	C_4H_{10}	NC4	petrochemical feedstock, gasoline blendstock
Isobutane	C_4H_{10}	IC4	petrochemical feedstock
Pentanes Plus (Natural Gasoline)	C_5H_{12} and heavier	C5+	gasoline, diluent, ethanol denaturant, petrochemical feedstock

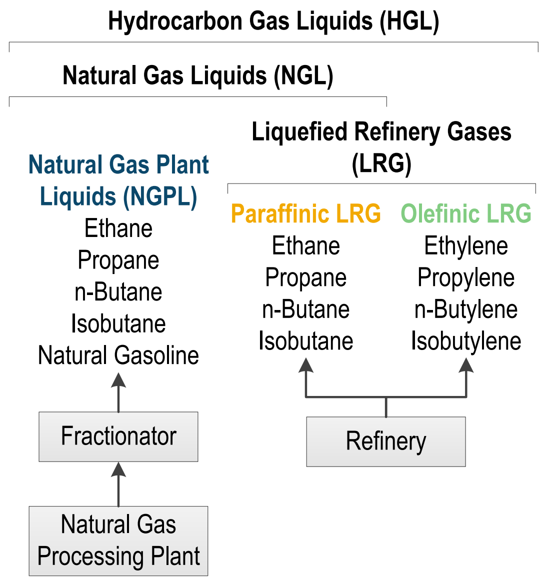
1.1 STRUCTURE OF THE NATURAL GAS LIQUIDS INDUSTRY

Natural gas liquids extracted from the wet natural gas stream at processing plants (called y-grade or raw NGLs) are transported in a mixed stream by truck, rail, or pipeline to fractionators. During fractionation, y-grade NGL is split into its individual purity products which can be stored above ground at surface temperature in pressurized tanks or below ground in salt caverns. There are two main locations in the U.S. where NGLs are stored belowground in large quantities with multiple interconnections, forming NGL trading hubs: Mont Belvieu, Texas and Conway, Kansas. Because of the seasonality of some purity product demand (e.g., propane for heating), storage is an integral component of the industry. The Conway hub distributes products to the Midwest, while Mont Belvieu primarily serves the Gulf Coast petrochemical facilities.

Refineries also supply alkanes and alkenes to the industry. Olefinic and paraffinic C2-C5 hydrocarbons from any source, when discussed together, are considered hydrocarbon gas liquids (HGLs). Natural gas liquids (NGLs) refer to C2-C5 alkane hydrocarbons regardless of their source and liquefied refinery gases (LRGs) indicate paraffin or olefin C2-C5 hydrocarbons from refinery streams. This terminology is illustrated in Figure 1-1.

Natural gas liquids are used in a variety of sectors. Ethane, when extracted from the natural gas stream, is transported by pipeline to be used almost entirely as a feedstock for ethylene production. C3 and heavier NGLs can be transported by pipeline, rail, or truck. Propane is used both as a petrochemical feedstock and for residential/commercial purposes (home heating, cooking, etc.). As the only NGL with direct consumer consumption, an integrated distribution system exists for marketers to sell propane to consumers. Normal butane is seasonally blended into the gasoline pool and also used as a chemical feedstock, while isobutane is utilized only as a chemical feedstock. Natural gasoline (consisting of C5 and heavier alkanes) is used for gasoline blending, as a blendstock for bitumen transport, and as a petrochemical feedstock.

Figure 1-1: Natural gas liquid terminology used in this work.



1.2 Recent Changes in the Natural Gas Liquids Industry

Between 2009 and 2015, production of NGLs in the United States has increased by more than 50%, as shown in Figure 1-2. Both natural gas production and crude oil refining contribute to NGL supply. However, the recent growth in NGL production has been due only to natural gas processing (NGPLs) with almost no change in the amount of LRGs produced by refineries (Figure 1-3).

Figure 1-2: Monthly U.S. natural gas plant field production, January 2005 – November 2015.[6]

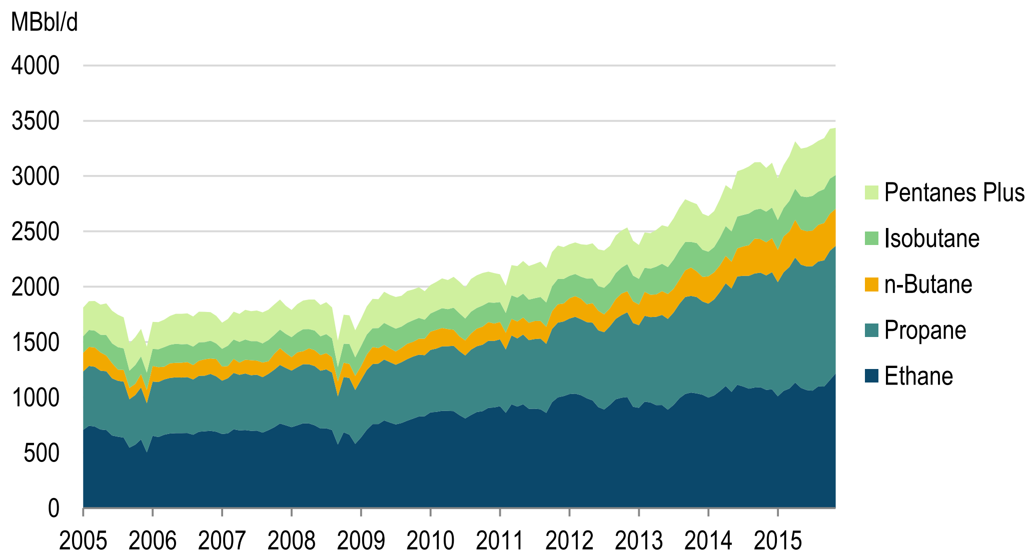
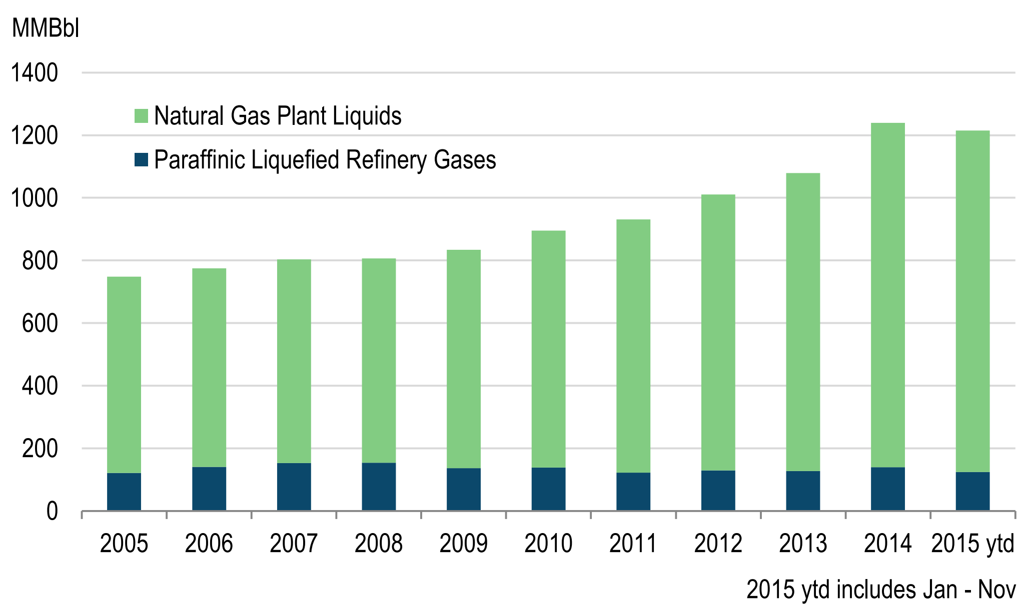


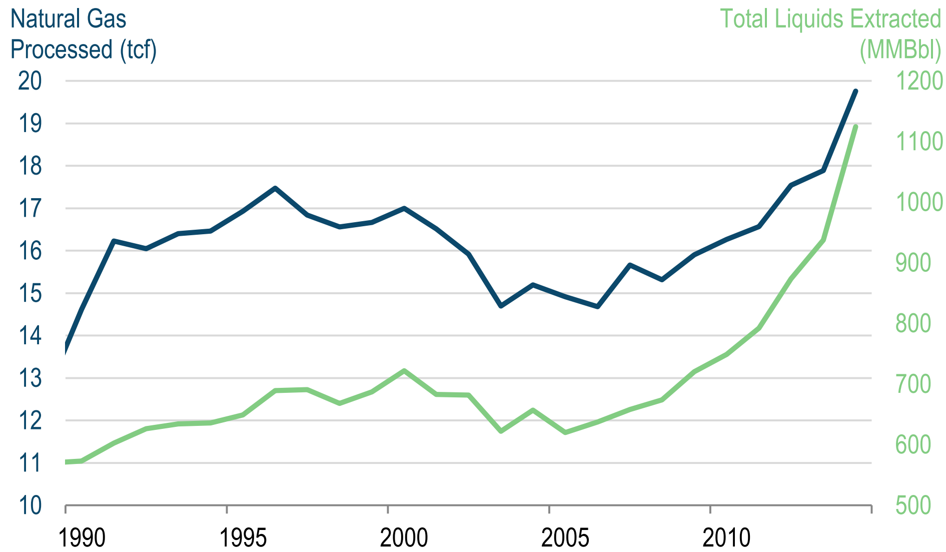
Figure 1-3: Natural gas liquids production from gas processing plants and refineries.[7,8,9]



As shown by Figure 1-3, NGL production from refineries has remained relatively constant since 2005, while production from the wet natural gas stream has increased. This shift can partly be attributed to the volume and type of natural gas processed. From 2006 to 2014, annual U.S. natural gas processing has increased by more than 5 trillion cubic feet (tcf).[10] This increase in gas processing has enabled an increase in the volume of liquids extracted. Natural gas plant liquids production from 2005 to the end of 2014 closely tracks the volume of natural gas processed, as shown in Figure 1-4, due to the change in composition of produced gas and favorable extraction economics. Recent production has been primarily from shale plays, which generally produce wetter gas than other natural gas sources. Due to a suppressed natural gas price and relatively high liquids prices during the last decade, producers increasingly targeted plays rich in liquids for production.[11] The economics of production can be improved when a larger portion of products are liquids because of their high market value on a BTU basis compared to dry natural gas. Relatively high oil prices and low natural gas prices make the liquids-rich portions of reservoirs more desirable, driving the increase in wet gas production.[12] During the high oil price period between 2010 and 2014, fractionation spreads[a] have been consistently above \$4.50/MMBtu, peaking above \$12/MMBtu in 2011, indicating the relative value of associated liquids production.[13] Increased production of wet gas, with favorable liquids pricing has driven increased natural gas processing and NGPL extraction.

[a] Fractionation spreads describe the value of processing natural gas to extract NGLs. A high spread indicates increased value realized by extracting NGLs from a wet natural gas stream.

Figure 1-4: Annual U.S. natural gas processing and liquids extraction, 1990 – 2014.[14]



With this increase in production, the NGL industry has experienced changes in purity product prices, transportation infrastructure, storage, and exports.

1.2.1 Changes in Natural Gas Liquids Production Locations

At the beginning of the shale era in the United States, a large portion of dry shale gas resource development occurred in the Barnett and Fayetteville basins. As liquid-rich areas were targeted, production began increasing in other regions. The first two basins targeted for development based on wet shale potential were the Bakken and Eagle Ford.[15] The Bakken development has mainly been focused on oil-rich shale, while Eagle Ford, Marcellus, and Utica were early players in NGL-driven production.

HGL production by PADD[b] is shown in Figure 1-5. While PADD 3 is still the dominant producing region (due primarily to the Permian and Eagle Ford Basins), the growth in production from PADDs 1 and 2 is significant when compared to historically minimal production. In just over five years, NGL production in PADD 1 grew from 24 MBbl/d in January 2010 to 292 MBbl/d in June 2015. In June 2015, natural gas plant field production of NGLs was more than 70% ethane and propane.[16] The increase in ethane and propane in PADD 1 is in the Marcellus Basin and part of the Utica Basin. This production is located closer to the major propane demand cities in the Northeast than production in PADD 3 and PADD 2. An ethane market has also started to emerge in the Marcellus region with multiple proposed ethylene cracker projects,[17,18] exports from Marcus Hook, PA,[19] and dedicated ethane take-away capacity on the Enterprise ATEX pipeline.[20]

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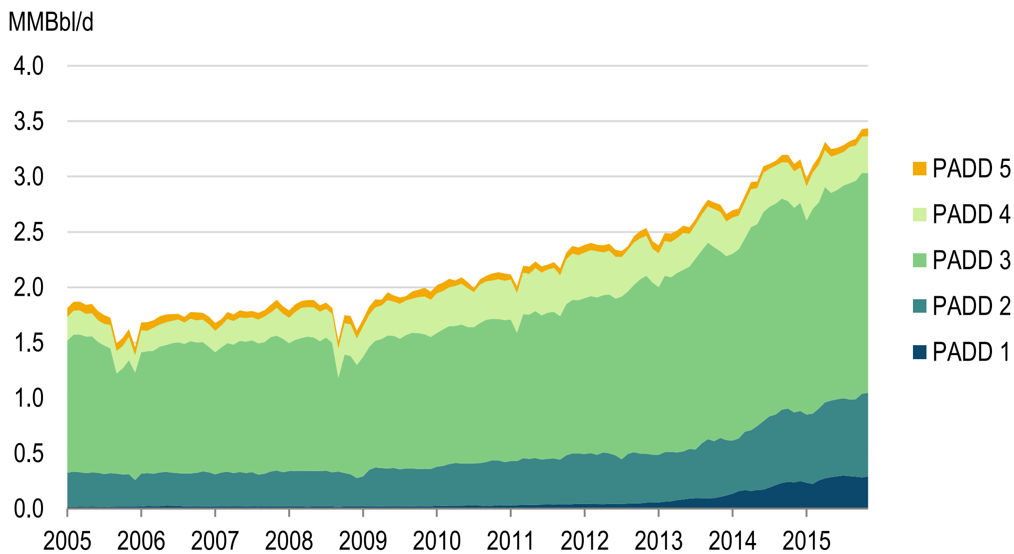
[b] The Petroleum Administration for Defense Districts (PADD) are regional groupings of the U.S. states into five districts:
PADD 1: The District of Columbia, Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut, New Jersey, Delaware, Maryland, Virginia, North Carolina, South Carolina, Georgia, Florida, New York, West Virginia, Pennsylvania
PADD 2: Indiana, Illinois, Kentucky, Tennessee, Michigan, Ohio, Minnesota, Wisconsin, North Dakota, South Dakota, Oklahoma, Kansas, Missouri, Nebraska, Iowa
PADD 3: Texas, Louisiana, Mississippi, Alabama, Arkansas, New Mexico
PADD 4: Montana, Idaho, Wyoming, Utah, Colorado
PADD 5: Washington, Oregon, California, Nevada, Arizona, Alaska, Hawaii

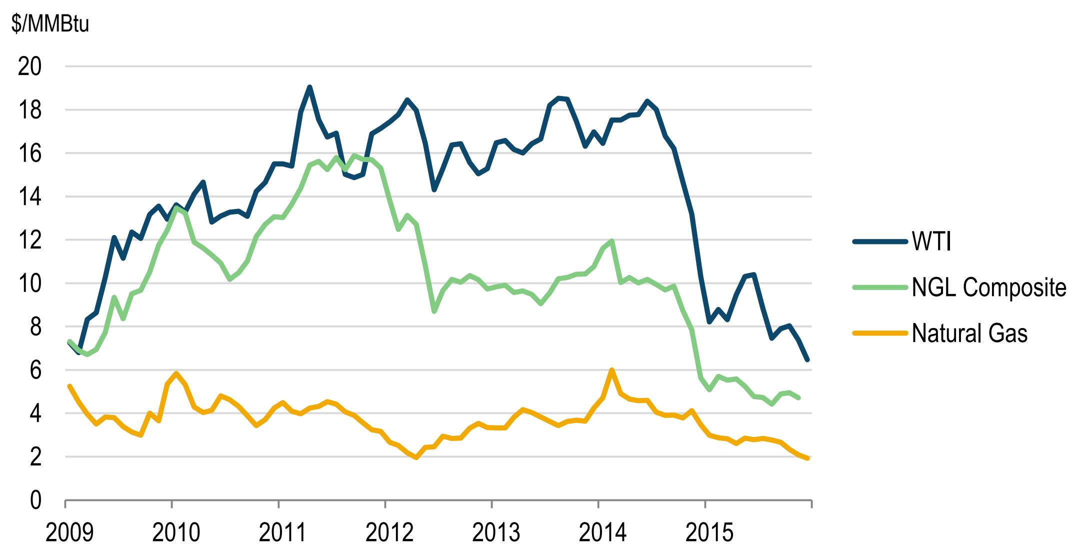
Figure 1-5: Monthly natural gas plant field production of hydrocarbon gas liquids, 2005 – 2015.[21]



1.2.2 Prices

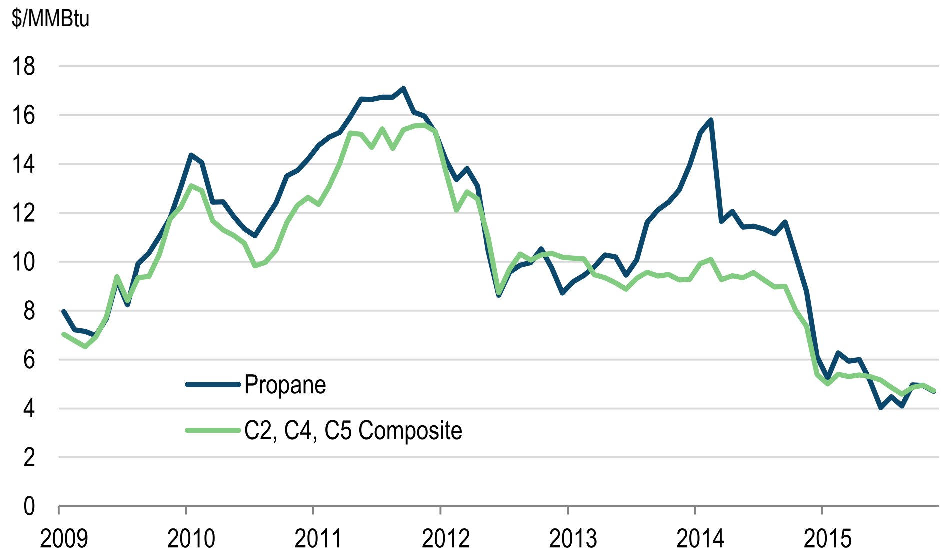
Along with significant changes in NGL production, NGL price dynamics have been altered dramatically over the past five years. Before 2012, NGL composite prices closely tracked crude oil prices on a BTU basis. Since 2012, NGL composite prices have decreased to fall between crude oil and natural gas spot prices (Figure 1-6).[22] Spot prices of individual NGL components have experienced different trends. Ethane spot prices have dropped from a high in August 2008 and throughout 2013 and 2014 traded near the Henry Hub natural gas spot price.[23] The natural gas price is an approximate price floor for ethane, as ethane can be sold as a component of natural gas if the price of ethane is too low to justify the cost of extraction (ethane rejection). With the increase in NGL supply, ethane and other NGL prices have decoupled from crude oil prices since mid-2012. Because ethane accounts for over 40% of the NGL composite price, the recent ethane price decrease is a major contributor to the drop in the NGL composite price.

Figure 1-6: Monthly spot price of crude oil (West Texas Intermediate (WTI) at Cushing, OK), NGL composite, and natural gas (Henry Hub), January 2009 – November 2015.[24,25,26]



The price of propane fell following the warm winter of 2011-2012 due to reduced home-heating demand and elevated stocks. The propane price rebounded in 2013 due to a large, wet corn harvest that severely depleted PADD 2 inventories. In January 2014, spot propane prices in the U.S. hit record levels due to multiple factors including colder than normal weather, high fall 2013 process needs for farmers, transportation bottlenecks, and higher export levels.[27] Propane prices compared to the other NGL components are shown in Figure 1-7.

Figure 1-7: Monthly propane Mont Belvieu spot price F.O.B. (free on board) and EIA NGPL composite price without propane, January 2009 – November 2015.[28,29,30]



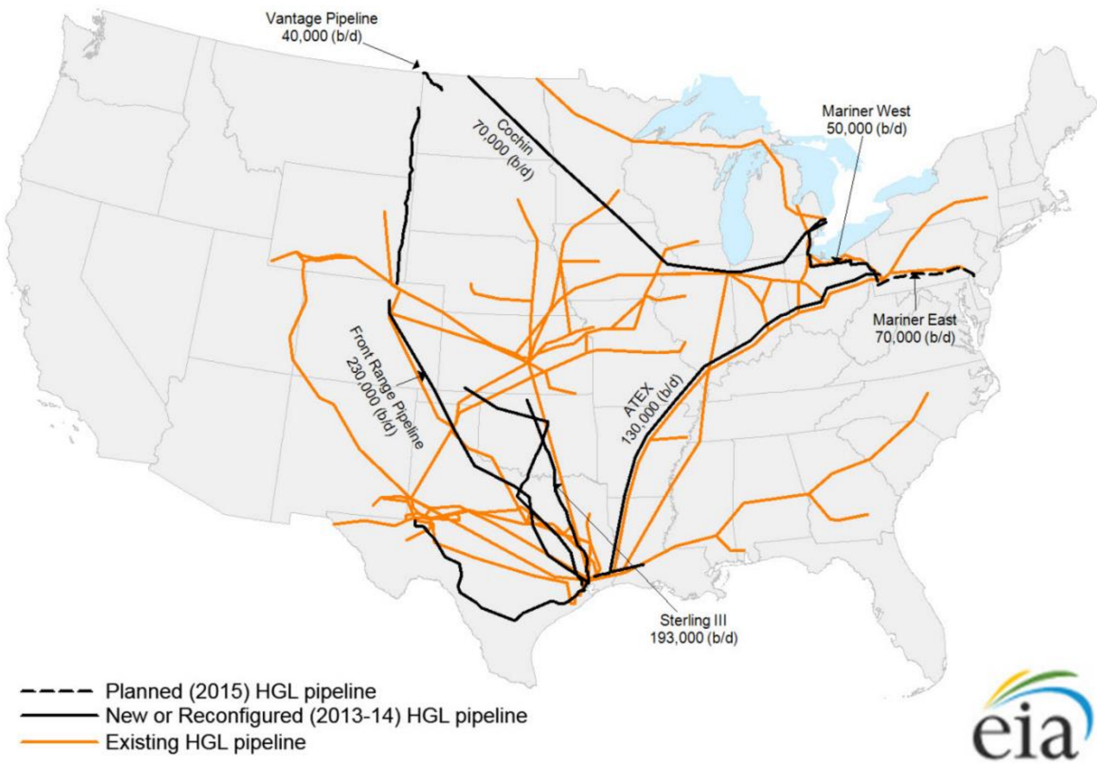
1.2.3 Infrastructure

As changes in NGL production have occurred since 2005, the flow pattern around the U.S. has evolved. Throughout the early 2000s, PADD 1 produced typically less than 30 MBbl/d of NGLs from natural gas processing plants. In less than four years (January 2012 – May 2015), PADD 1 NGL production has increased nearly 10 fold. PADDs 2 and 3 have also seen a large increase in production.[31]

The changing production locations of NGLs have necessitated changes in NGL transportation infrastructure. To serve the increasing ethane production in the Marcellus region, Enterprise Products recently began operation of the ATEX (Appalachia to Texas) Pipeline, which brings Marcellus/Utica ethane to petrochemical markets near Mont Belvieu.[32] The Cochin pipeline (which originally transported propane from Canada to

PADD 2) was reversed in April 2014 to ship light petroleum liquids from Illinois to western Canada.[33] Recent and projected pipeline changes are shown in Figure 1-8.

Figure 1-8: Changes to hydrocarbon gas liquid (HGL) pipeline infrastructure.[34]

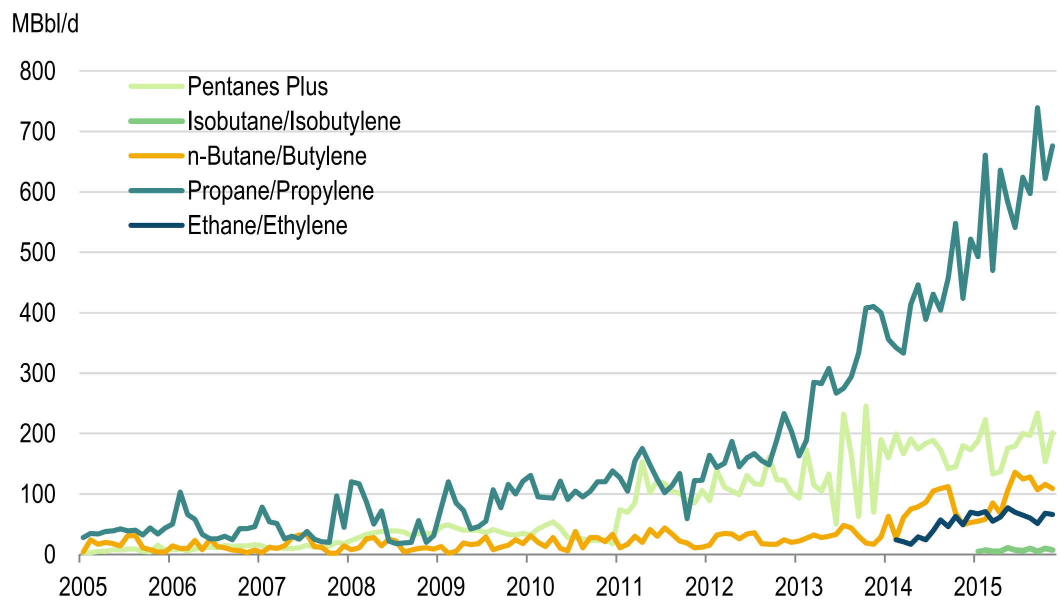


1.2.4 Storage and Exports

The NGL market is balanced using storage and exports. With increasing levels of NGL production, and a comparatively small amount of available storage, a large portion of production is exported if local demand is not sufficient or accessible. Because of these constraints and favorable international price spreads, HGL exports have increased significantly since 2010, with propane/propylene exports seeing the largest increase

(Figure 1-9). The EIA data does not differentiate between the alkane and alkene component of export volumes.

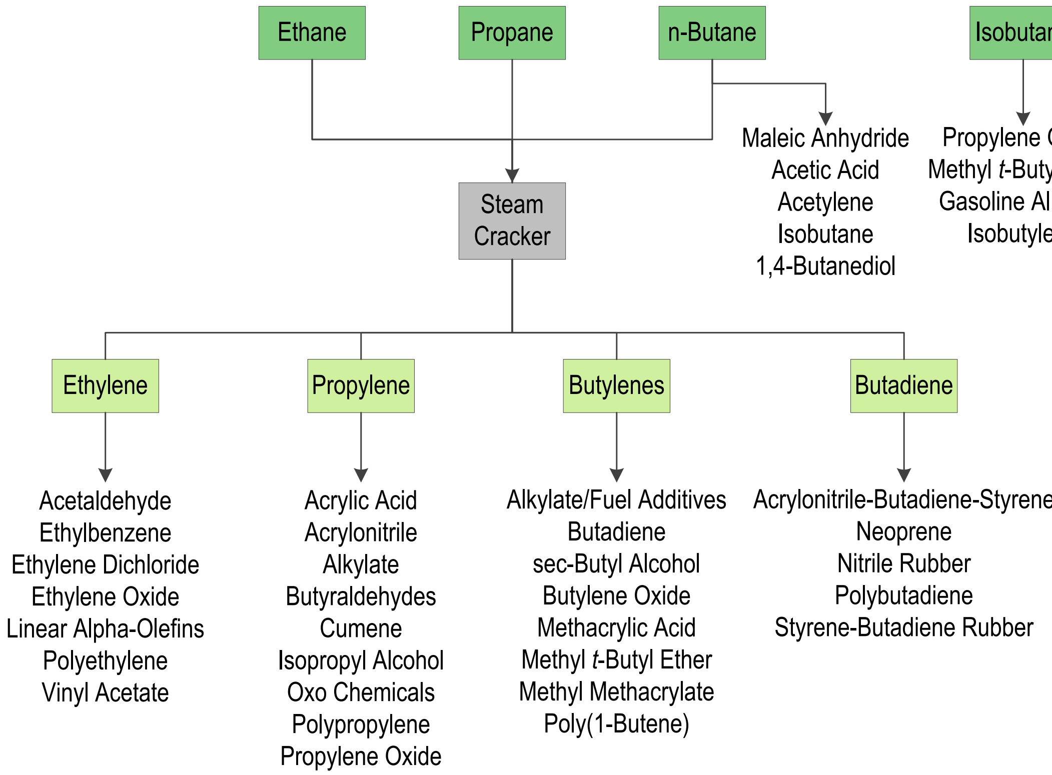
Figure 1-9: Monthly U.S. exports of hydrocarbon gas liquids, January 2005 – November 2015.[35]



1.3 Use of Natural Gas Liquids in the Petrochemical Industry

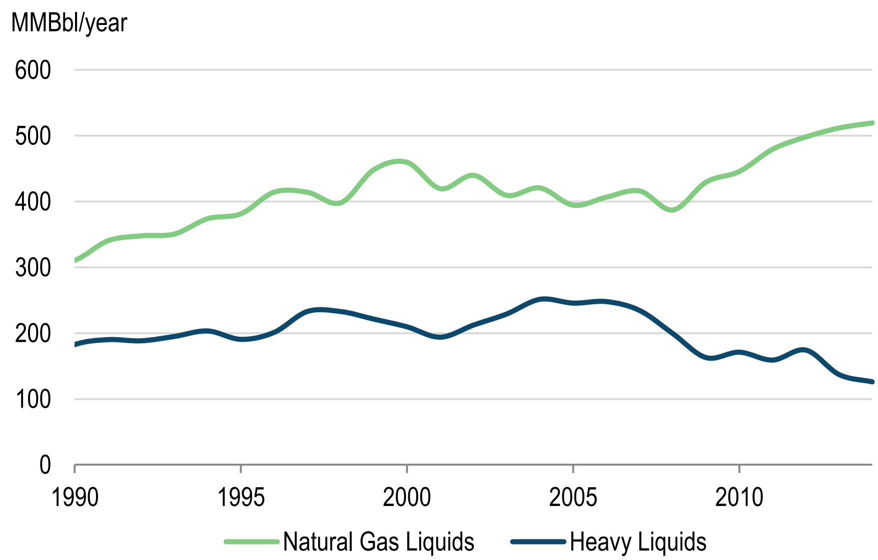
While NGLs are used for fuel blending and residential use, the single largest consumption sector is the petrochemical industry, accounting for 50-60% of NGL use.[36] The petrochemical industry uses NGLs as a feedstock to produce a wide variety of intermediate and final end products. The most common intermediate use is to convert NGLs into olefins through steam cracking or dehydrogenation. These olefins are then used in the production of many other chemicals. Select examples of commodity chemicals derived from NGLs are shown in Figure 1-10.

Figure 1-10: Select chemicals derived from natural gas liquids.



The U.S. chemical industry has already begun adapting to the increased availability, at low cost, of natural gas and NGLs. From 2005 to 2014, the use of NGLs for feedstocks has increased more than 30%, while the use of heavy liquids (such as naphtha from petroleum processing) has decreased almost 50%.[37] The distribution of feedstock use in the chemical industry between NGLs and heavy liquids is shown in Figure 1-11. On-going changes in the availability and price of methane, ethane, propane, butanes, and pentanes have the potential to influence the structure of the United States commodity chemical manufacturing industry. Because of their current low cost and high domestic availability, there is an incentive for manufacturers to use NGLs as a feedstock where possible, replacing heavy liquids such as naphtha. One impact of using these different feedstocks is changing byproduct slates. For example, cracking naphtha to ethylene produces higher yields of C5 components than cracking ethane to ethylene. Also, NGLs are recovered at geographically distributed processing facilities instead of centralized petroleum refinery locations. This difference in feedstock geography may affect the scale and location of future chemical manufacturing operations. Because of the large number of chemical supply chains that originate from NGLs, structural changes in the industry have the potential to propagate throughout the chemical network, impacting production costs, product prices, and manufacturing technologies used for many final end products.

Figure 1-11: Annual feedstock sources in the United States chemical manufacturing industry, 1990 – 2014.[37]



1.4 Research Objectives

With the surge in domestic NGL production, the U.S. has been presented with an unprecedented opportunity to spur growth and innovation in the chemical industry. The U.S. has already seen changes in manufacturing due to increased shale gas and associated liquids production. Over $145 billion worth of investment projects linked to shale gas have been publicly announced, which would contribute to more than 700,000 long-term, permanent jobs in the U.S.[38] Methane-to-chemicals technologies have seen a resurgence, with BASF announcing the potential for a new propylene plant to be built in the U.S. by 2019 – the first utilization of a methane-to-propylene technology outside of China.[39] With a forecasted increase in NGPL production from 2015 levels (even under an oil price contraction scenario),[40] the chemical industry will continue to adapt to using more NGLs. Because of the diversity of NGL end uses, large lead times for infrastructure development, and interdependencies with other energy markets, the industry will face challenges as it grows. For example, because of propane's use as a home heating fuel, ensuring delivery to residential consumers during the winter is a crucial task of the industry, but the seasonality of demand poses a challenge for infrastructure management and long-term export planning.

This thesis examines structural changes to the chemical manufacturing industries in the United States that may occur as the result of expanded availability of low cost NGLs. Industry-wide modeling, coupled with region-specific analysis, is used to highlight the challenges and opportunities for chemical manufacturing and U.S. energy policy as NGLs continue to expand their influence in the chemical manufacturing industry. Because of the interconnected nature of the industry, the manufacturing costs of upstream chemicals can have a significant impact on a wide range of final end product and consumer prices. **Objective 1 was to use industry-wide input-output models to**

estimate the potential magnitude of cost changes for a range of chemicals based on fluctuations in natural gas and NGL prices.

As the chemical industry evolves to take advantage of abundant domestic feedstocks, new technologies may be introduced. **Objective 2 was to identify new reaction pathways that may become viable as the industry evolves.** The impact of these new technologies on related manufacturing processes was determined using network models of the industry.

With the production, price, and transport changes occurring in the NGL and petrochemical industries, there is an opportunity to reevaluate the traditional chemical manufacturing system in the United States. With the abundance of natural gas and NGLs now produced in areas removed from the Gulf Coast, a distributed manufacturing system may be feasible. **Using the Four Corners region as a case study, Objective 3 was to develop and implement an analytic process for evaluating greenfield manufacturing based on specific feedstock availability and global chemical markets.**

Economic and operational decisions faced by entities in the NGL industry are complicated to forecast because of the size of the industry and competing sector goals. **Objective 4 was to understand the interplay between economic decisions made concerning exports, midstream infrastructure, supply, and new chemical demand.**

1.5 DISSERTATION OVERVIEW

This dissertation is organized into seven chapters. The first chapter has provided an introduction to the NGL industry and described the importance of NGLs for chemical manufacturing. Chapter 2 consists of a literature review of modeling techniques used to understand the industry's behavior followed by a review of federal policy initiatives that impact NGLs and chemical manufacturing. Chapter 3 describes a linear program developed to understand the impact of NGL prices on chemical manufacturing costs. The fourth chapter uses that same linear program in a different context – using cost points to design a new technology that will optimally fit into the existing industry. Chapter 5 explores the possibility for greenfield manufacturing using resources close to their production areas, with methane production in the Four Corners as a case study. Chapter 6 motivates the development of an agent-based model to be used to analyze the economic interactions between entities in the NGL industry – from production to secondary chemical consumption. Chapter 7 presents a summary of conclusions and outlines recommendations for future work conducted to understand the continuing changes in the NGL and chemical manufacturing industries. Finally, addressing the core objectives of this thesis required development of analytic tools that have broad application. Appendices to this thesis frame some of the analytic tools developed in this work in a broader context.

1.6 References

1. U.S. Energy Information Administration (EIA), *Natural Gas Gross Withdrawals and Production,* http://www.eia.gov/dnav/ng/ng_prod_sum_a_EPG0_FGW_mmcf_m.htm (accessed August 24, 2015).
2. U.S. Energy Information Administration (EIA), *Crude Oil Production*, http://www.eia.gov/dnav/pet/pet_crd_crpdn_adc_mbbl_m.htm (accessed August 24, 2015).
3. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production,* http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_m.htm (accessed August 24, 2015).
4. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production,* http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_m.htm (accessed August 24, 2015).
5. U.S. Energy Information Administration (EIA), *Today in Energy: What are natural gas liquids and how are they used*, April 20, 2012, https://www.eia.gov/todayinenergy/detail.cfm?id=5930 (accessed August 24, 2015).
6. U.S. Energy Information Administration (EIA), *U.S. Natural Gas Plant Field Production*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbblpd_m.htm (accessed August 24, 2015).
7. U.S. Energy Information Administration (EIA), *Hydrocarbon Gas Liquids (HGL): Recent Market Trends and Issues*, November 2014, http://www.eia.gov/analysis/hgl/pdf/hgl.pdf (accessed August 25, 2015).
8. U.S. Energy Information Administration (EIA), *Refinery Net Production (Annual-Thousand Barrels* and *Monthly-Thousand Barrels)*, http://www.eia.gov/dnav/pet/pet_pnp_refp2_dc_nus_mbbl_a.htm (accessed August 25, 2015).
9. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Annual-Thousand Barrels* and *Monthly-Thousand Barrels)*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_a.htm (accessed August 25, 2015).
10. U.S. Energy Information Administration (EIA), *Natural Gas Plant Processing*, http://www.eia.gov/dnav/ng/ng_prod_pp_a_EPG0_ygp_mmcf_a.htm (accessed August 25, 2015).
11. National Petroleum Council, *NPC NGL Study: NGL Supply and Demand through 2035*, Paper #1-13 of the NPC North American Resource Development Study, September 15, 2011.
12. Troner, A. *Natural Gas Liquids in the Shale Revolution*, James A. Baker III Institute for Public Policy, Rice University, April 29, 2013.

13. RBN Energy, *Spotcheck: Gas Processing Frac Spread*, October 2013.

14. U.S. Energy Information Administration (EIA), *Natural Gas Plant Processing (Natural Gas Processed* and *Total Liquids Extracted)*, http://www.eia.gov/dnav/ng/ng_prod_pp_a_EPG0_ygp_MMcf_a.htm (accessed August 25, 2015).

15. Troner, A. *Natural Gas Liquids in the Shale Revolution*, James A. Baker III Institute for Public Policy, Rice University, April 29, 2013.

16. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Monthly-Thousand Barrels per Day*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_r10_mbblpd_m.htm (accessed September 30, 2015).

17. Oil & Gas Journal, *Ethane, polyurethane processing to grow in West Virginia*, November 15, 2013, http://www.ogj.com/articles/2013/11/ethane-polyurethane-processing-to-grow-in-west-virginia.html (accessed September 30, 2015).

18. Shell Appalachian petrochemical project, http://www.shell.us/about-us/projects-and-locations/appalachian-petrochemical-project.html (accessed September 30, 2015).

19. ICIS Chemical Business, *AFPM: Ethane exports begin to build*, March 20, 2015, http://www.icis.com/resources/news/2015/03/20/9869769/afpm-ethane-exports-begin-to-build/ (accessed September 30, 2015).

20. Enterprise Products Partners, L.P., *NGL Pipelines*, http://www.enterpriseproducts.com/operations/nglPipelines.shtm (accessed September 30, 2015).

21. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Monthly-Thousand Barrels per Day*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_r10_mbblpd_m.htm (accessed September 30, 2015).

22. U.S. Energy Information Administration (EIA), *Today in Energy: High value of liquids drives U.S. producers to target wet natural gas resources.* May 8, 2014, http://www.eia.gov/todayinenergy/detail.cfm?id=16191 (accessed August 25, 2015).

23. RBN Energy, *Spotcheck: Ethane to HH Gas Ratio*, July 2015.

24. U.S. Energy Information Administration (EIA), *Today in Energy: High value of liquids drives U.S. producers to target wet natural gas resources.* May 8, 2014, http://www.eia.gov/todayinenergy/detail.cfm?id=16191 (accessed August 25, 2015).

25. U.S. Energy Information Administration (EIA), *Natural Gas Spot and Futures Prices (NYMEX),* http://www.eia.gov/dnav/ng/ng_pri_fut_s1_m.htm (accessed August 25, 2015).

26. U.S. Energy Information Administration (EIA), *Spot Prices – Monthly,* http://www.eia.gov/dnav/pet/pet_pri_spt_s1_m.htm (accessed August 25, 2015).

27. U.S. Energy Information Administration (EIA), *Today in Energy: Midwest propane markets tighten further on cold weather*, January 23, 2014, http://www.eia.gov/todayinenergy/detail.cfm?id=14711 (accessed August 25, 2015).

28. U.S. Energy Information Administration (EIA), *Spot Prices for Crude Oil and Petroleum Products*, http://www.eia.gov/dnav/pet/pet_pri_spt_s1_m.htm (accessed September 22, 2015).

29. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Monthly-Thousand Barrels)*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_m.htm (accessed September 22, 2015).

30. U.S. Energy Information Administration (EIA), *Natural Gas Spot and Futures Prices (NYMEX),* http://www.eia.gov/dnav/ng/ng_pri_fut_s1_m.htm (accessed September 22, 2015).

31. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Annual-Thousand Barrels* and *Monthly-Thousand Barrels)*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_a.htm (accessed August 25, 2015).

32. Enterprise Products Partners, *NGL Pipelines,* http://www.enterpriseproducts.com/operations/nglPipelines.shtm (accessed August 25, 2015).

33. U.S. Energy Information Administration (EIA), *Today in Energy: Without the Cochin pipeline, western Canadian propane seeks new outlets,* March 27, 2015, http://www.eia.gov/todayinenergy/detail.cfm?id=20552 (accessed August 25, 2015).

34. U.S. Energy Information Administration (EIA), *Hydrocarbon Gas Liquids (HGL): Recent Market Trends and Issues*, November 2014, http://www.eia.gov/analysis/hgl/pdf/hgl.pdf (accessed August 25, 2015).

35. U.S. Energy Information Administration (EIA), *Exports (Monthly-Thousand Barrels per Day)*, http://www.eia.gov/dnav/pet/pet_move_exp_dc_NUS-Z00_mbblpd_m.htm (accessed August 25, 2015).

36. National Petroleum Council, *NPC NGL Study: NGL Supply and Demand through 2035*, Paper #1-13 of the NPC North American Resource Development Study, September 15, 2011.

37. American Chemistry Council, *Business of Chemistry Annual Data*, 2015.

38. American Chemistry Council, *U.S. Chemical Investment Linked to Shale Gas: $145 Billion and Counting*, June 2015, http://www.americanchemistry.com/Policy/Energy/Shale-Gas/Fact-Sheet-US-Chemical-Investment-Linked-to-Shale-Gas-145B-and-Counting.pdf (accessed August 28, 2015).

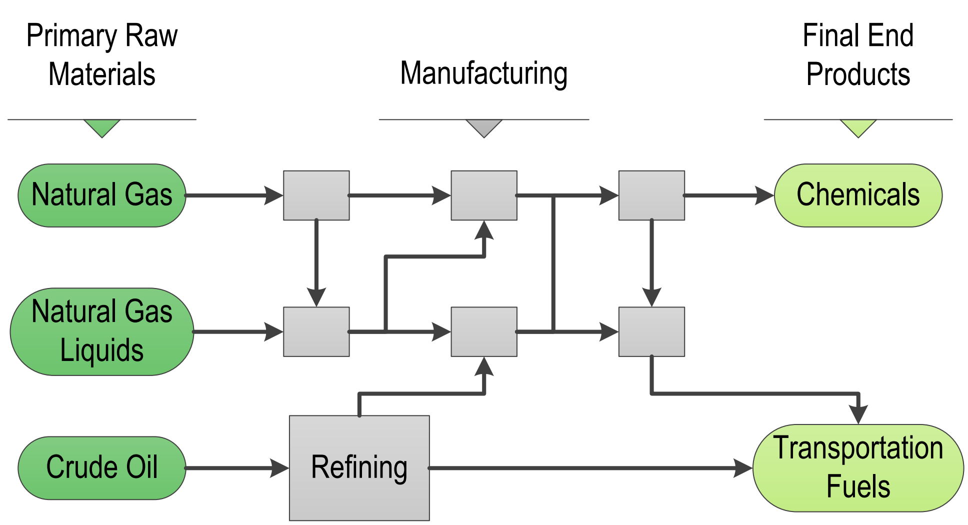
39. Carr, C. *BASF Chemical Evaluates Investment in World-Scale Methane-to-Propylene Complex on U.S. Gulf Coast*, IHS Chemical Research Note, May 5, 2014, https://www.ihs.com/pdf/Research-Note-BASF-Propylene_186332110913049832.pdf (accessed August 28, 2015).

40. RBN Energy, *It's Not Supposed to Be That Way – Part 1*, Drill Down Report, June 2015.

Chapter 2: Modeling the Chemical Industry

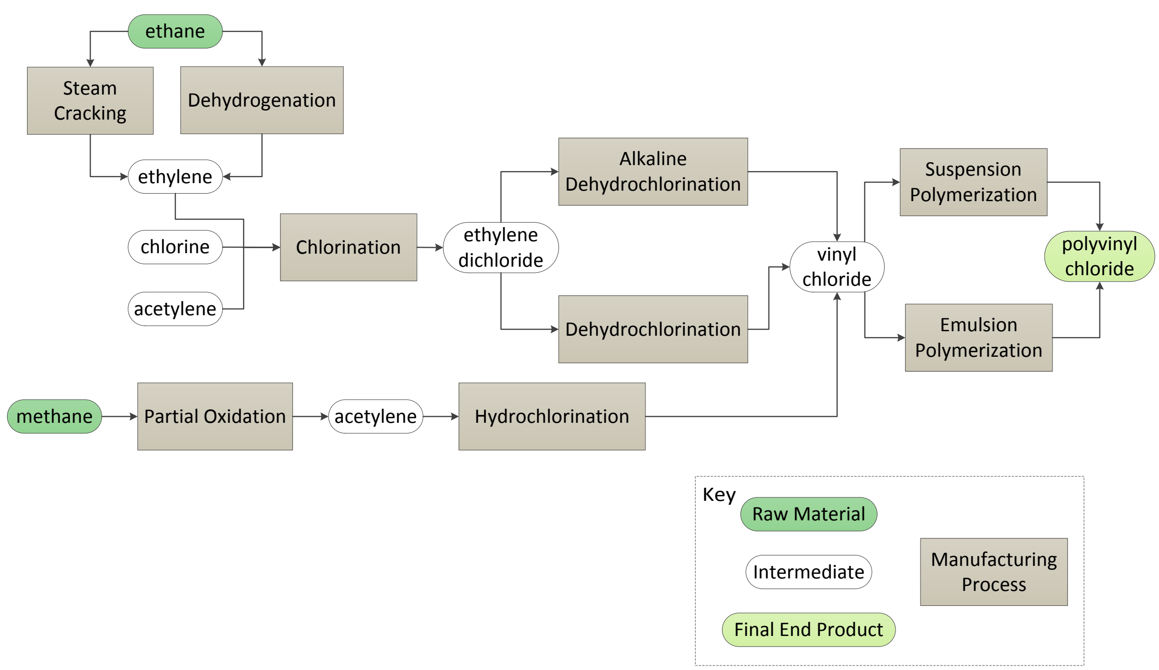
The chemical industry in the United States is designed to convert primary raw materials into intermediates and then into a variety of final end products. The primary raw materials are extracted hydrocarbons and can be classified into three groups: natural gas, natural gas liquids (NGLs), and crude oil. A large number of final end products are produced, with uses in many sectors of the economy. Common final end products include transportation fuels (gasoline, diesel, etc.), plastic materials (polyethylene, polyvinyl chloride), fertilizers (ammonia, urea), and fibers (nylon, polyester). The conversion of raw materials to final end products is achieved through a series of refining and chemical manufacturing processes that form the structure of the petrochemical industry, illustrated in Figure 2-1.

Figure 2-1: Structure of the petrochemical industry.



The processes in the chemical manufacturing industry form a complex network, designed to convert the small number of feedstocks into a diverse array of intermediate chemicals and final end products. In many cases, different technologies have been developed to produce the same material. These "dissimilar chemical routes" add to the complexity of the network, introducing multiple pathways for manufacturing between one starting chemical and its respective end products.[1] Figure 2-2 shows a portion of the network to produce polyvinyl chloride using different starting materials and technologies.

Figure 2-2: Process pathways to produce polyvinyl chloride.[2]



Two different techniques were utilized in this work to model the chemical industry: optimization and agent-based modeling. Each modeling technique conceptualizes the industry as a network in a different way. Optimization models typically represent technology choices as nodes and the type of chemical as a connection.

This is the representation shown in Figure 2-2. Agent-based models used in this work conceptualize physical plant locations as nodes (with inherent technologies for material conversion) and chemical shipments as connections. This chapter first describes the scientific development of these two modeling areas applied to the chemical industry. Then, to illustrate how these analytic tools can inform decisions, a review of United States policies related to NGLs is presented, including the analytical framework for federal policies in the United States.

2.1 Optimization Models of the Petrochemical Industry

Models of chemical manufacturing networks originated with Stadtherr and Rudd[3] and were described in detail by Rudd et al.[1] Stadtherr describes the benefit of large-scale, integrated models of the industry:

> The many segments of this [petrochemical] system interact by competing for raw materials and markets, and by developing and licensing competing process technologies. Thus, if particular segments of the industry are examined in isolation, there is no guarantee that the conclusions reached will be significant when the performance of the overall system is of importance. In such a large, interactive system, the whole is not necessarily made more efficient if one particular part is improved. In fact, local inefficiencies may be necessary if the overall system is to operate at maximum efficiency.[4]

Stadtherr shows that modeling the petrochemical system on a national scale enables an understanding of the system as a whole that may not be possible when studying specific technologies or individual supply chains. These models generally build a network around process stoichiometry instead of individual facilities. In order to identify macro-level trends, optimization models of the petrochemical industry are designed to approximate the general behavior of the industry while ignoring local economic-driven decisions.[4]

2.1.1 Mathematical Representation of the Industry

Because the optimization networks are built around stoichiometric connections between technologies, the framework for a mathematical representation is a material balance around each chemical present in the industry. For chemical i in process j, the material balance is

$$F_i + \sum_j a_{i,j} X_j - Q_i = 0$$

where F represents primary feedstock supply, X_j is the utilization rate of process j (in units of the primary product of the process), Q is the amount of final end product produced, and $a_{i,j}$ is the input-output coefficient. The input-output coefficient describes the mass of i consumed (negative coefficient) or produced (positive coefficient) in process j per unit mass of primary product for that process. Two major constraints, relating to supply of the primary feedstocks (S) and demand of the final end products (D), will be applied to the system. For chemical i, the constraints are represented as

$$0 \leq F_i \leq S_i$$

$$Q_i \geq D_i$$

The amount of chemical i used as a primary feedstock must be less than or equal to the amount supplied annually, and the amount of final end product, Q, must be greater than or equal to demand in the represented market.[1,2,5,6,7]

A linear program is formulated based on stoichiometry, supply, and demand. The solution determines the set of chemical flows and technologies that use available primary raw materials and supply required final end products while minimizing production cost of the entire industry as the objective function. As discussed below, other objective functions besides minimizing production cost have also been used.

With the modeling framework used in this work, the optimal structure of the industry is based entirely on production cost (which includes capital and variable costs) but does not include costs of shared infrastructure. Off-site infrastructure costs for each technology are included as part of the unit production cost (refrigeration, utilities, waste, storage, and tankage) and general service facilities are assumed to cost 20% of battery limits plus utilities and tankage, based on the IHS Process Economics Program Yearbook methodology, which is the primary data source. However, large-scale shared infrastructure (pipelines, railways, loading and unloading facilities) that are typically owned by midstream or other companies have costs that are not included as part of the process cost. Shared infrastructure investments are an important component of industry operation and can serve as driving forces for new plants and new technology buildout. Minimizing overall production cost provides no feedback about how infrastructure impacts evolution of the industry's structure. New technologies may require new piplines or rail terminals, and these costs are not included in the unit production costs for each technology.

2.1.2 Applications of the Linear Model

This fundamental representation of the industry has been utilized for a variety of applications. Rudd et al. developed a model of the 1977 U.S. chemical industry and used it to project a 1985 industry involving 131 chemicals and 182 processes. The projections discovered what specific process pathways would need to be expanded to meet 1985 demand, how new chemical technology would fare in the 1985 industry, and how changes in energy consumption and primary feedstock availability would impact the industry structure. Rudd et al. also developed a model based solely on primary feedstock and final end product prices, with no inherent information about intermediate prices. This model is shown to be useful when pricing information is limited. This "integrated model" is used to explore the price point at which a new feedstock and process can be competitive in the existing industry.[1]

Fathi-Afshar and Rudd also utilized the model to analyze how the introduction of new technologies could impact price projections, showing that chemical shadow prices from the dual problem are generally representative of the chemical's market value.[8] By utilizing the dual linear program, the model can be used to estimate the effectiveness of a new technology by comparing the shadow price of a chemical in a hypothetical environment to the market prices of chemicals in the business-as-usual environment.

Chang and Allen utilized a network model to assess the environmental impact of the chemical manufacturing system as a whole. By exploring the trade-off between total industry cost and total use of chlorine, Chang and Allen quantified the impact of lessening chlorinated intermediates on the industry's total production cost. A multi-objective optimization framework was utilized to screen new technologies that could reduce chlorine use, identifying the magnitude of their impact when considered as part of the integrated industry.[5]

Another application of optimization models in the chemical industry is in long-term planning for specific investment decisions. Sahinidis et al. developed a mixed integer linear program (MILP) that optimized plant construction and expansion schedules based on forecasts of chemical prices and demand. Sahinidis et al. implemented an optimization strategy to maximize net present value of a project over a number of time periods, by optimally allocating constrained capital to capacity expansions of individual plants. The authors explored a variety of solution strategies for their MILP, determining that integer cuts, strong cutting plane generation, and branch and bound methods are most suited to large petrochemical networks.[9]

An important characteristic of many chemical plants is their ability to switch feedstocks or reaction conditions to alter their product mix without any capital investment or down-time. For example, some ethylene production facilities can crack a combination of feedstocks (ethane, propane, n-butane, naphtha). The quantity of feedstocks used is determined based on availability, price, and distribution of coproducts and their respective prices/demand. Sahinidis and Grossmann have expanded their original investment MILP to include flexible plants. The flexible plants are continuous or batch facilities that can utilize a different combination of feedstock (and potentially produce a different distribution of products) in each time step. The representation of process flexibility is achieved by separating the plant capacity variable from the main product production rate (X_j, above). All alternative production schemes must be enumerated for each flexible process.[10,11] Near-term operational decisions of flexible plants require a different algorithm and solution procedure, as shown by Bok et al.[12]

Network models in general can be used in many different applications. Floudas et al. document the use of network models as part of multi-scale systems studies in the energy industry.[13] Supply chain network models have been developed and optimized for sectors such as biomass resource supply[14] and CO_2 capture, utilization, and sequestration.[15] The multi-scale framework involves a number of steps to design a system, beginning with screening optimal materials for individual technologies and processes and eventually building up an entire supply chain network model to be optimized.[13]

2.2 AGENT-BASED MODELING AND SIMULATION

Agent-based models are used to take information about individual processes and entities and discover system-wide behaviors that emerge from individual interactions. Agent-based models do not optimize the entire industry, but instead allow individual firms to optimize their operation, and explore how the industry as a whole behaves. A model begins by mathematically representing a system's components as firms and defining each firm's behaviors. A simulation then enables connections between components to form a complete system, representing an entire industry or event. The goal of an agent-based simulation is to discover "the ties between micro-level behavior and macro-level results."[16] This review will only describe agent-based modeling (ABM) in the context of the chemical and related industries.

The individual entity represented in agent-based models of the chemical industry is a chemical plant. This one enterprise-firm (an agent) encompasses representations of different business units in a plant, each with a mathematical representation of a decision-making framework with an ability to choose an optimal course of action when faced with choices. Anything within a firm that can make a business decision is then classified as a sub-agent within that firm. For example, a buying sub-agent for a chemical plant makes a decision about what raw materials to purchase. The buyer sub-agent is given specific quantities of materials to purchase and can calculate an optimal purchase procedure when presented with multiple options for chemicals to buy in the market from different sellers.

Individual plant agents are given specific rules to follow as they perform their tasks. These rules govern the interactions between agents at one plant and agents at other plants and how agents respond to new information. The fundamental goal of an agent-based model is to discover how those individual interactions between agents form a complex system with behavior on a whole that is different than behavior of the constituent parts.[16] The basis for understanding results is that the system as a whole adapts to exogenous changes in ways that cannot be discerned by just studying an individual plant or other component. This is because each agent has limited influence on the system as a whole, but the collective outcome of the system relies on each agent.[16]

Many components of supply chain systems have been modeled using an agent-based framework. Garcia-Flores and Wang constructed an ABM to simulate dynamic behavior of cooperating agents along a single supply chain.[17] The specific operation of a warehouse system was modeled by Ito and Abadi.[18] Models of refinery supply chains have been used to determine optimal business processes and configurations in one specific plant.[19,20]

All of these modeling techniques of specific behaviors can then be combined to represent an entire, dynamic chemical system. The U.S. Department of Homeland Security National Infrastructure Simulation and Analysis Center (NISAC) developed the NISAC Agent-Based Laboratory for Economics (N-ABLE) to conduct economic analysis of "homeland security-related disruptive events."[21] N-ABLE has been used to simulate the impact of disruptive events (both natural and man-made disasters) on the chemical industry. This framework effectively represents plant-level operations and the system-wide behaviors of the entire U.S. chemical industry. Ehlen et al. describe the theoretical basis for a number of different sub-agents of an enterprise-firm.[22] The production supervisor for the plant solves a linear program (LP) for production levels of technologies in the plant given unit capacities, how production units are connected to one another (utilizing byproducts), and current inventories of raw materials and products. The LP is designed to balance meeting optimal production targets for desired chemicals with the cost of storing materials in a warehouse for undesired chemicals (generally undesired chemicals are byproducts that cannot be sold at a profit).

Each of these enterprise-firms operating on a daily production schedule then interact with other plant agents in a market environment by buying from or selling to other plants. The ability for two agents to carry out a transaction depends on the specific chemical, market region, and transportation mode. The chemical flows between plants in a simulation form a supply chain, with plants as nodes, chemical flows as connections, and transport infrastructure as the connection pathways.

Ehlen et al. have utilized the N-ABLE framework with a chemical data model to simulate thousands of chemical plants and related firms in the U.S. As an example, they extracted data about the 1,4-butanediol supply chain and used the model to simulate potential behavior during a disruption event (a hurricane making landfall near New Orleans). By comparing agent behavior (production quantities, inventories, and shipments) from a baseline supply chain to a disrupted supply chain, the impact on shipments of other chemicals in the butanediol supply chain can be quantified. Their results show that for some chemicals in the supply chain in this scenario, sales recover to baseline levels in 60 days, while other chemicals take closer to 200 days to recover.[22] These results can be used to identify target chemicals for inventory build ups before a known disaster or to show which transportation infrastructure is most critical to repair after an event. Similar studies also conducted at NISAC show resilience of the entire petrochemical industry to other hurricane scenarios.[23]

2.3 United States Energy Policy Related to Hydrocarbon Gas Liquids

In general, the United States Federal Government has a limited role in regulating the HGL industry. Production of NGPLs, up to separation at a gas processing plant, is regulated as natural gas production. Transportation by pipeline is subject to standard hazardous liquid pipeline transport regulations. Federal Energy Regulatory Commission (FERC) jurisdiction over transportation of purity ethane, propane, and butane is handled on a case-by-case basis and is decided based on three factors: whether the material is a commodity subject to the Interstate Commerce Act (ICA), the pipeline is a common carrier, or the pipeline is involved in interstate commerce.[24] The ICA applies to "oil" transportation, but FERC's "ICA jurisdiction applies where oil or petroleum products that can be used for energy purposes are moved in interstate commerce."[25] There was a period of uncertainty surrounding transport of NGLs for non-energy purposes (chemical manufacturing). However, in FERC's declaratory order on Williams Olefins Feedstock Pipelines L.L.C.'s petition, purity ethane transport by pipeline was determined to be within its jurisdiction because "it is unquestionably a naturally-occurring hydrocarbon that is used for current energy purposes and will be used for future purposes."[25] Williams claimed that their ethane pipelines should not fall into FERC jurisdiction because ethane is not used as a fuel and will only be used as a petrochemical feedstock in this instance.[26,27] FERC notes the that the high BTU content of ethane enables potential blending with natural gas, and because Williams "does not have title to the ethane in its pipeline…it cannot be certain of the ultimate disposition of the ethane."[25] This reasoning led FERC to its conclusion to regulate ethane interstate transport even for petrochemical end uses, similar to the conclusion reached in other recent findings (*Enterprise Liquids Pipeline, LLC*, 144 FERC ¶ 61,083 (2013) and *Sunoco Pipeline, L.P.*, 142 FERC ¶ 61, 087 (2013)).[25]

The Energy Policy and Conservation Act of 1975 defines petroleum products as including "any natural gas liquid product."[28] Also, the U.S. Department of Commerce Bureau of Industry and Security (BIS) specifically includes propane, butanes, ethylene, propylene, butylene, butadiene, and liquefied petroleum gases in the definition of petroleum products.[29] Since October 1981, the U.S. Department of Commerce no longer restricts exports of petroleum products.[30] U.S. Department of Energy (DOE) permitting requirements for export of natural gas, as specified by Section 3 of the Natural Gas Act, do not pertain to NGLs. Therefore, exports of NGLs are allowed without a permit, unlike crude oil and natural gas. Petroleum products are still subject to "restriction(s)," however, as determined by the executive branch.[31]

The propane market is monitored differently than other HGLs because of propane's use as a residential home heating fuel. Because of the necessity of supply during the winter and extreme weather events, the federal government monitors propane availability and price. During the winter, EIA publishes wholesale and residential propane prices for 38 states.[32] The Reliable Home Heating Act, enacted on June 30, 2014, requires the EIA Administrator to notify state governors if propane inventories in their PADD are "below the most recent 5-year average for more than 3 consecutive weeks."[33] The Act also extends exemptions from Federal motor carrier safety regulations[34] for heating fuel delivery by commercial motor vehicles during a state of emergency declared by state governors in addition to a Presidential or Federal Motor Carrier Safety Administration declaration.[35]

The Northeast Home Heating Oil Reserve (NEHHOR) is a federal petroleum reserve operated by the U.S. Department of Energy. Ultra-low sulfur distillate is stored at locations in Connecticut and Massachusetts to supply home heating oil to residential consumers when allowed under the Energy Policy and Conservation Act.[36] The state of New York also maintains a distillate fuel oil reserve. Unlike heating oil, there is no federally maintained storage of propane to be used for emergencies. This was one of the driving factors for the legislation encouraging communication about inventory levels between EIA and the states.

Gasoline is blended to meet different federal specifications depending on the time of year and location in the United States. The two major specifications used in gasoline blending are octane and Reid Vapor Pressure (RVP). n-Butane demand as a motor gasoline blending component is driven primarily by the RVP requirement.[37] The optimal RVP of gasoline varies based on the time of year so n-butane is used seasonally. Blender net inputs of n-butane are near zero during the summer but peak in October (at levels as high as 77,000 bbl/d during October 2015).[38] Isobutane is used as a feedstock for alkylate, which impacts the octane rating of a fuel.[37]

2.3.1 Modeling Tools Used to Inform Federal Policy

The U.S. Department of Energy utilizes a number of modeling platforms to understand HGL markets and inform their policy decisions.

2.3.1.1 EIA Annual Energy Outlook

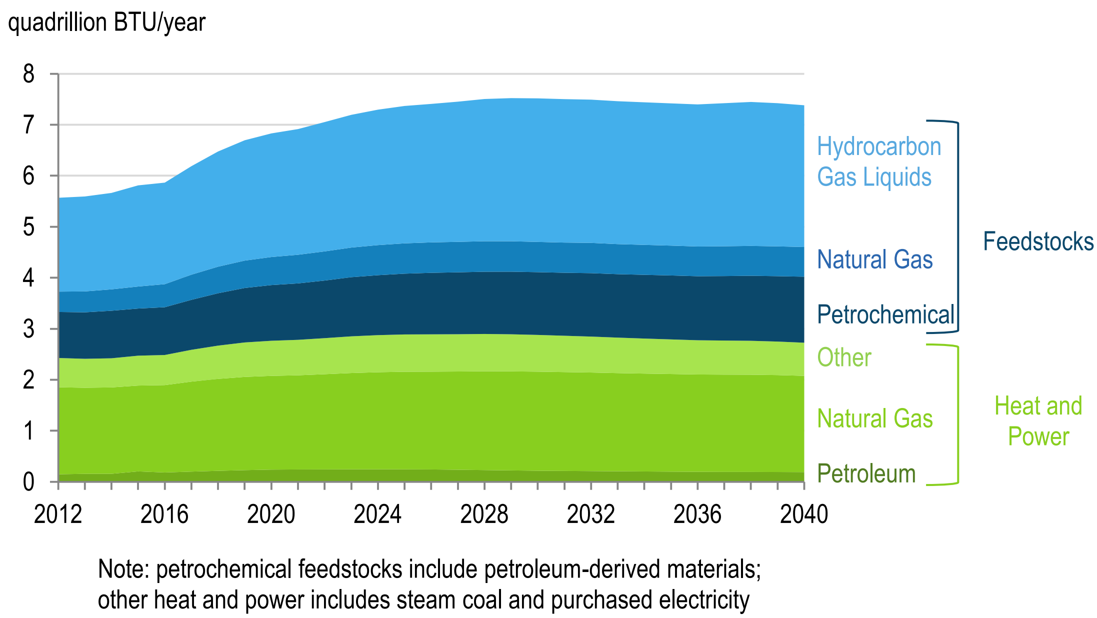
The most commonly referenced platform for projections is the EIA Annual Energy Outlook (AEO). The AEO utilizes exogenous assumptions of the world oil price and macroeconomic growth baseline as inputs to the National Energy Modeling System (NEMS) to model specific scenarios. NEMS is a general equilibrium model of energy-economy interactions.[39] Each year, the AEO publishes NGPL production projections for six cases. The cases utilize different exogenous assumptions of economic growth, world oil prices, and oil and gas resources.

Bulk chemical production is forecast in the AEO by the Industrial Demand Module (IDM). The IDM is a dynamic accounting model that takes as input "fuel prices, employment data, and the value of industrial shipments" from other NEMS components and returns "projections of industrial sector energy demand" by fuel/feedstock type for different industrial sectors.[40] In the model, NGLs can be a fuel source (typically as liquefied petroleum gas, LPG) or a feedstock for nonfuel applications. Chemical manufacturing is grouped by NAICS code[a] and includes four subcategories (organic chemicals, inorganic chemicals, resins, and agricultural chemicals), where fuel and feedstock demand is estimated for each category. The model includes a feedstock selection algorithm to estimate substitution of NGLs for naphtha in the organic chemicals subcategory. The baseline distribution of NGLs versus naphtha use is determined based on the 2010 Manufacturing Energy Consumption Survey. Incremental feedstock demand is then satisfied by NGLs, naphtha, or propylene (where applicable). The magnitude of incremental market share captured by each potential feedstock is determined based on relative pricing and then NGL demand is filled by each NGL component as available. The NGL and naphtha feedstocks also compete against propylene on an economic basis. Propylene price is determined from propylene production cost calculated in the Liquid Fuels Market Model (another module included in NEMS).[40]

This representation of the bulk chemical manufacturing industry enables EIA to project heat and power use by fuel and feedstock use by fuel for different scenarios. Results from the 2015 AEO reference case are shown in Figure 2-3. In this instance, there is very little difference between the three oil price cases (high oil price, low oil price, and the reference case), so only the reference case is shown.

[a] The North American Industry Classification System (NAICS) classifies businesses into different industries for data collection.

Figure 2-3: Annual feedstock and heat and power consumption by fuel for the bulk chemicals industry in the AEO2015 reference case, 2012 – 2040.[41,42]



EIA notes that feedstock use over time generally tracks end product demand growth only and does not represent changes in efficiency, since reaction stoichiometry is constant.[40] Demand growth for natural gas as a feedstock, reflective of growing demand for nitrogenous fertilizers, methanol, and hydrogen gas, is projected at 3% per year from 2012 through 2025 in the AEO reference case. Growth of HGL feedstock consumption is projected through 2025 at 2% per year and growth of petrochemical feedstock consumption is projected at 3% per year.[43]

2.3.1.2 Other Industry Models

To understand infrastructure requirements and potential build-outs, forecasted production volumes of NGPLs are derived from forecasts of natural gas production. Many different industrial models forecast production. For example, the Bentek CellCast natural gas production model incorporates production profiles of each well in a basin/play to aggregate up to regional and national projections that then use pipeline constraints and demand projections to balance the forecast. Using estimated wet gas composition, Bentek has forecast demand for processing and fractionation capacity by basin.[44]

Two studies moved one step further than production forecasts to quantify capital expenditures in NGL infrastructure needed to reach forecasted production. An IHS Global study conducted for the American Petroleum Institute projected direct capital investments from 2014-2025 for NGL and LPG processing, pipelines, storage, rail and marine infrastructure.[45] An ICF International report prepared for the Interstate Natural Gas Association of America provided a similar analysis, shown in Table 2-1.[46] Note that these assessments were conducted before the global crude oil price drop that began in July 2014.

Table 2-1: ICF projection of capital expenditures for natural gas liquids infrastructure, 2014 – 2035.[46]

Infrastructure Category	**Capital Expenditures (billions of real 2012 dollars)**
Transmission Mainline Pipe	26.4
Transmission Mainline Pump	2.5
Fractionation	21.1
Export Facilities	5.9
Total	**56.0**

2.3.1.3 Federal Policy Development

These industry- and economy-wide models are utilized by federal agencies to evaluate policy proposals and identify potential future problems as development progresses. For example, the EIA, Bentek, IHS, ICF, and other models were all used to inform the recommendations in the Quadrennial Energy Review (QER). In January 2014, President Obama issued a Presidential Memorandum "directing the administration to conduct a Quadrennial Energy Review."[47] The QER has launched a comprehensive review of domestic energy services designed to "identify the threats, risks, and opportunities for U.S. energy and climate security."[47] Over four years, DOE will coordinate interagency activities producing one report each year about a different component of energy infrastructure with recommendations for policy development.

In the first release of the QER (April 2015), one recommendation related to NGLs was included:

> Continue to monitor propane storage, use, and exports: Given the changes occurring in propane TS&D [transmission, storage, and distribution] infrastructure, DOE should ensure adequate support for EIA's data collection and analysis relative to domestic propane storage and use, as well as propane exports, going forward.[48]

The modeling work conducted for the QER indicated the potential for further disruptions to propane supply, especially in light of the 2013-2014 winter propane price spikes, so DOE and the Administration advocated for EIA's propane analysis in a monitoring role.

2.3.1.4 RBN Energy Propane Model

The Propane Education & Research Council (PERC) is a congressionally authorized, industry-funded council that provides consumer education, research and development, and safety and training.[49] RBN Energy developed a propane forecast for PERC to forecast propane supply/demand balances on the PADD level. The model was utilized to examine “supply, demand, logistics, and pricing” in the near future.[50] Based on announced infrastructure build-outs and two different production scenarios (contraction and growth), RBN Energy projected propane supply and demand by PADD. With the addition of new infrastructure and new chemical demand, the model was used to forecast how the propane market would adapt to a polar vortex event in 2016-207. RBN’s analysis determined that PADD 3 propane exports are the “balancing sector” in a 2016-2017 polar vortex event, not chemical demand.[51]

2.4 References

1. Rudd, D. F.; Fathi-Afshar, S.; Trevino, A. A.; Stadtherr, M. A. *Petrochemical Technology Assessment*; Wiley Series in Chemical Engineering; Wiley: New York, 1981.
2. Chang, D. Minimization of Production Cost and Chlorine Use in the Petrochemical Industry. Master's Thesis, University of California Los Angeles, Los Angeles, CA, 1996.
3. Stadtherr, M.; Rudd, D. F. Systems study of the petrochemical industry. *Chem. Eng. Sci.* 1976, 31, 1019−1028.
4. Stadtherr, M.A. A Systems Study of the Petrochemical Industry. Ph.D. Thesis. The University of Wisconsin – Madison, Madison, WI, 1976.
5. Chang, D.; Allen, D. T. Minimizing chlorine use: Assessing the trade-offs between cost and chlorine reduction in chemical manufacturing. *J. Ind. Ecol.* 1997, 1, 111−134.
6. Al-Sharrah, G. K.; Alatiqi, I.; Elkamel, A.; Alper, E. Planning an integrated petrochemical industry with an environmental objective. *Ind. Eng. Chem. Res.* 2001, 40, 2103−2111.
7. Jimenez, A.; Rudd, D. F.; Meyer, R. R. A study of the development of a Mexican petrochemical industry using mixed-integer programming. *Comput. Chem. Eng.* 1982, 6, 219−229.
8. Fathi-Afshar, S.; Rudd, D. F. The economic impact of new chemical technology. *Chem. Eng. Sci.* 1981, 36, 1421−1425.
9. Sahinidis, N. V.; Grossman, I. E.; Fornari, R. E.; Chathrathi, M. Optimization model for long range planning in the chemical industry. *Comp. Chem. Eng.* 1989, 13, 1049-1063.
10. Sahinidis, N. V.; Grossman, I.E. Multiperiod investment model for processing networks with dedicated and flexible plants. *Ind. Eng. Chem. Res.* 1991, 30, 1165-1171.
11. Norton, L. C.; Grossman, I. E. Strategic planning model for complete process flexibility. *Ind. Eng. Chem. Res.* 1994, 33, 68-76.
12. Bok, J-K; Grossman, I. E.; Park, S. Supply chain optimization in continuous flexible process networks. *Ind. Eng. Chem. Res.* 2000, 39, 1279-1290.
13. Floudas, C.; Niziolek, A. M.; Onel, O.; Matthews, L. R. Multi-scale systems engineering for energy and the environment: challenges and opportunities. *AIChE Journal*, 2016, 62, 602-623.

14. Elia, J. A.; Baliban, R. C.; Floudas, C. A.; Gurau, B.; Weingarten, M. B.; Klotz, S. D. Hardwood biomass to gasoline, diesel, and jet fuel: 2. Supply chain optimization framework for a network of thermochemical refineries. *Energy & Fuels*, 2013, 27, 4235-4352.

15. Hasan, M. M. F.; Boukoubvala, F.; First, E. L.; Floudas, C. A.; Nationwide, regional, and statewide CO_2 capture, utilization, and sequestration supply chain network optimization. *Ind. Eng. Chem. Res.* 2014, 53, 7489-7506.

16. North, M. J.; Macal, C. M. *Managing Business Complexity: Discovering Strategic Solutions with Agent-Based Modeling and Simulation*; Oxford University Press: New York, 2007.

17. Garcia-Flores, R.; Wang, X. Z. A multi-agent system for chemical supply chain simulation and management support, *OR Spectrum*, 2002, 24, 343-370.

18. Ito, T.; Mousavi Jahan Abadi, S. M. Agent-based material handling and inventory planning in warehouse, *Journal of Intelligent Manufacturing*, 2002, 13, 201-210.

19. Srinivasan, R.; Bansal, M.; Karimi, I. A. A multi-agent approach to supply chain management in the chemical industry. In B. Chaib-draa and J. Muller (Eds.), *Multiagent Based Supply Chain Management* (p 419-450). Berlin: Springer, 2006.

20. Julka, N.; Karimi, I.; Srinivasan, R. Agent-based supply chain management: Framework and a refinery application. *Comp. Chem. Eng.* 2002, 26, 1755-1769.

21. Ehlen, M. *Economics Definitions, Methods, Models, and Analysis Procedures for Homeland Security Applications*, Sandia National Laboratories SAND2010-4315, Prepared for The Science and Technology Directorate, U.S. Department of Homeland Security Chemical Sector and Resilience Project, January 29, 2010.

22. Ehlen, M. A.; Sun, A. C.; Pepple, M. A.; Eidson, E. D.; Jones, B. S. Chemical supply chain modeling for analysis of homeland security events, *Comp. Chem. Eng.* 2014, 60, 102-111.

23. Vugrin, E. D.; Warren, D. E.; Ehlen, M. A. A resilience assessment framework for infrastructure and economic systems: quantitative and qualitative resilience analysis of petrochemical supply chains to a hurricane, *Process Safety Progress*, 2011, 30.

24. Boudreaux, M. T.; Hoff, A. L. FERC/Not FERC? Determining Jurisdictional Status of NGL Pipeline Service, *Natural Gas & Electricity*. November 2013, 30, 15-20.

25. Declaratory Order re Williams Olefins Feedstock Pipelines, L.L.C., FERC Docket No. OR13-29.

26. Boudreaux, M. T.; Hoff, A. L. FERC/Not FERC? Determining Jurisdictional Status of NGL Pipeline Service, *Natural Gas & Electricity*. November 2013, 30, 15-20.

27. Petition for Declaratory Order of Williams Olefins Feedstock Pipelines, L.L.C., FERC Docket No. OR13-29.

28. 42 USS §6202(3)

29. Supplement No. 1 to 15 CFR Part 754 – Crude Petroleum and Petroleum Products, http://www.ecfr.gov/cgi-bin/text-idx?SID=da7d61ba2719e58b59fd62abf2bde661&mc=true&node=ap15.2.754_17.1&rgn=div9 (accessed September 25, 2015).

30. Kemp, J. Column-History of controls on U.S. oil exports. *Reuters*, October 23, 2014, http://www.reuters.com/article/2014/10/23/usa-oil-export-controls-kemp-idUSL6N0SI37X20141023 (accessed September 25, 2015).

31. Vann, A. Applicability of Federal Export Requirements to Natural Gas Liquids and Condensate [Memorandum]. Senate Committee on Energy and Natural Resources Committee, January 6, 2014, http://www.energy.senate.gov/public/index.cfm/files/serve?File_id=3e18847c-cf43-48f6-ad3a-f8f896a5cc5c (accessed September 25, 2015).

32. U.S. Energy Information Administration (EIA), *Hydrocarbon Gas Liquids (HGL): Recent Market Trends and Issues*, November 2014, http://www.eia.gov/analysis/hgl/pdf/hgl.pdf (accessed September 28, 2015).

33. S. 2086, Sec. 3, http://www.gpo.gov/fdsys/pkg/BILLS-113s2086rfh/pdf/BILLS-113s2086rfh.pdf (accessed September 28, 2015).

34. 49 CFR Chapter III, Parts 390-399.

35. National Propane Gas Association (NPGA), *New law helps propane consumers during winter emergencies; mandates early warning system*, July 1, 2014, https://www.npga.org/i4a/pages/index.cfm?pageid=1867 (accessed September 28, 2015).

36. U.S. Department of Energy, *Heating Oil Reserve*, http://energy.gov/fe/services/petroleum-reserves/heating-oil-reserve (accessed September 28, 2015).

37. Eastman, A. D.; Mears, D. Hydrocarbons, C1-C6. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2000.

38. U.S. Energy Information Administration (EIA), *Blender Net Input*, http://www.eia.gov/dnav/pet/pet_pnp_inpt3_dc_nus_mbblpd_m.htm (accessed January 8, 2015).

39. U.S. Energy Information Administration (EIA), *Integrating Module of the National Energy Modeling System: Model Documentation 2013*, June 2013.

40. U.S. Energy Information Administration (EIA), *Model Documentation Report: Industrial Demand Module of the National Energy Modeling System*, August

2014, http://www.eia.gov/forecasts/aeo/nems/documentation/industrial/pdf/m064(2014).pdf (accessed September 28, 2015).

41. U.S. Energy Information Administration (EIA), *Today in Energy: Bulk chemical feedstock use a key part of increasing industrial energy demand*, May 29, 2015, http://www.eia.gov/todayinenergy/detail.cfm?id=21432 (accessed September 29, 2015).

42. U.S. Energy Information Administration (EIA), *Annual Energy Outlook 2015*, Table: Bulk Chemical Industry Energy Consumption, Case: Reference Case, http://www.eia.gov/beta/aeo/#/?id=38-AEO2015&cases=ref2015 (accessed September 29, 2015).

43. U.S. Energy Information Administration (EIA), *Today in Energy: Bulk chemical feedstock use a key part of increasing industrial energy demand*, May 29, 2015, http://www.eia.gov/todayinenergy/detail.cfm?id=21432 (accessed September 29, 2015).

44. Bentek Energy, *The Future of U.S. Natural Gas: Supply, Demand & Infrastructure Developments*, July 9, 2014. Prepared for the U.S. Department of Energy Quadrennial Energy Review, http://energy.gov/sites/prod/files/2015/04/f22/QER%20Analysis%20-%20The%20Future%20of%20U.S.%20Natural%20Gas%20Supply%2C%20Demand%20%26%20Infrastructure%20Developments.pdf (accessed September 28, 2015).

45. IHS Global, *Oil & Natural Gas Transportation & Storage Infrastructure: Status, Trends, & Economic Benefits*, Prepared for American Petroleum Institute, December 2013, http://www.api.org/~/media/Files/Policy/SOAE-2014/API-Infrastructure-Investment-Study.pdf (accessed September 28, 2015).

46. Interstate Natural Gas Association of America (INGAA) Foundation, *North American Midstream Infrastructure through 2035: Capitalizing on Our Energy Abundance*, Prepared by ICF International, March 18, 2014, http://www.ingaa.org/File.aspx?id=21498 (accessed September 28, 2015).

47. The White House, Office of the Press Secretary, *Presidential Memorandum – Establishing a Quadrennial Energy Review*, https://www.whitehouse.gov/the-press-office/2014/01/09/presidential-memorandum-establishing-quadrennial-energy-review (accessed September 28, 2015).

48. U.S. Department of Energy, QER Report: Energy Transmission, Storage, and Distribution Infrastructure, April 2015, Chapter 4 Page 13, http://energy.gov/sites/prod/files/2015/07/f24/QER%20Full%20Report_TS%26D%20April%202015_0.pdf (accessed September 28, 2015).

49. U.S. Government Accountability Office, Propane and Heating Oil: Federal Oversight of the Propane Education and Research Council and National Oilheat Research Alliance Should Be Strengthened, GAO-10-583, June 2010, http://www.gao.gov/assets/310/306329.pdf (accessed September 28, 2015).

50. RBN Energy, Can't Get Next to You (But Now I Can!) – Propane Supply Growth Close to Largest Centers of Demand, Rusty Braziel, September 1, 2015, https://rbnenergy.com/can-t-get-next-to-you-but-now-i-can-propane-supply-growth-close-to-largest-centers-of-demand (accessed September 28, 2015).

51. RBN Energy, Can't Get Next to You Part 7 – Weather the Next Worst-Case Propane Market Scenario, Sandy Fielden, September 27, 2015, https://rbnenergy.com/can-t-get-next-to-you-part-7-weathering-the-next-worst-case-propane-market-scenario (accessed September 28, 2015).

Chapter 3: Impact of Natural Gas and Natural Gas Liquids Supplies on the U.S. Chemical Manufacturing Industry: Production Cost Effects and Identification of Bottleneck Intermediates

DeRosa, S.E. and D.T. Allen. *ACS Sustainable Chemistry & Engineering*, 2015, 3 (3), 451-459, DOI: 10.102/sc500649k[a]

Primary feedstocks to the U.S. chemical manufacturing industry include ethane, propane, butanes, and pentanes (commonly known as C2-C5 alkanes or natural gas liquids, NGLs). These materials are converted into more reactive olefins and then into a variety of commodity chemicals. Natural gas liquids are sourced from byproducts of natural gas processing (called natural gas plant liquids, NGPLs) or from petroleum crude processing (called paraffinic liquefied refinery gases, LRGs).

Over the past few decades, petroleum processing has been a prominent source of C2-C5 alkanes. However, recent advancements in and applications of horizontal drilling and hydraulic fracturing in tight oil and shale formations have led to an increase in the availability of wet natural gas (NG) and therefore NGPLs in the U.S.

The U.S. chemical industry has already begun adapting to the increased availability, at low cost, of natural gas and NGLs. Since 2009, the use of NGLs for feedstocks has increased dramatically, while the use of heavy liquids (such as naphtha from petroleum processing) has decreased at a similar rate. The distribution of feedstock use in the chemical industry between NGLs and heavy liquids is shown in Figure 3-1.

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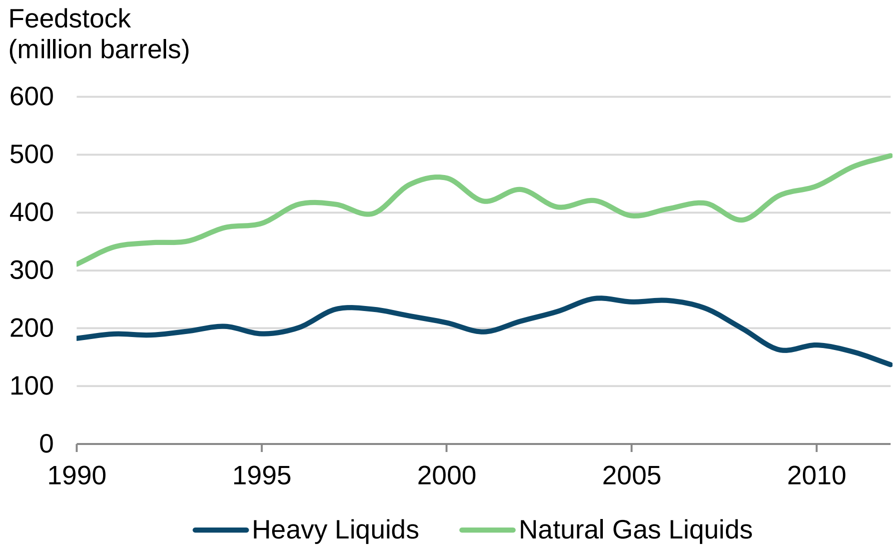
[a] SED designed the model, completed the analysis, and wrote the manuscript; DTA advised development of the model, contributed to the analysis, and edited the manuscript. The authors thank Dr. Jennifer Li, U.S. Department of Energy, for her valuable help in the preparation of this manuscript, and Dr. Michael Baldea, The University of Texas at Austin, for his assistance in developing the solution algorithm.

Figure 3-1: Feedstock sources in the U.S. chemical manufacturing industry.[1]



In addition to using natural gas liquids, the chemical manufacturing industry uses natural gas (primarily methane), depending on the process, as a fuel source or as a chemical feedstock. In 2012, 78.6% of natural gas used in the U.S. chemical industry was for fuel and power, while 21.4% was used directly as a feedstock.[1] Total natural gas use by the chemical industry has increased 13.64% from 2009 to 2012, driven by an increase in the portion of fuel and power provided by natural gas in the industry as a whole.[1] The substitution of natural gas for other fuels in chemical manufacturing was originally driven by fuel price economics, similar to the fuel switching seen in electricity generation.[2] The change in the amount of natural gas used as a fuel impacts the production costs of chemical products.

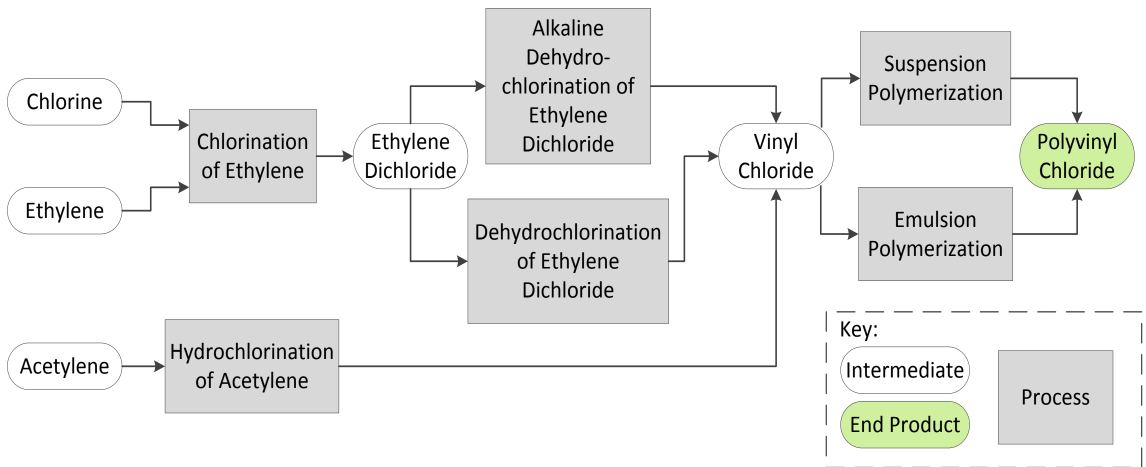
On-going changes in the availability and price of methane, ethane, propane, butanes, and pentanes have the potential to influence the structure of the U.S. commodity chemical manufacturing industry. Because of their low cost and high domestic availability, there is an incentive for manufacturers to use NGLs as a feedstock where possible, replacing heavy liquids such as naphtha. One impact of using these different feedstocks is changing byproduct slates. For example, cracking naphtha to ethylene produces higher yields of C5 components than cracking ethane to ethylene. Also, NGLs are recovered at geographically distributed processing facilities instead of centralized petroleum refinery locations. This difference in feedstock location may affect the scale of chemical manufacturing operations. Because of the material interconnections in the industry, structural changes will not be restricted to the direct supply chains of NGL use, but will also propagate throughout the network of chemical manufacturing operations. For example, butadiene, a byproduct of ethylene cracking, is used in synthetic elastomer production, so changes in ethylene cracking technology could impact supply and cost of raw materials for rubber production.

This work uses a network model of the U.S. chemical industry to identify changes that are occurring or might occur in the industry as a result of high volumes of NGLs becoming available at low cost. The model is used to explore the connections between natural gas, NGLs, and crude oil starting materials with downstream intermediate and end products (alkenes, alcohols, polymers, resins, fertilizers, etc.).

3.1 Model Development

The processes in the chemical manufacturing industry form a complex network, designed to convert a small number of feedstocks into a diverse array of intermediate chemicals and final end products. The network of chemical reactions allows for multiple pathways to exist between one starting chemical and its respective end products. Figure 3-2 shows a portion of the network to produce polyvinyl chloride using different starting materials and technologies. The material flows between technologies form the structure of the network. Due to this interdependent nature of the industry, changes in feedstock availability and price can have impacts that propagate throughout the entire network, influencing production costs and the feasibility of specific processing pathways.

Figure 3-2: Process pathways to produce polyvinyl chloride.[3]



Models of chemical manufacturing networks originated with Stadtherr and Rudd[4] and were expanded by Rudd et al.[5] Many iterations of the original industry model have been constructed that introduce other metrics besides the carbon content basis used by Stadtherr and Rudd, which allowed for minimization of raw material consumption. Fathi-Afshar and Rudd analyzed how the introduction of new technologies could impact price projections, showing that shadow prices from the Rudd et al.[5] model environment are generally representative of market value.[6] Chang and Allen show how the chemical manufacturing technologies chosen as part of the optimal solution vary as the quantity of chlorine used in the industry is minimized.[7] Different industry objective functions were also used in the linear program by designing the optimal industry structure to minimize toxicity of production methods.[8] Environmental objectives were further expanded upon by Al-Sharrah et al., using health indices of chemicals to judge process sustainability.[9] The linear program can be expanded to a mixed-integer problem to make an investment decision using economies of scale for individual plants optimized against importing products from international markets.[10] The linear programming approach has been applied to other industries: Elia et al. utilized mixed-integer linear programming to choose strategic locations for gas-to-liquids refineries.[11]

These previously developed models seek to discern the optimal industry structure (technologies chosen to meet all constraints) in different scenarios. The traditional model structure used in previous work is designed largely to extract information about technologies chosen as part of the optimal solution. This work determines the effect that primary raw material price changes have not only on the chosen technologies, but also on the production costs of all downstream materials using those technologies. Understanding which downstream materials are impacted by primary raw material prices *and* the magnitude of that cost effect is important because the relationship between the upstream raw material price and production cost for farther downstream materials is not always apparent. For example, a reduction in ethane feedstock price for an ethylene cracker does not mean that every product from the cracking operation will become cheaper (butadiene, extracted as a byproduct, actually becomes more expensive to produce). Through the pricing scenarios explored in this paper, the relationship between upstream primary raw materials and downstream intermediate/end product production costs is presented.

The network used in this work to represent U.S. chemical manufacturing sector consists of 873 chemical processes that produce 283 different materials. Process data was obtained from the IHS 2012 Process Economics Program Yearbook. The chemicals used are shown in Table A-1. Natural gas, NGLs, and crude distillate products as primary raw materials are used to manufacture intermediate chemicals, which are then used to manufacture final end products. A linear programming model using a series of mass balances to model material flows between processes was constructed. For chemical i in process j, the material balance is:

$$F_i + \sum_j a_{i,j} \cdot \chi_j - Q_i = 0 \tag{1}$$

where F represents primary feedstock, χ_j represents the utilization rate of process j, Q is the amount of final end product, and $a_{i,j}$ is the input-output coefficient. The input/output coefficient describes the mass of i consumed (negative coefficient) or produced (positive coefficient) in process j per unit mass of primary product. The summation is over every process, j=1, 2, …, 873, and the mass balance is applied to every chemical, i = 1, 2, …, 283. Two major constraints, relating to supply of primary feedstocks (S) and demand of final end products (D), will be applied to the system. For chemical i the constraints are represented as

$$0 \leq F_i \leq S_i \tag{2}$$

$$Q_i \geq D_i\ . \tag{3}$$

The amount of chemical i used as a primary feedstock must be less than or equal to the amount supplied annually, and the amount of final end product, Q, must be greater than or equal to demand in the represented market.[3,5,7,9,10]

3.2 Problem Statement

The problem can be stated as

$$\min Total\ Cost = \sum_j C_j \cdot X_j \tag{4}$$

where C_j is the cost of process j in ¢/pound, and X_j is the production level of process j in pounds/year. The summation is taken over all chemical manufacturing processes included in the model, j = 1, 2, …, 873. Process cost is the sum of capital, operating, and variable costs, as reported in the IHS 2012 Process Economics Program Yearbook. Variable cost consists of raw material cost, byproduct credits, and utility costs. Byproduct credits are reductions in process cost due to the sale or use of a co-product. Utility costs include consumption of cooling water, electricity, fuel, inert gas, natural gas, process water, and steam. Operating and variable costs are further discussed in Appendix A.

The problem is subject to the following material constraints:

$$-\sum_j a_{i,j} \cdot X_j < S_i \quad for\ i \in \{Primary\ Raw\ Materials\} \tag{5}$$

$$\sum_j a_{i,j} \cdot X_j > 0 \quad for\ i \in \{Intermediate\ Materials\} \tag{6}$$

$$\sum_j a_{i,j} \cdot X_j > D_i \quad for\ i \in \{Final\ End\ Products\} \tag{7}$$

where D_i is the annual demand for chemical i, S_i is the annual supply of chemical i, and $a_{i,j}$ is the input/output coefficient of chemical i in process j. Primary raw materials are natural gas, NGLs, and distillate products. The set of final end products is shown in Table A-3. Supply and demand of all components was constrained using 2012 data, shown in Appendix A and Tables A-2 and A-3. The objective function is the minimization of total industry cost, and the problem was modeled using General Algebraic Modeling System (GAMS) using the BDMLP solver to find optimal values of X_j, the production level of each process j, to satisfy the total U.S demand of all end products. The model consists of 886 variables and 888 constraints.

Previous models use fixed material prices to calculate the cost of each process, allowing for optimization of the petrochemical network for constant cost data. However, in order to utilize projections of future natural gas and NGL prices, the variable cost for each process must reflect changing raw material prices. This model calculates production cost changes of each material based on changes in natural gas, NGL, or crude oil prices. The model begins by calculating upstream material price changes, and then recognizes how those materials, both as byproducts and raw materials, may affect downstream process costs. Changes in raw material costs and byproduct credits from the data provided were calculated as

$$\Delta Cost_{raw\ materials} = \sum_{i \cap j} -a_{i,j} \cdot \Delta B_i \tag{8}$$

where $a_{i,j}$ is the input/output coefficient of chemical i in process j, and ΔB_i is the change in cost of chemical i from a baseline 2012 price. For example, a price change in ethane will cause ethylene production costs to change (ethane as a raw material contributes to the variable cost of ethylene production). A change in ethylene price will then affect the cost of downstream polyethylene processes, eventually leading to a potential change in polyethylene production cost. A detailed explanation of the approach is provided in Appendix A. It is recognized that these reported changes in final end product production cost do not represent a change in market price, but are intended to represent the general features of variable cost impacts.

3.3 Model Limitations

The model is designed to be illustrative of industry structure, but not to represent individual plants throughout the U.S. An average capital cost for each technology represents all uses of that technology in the model, so economies of scale across plants are not represented. There are no constraints on the volume of technology utilization, and while it is recognized that some technologies have licensing limitations that dictate their availability for use, all technology options are included for which data is available.

The model is intended to only show immediate cost effects on downstream materials due to changing raw material costs/byproduct credits and does not take into account all market conditions. The model does not incorporate competition from international markets or shifting product demand as a result of material price changes due to changes in production cost. The studies carried out with this model assume a constant demand for intermediate and end products unaffected by production cost changes. The model simulations presented in this work also assume that supplies of primary raw materials remain fixed at 2012 levels and the model simulations focus on impacts of feedstock price changes.

The objective function minimizes production cost for every necessary intermediate and end product. Different objective functions for the industry are possible and would represent different industry-wide strategies. For example, profit maximizing across an entire supply chain would also be a viable objective function, which would represent market prices instead of the production costs used here. This current model does not use market price as part of the objective function, but minimizes overall production cost for the industry.

Use of the model is limited to materials where data is available. The model is designed to work with 141 final end products. However, annual demand and production data is only available for 53 final end products, limiting the number of constraints in the form of Equation 3. Demand values used are provided in Table A-3. The 53 final end products represent 42% of U.S. chemical industry shipments in 2012.[1]

3.4 Results

The constructed model was calibrated to 2012 data for raw material supply and price, utility prices, and demand of final end products. The solution to this baseline case represents the optimal industry structure in 2012 to minimize total cost. A variety of case studies were then conducted by changing the prices of methane, ethane, propane, butanes, and pentanes (primary raw materials) and natural gas (as a utility) to identify downstream cost changes in the model industry. The optimal industry structure in these case studies is compared to the baseline. Production cost changes of all materials in the model are calculated as increases or decreases from 2012 levels.

The price of NGLs has a large impact on total industry cost and the costs of intermediate materials. An increase in NGL prices impacts total industry cost more than a similar magnitude increase in natural gas cost. Of the 283 distinct chemicals included in the model, 32 show production cost responses when natural gas costs change (14 intermediates and 18 final end products), while 65 (non-exclusive) materials show production cost responses when NGL costs change (31 intermediates and 34 final end products), as shown in Table 3-1 and Table 3-3, respectively. The end products are either affected directly by a price change in methane or an NGL as a raw material, by natural gas as a utility, or by a change in an intermediate's production cost. The changes shown for each material represent only the cost impact due to changing natural gas/NGL costs. Effects of natural gas price changes are first discussed, followed by NGL effects.

3.4.1 Effect of Changing Natural Gas Prices

Two different natural gas price scenarios are used to determine the effect on chemical production costs. These two scenarios use the United States Energy Information Administration's Annual Energy Outlook (AEO) 2014 Reference Case Henry Hub prices for two different years as representative natural gas prices. The market conditions in the AEO are not fully represented here – the goal is to understand how chemical production costs change, and the optimal industry structure adapts, as natural gas prices increase to levels consistent with AEO projections.

As natural gas prices near projected 2018 values ($4.80/MMBtu, in 2012 dollars)[12] from a representative 2012 price of $3.80/MMBtu,[13] affected materials show production cost increases between -0.04 and 5 cents per pound above 2012 levels (Table A-5). Using a projected 2040 natural gas price ($7.65/MMBtu, in 2012 dollars),[12] affected materials show changes between -0.1 and 18 cents per pound from 2012 production cost levels. The changes for this scenario are shown in Table 3-1. The table is divided to show separately the cost impacts when natural gas is used for process power as a utility and when methane is used as a raw material. The sum of these two effects is the total impact of natural gas price changes. Predicted effects of natural gas as a utility do not take changing electricity prices into account, only natural gas used directly for process power.

Table 3-1: Magnitude of production cost changes (in 2012 dollars) from 2012 values when methane price increases from a representative 2012 level ($3.80/MMBtu) to a projected 2040 value ($7.65/MMBtu, in 2012 dollars).

Material	Effect of Natural Gas as a Utility (¢/lb)	Effect of Methane as a Raw Material (¢/lb)	Total Impact (¢/lb)
Intermediates			
Acetylene	0.22	15	15.22
Acrylamide	0.00	1.9	1.9
Acrylic acid (glacial)	0.00	11	11
Acrylonitrile	0.00	2.5	2.5
Adipic acid	0.00	0.73	0.73
Ammonia	1.2	2.9	4.1
1,4-Butanediol	0.00	5.2	5.2
Carbon dioxide	0.00	0.99	0.99
Carbon monoxide	0.00	9.3	9.3
Methyl methacrylate	0.00	1.9	1.9
Nitric acid (60%)	0.00	1.2	1.2
Synthesis gas (2:1)	0.15	5.5	5.65
Synthesis gas (3:1)	0.00	7.6	7.6
Tetrahydrofuran	0.00	-0.14	-0.14
Final End Products			
ABS resin	0.15	0.36	0.51
Ammonium nitrate fertilizer	0.00	1.7	1.7
Copolyester ether elastomer	1.2	0.10	1.3
Diammonium phosphate	0.065	0.83	0.895
Kerosene jet fuel	0.87	3.6	4.47
Methylene diphenylene isocyanate	0.00	4.1	4.1
Monoamonium phosphate	0.00	0.52	0.52
Nitrile barrier resin	0.00	1.7	1.7
Nylon 6,6 chips	0.00	0.48	0.48
Polyacrylamide	0.00	1.8	1.8
Polyacrylate latex	0.00	0.67	0.67
Polyacrylate pellets	0.00	1.7	1.7
Polycarbonate	0.28	0.79	1.07
Polymethyl methacrylate	0.00	1.7	1.7
Polypropylene	0.00	18	18

Table 3-1, cont.

Material	Effect of Natural Gas as a Utility (¢/lb)	Effect of Methane as a Raw Material (¢/lb)	Total Impact (¢/lb)
Polyurethane elastomer	0.00	1.6	1.6
SAN resin	0.14	0.49	0.63
Urea (agricultural grade)	0.00	3.1	3.1

3.4.1.1 Tetrahydrofuran

Tetrahydrofuran is the only material that shows a small decrease in production cost because of an increase in natural gas price. The model selects tetrahydrofuran production to proceed by a maleic acid route over a Pd-Re catalyst. Byproducts of this process include 1,4-butanediol, n-butanol, and n-propanol. In this scenario, the production cost of 1,4-butanediol increases, which increases its byproduct credit, lowering the overall cost of the tetrahydrofuran process.

3.4.1.2 Utility Use

To understand changes in utility use between the base scenario and the optimal industry structure with an increased natural gas price, the total utility use for all chosen processes was calculated. As natural gas prices increase to the projected 2040 levels, total observed industry-wide consumption of cooling water, fuel oil, and inert gas does not change. This is a result of the very few structural changes in technology pathways between the baseline solution and the solution for the increased natural gas price scenario. Total industry-wide use of natural gas as a fuel decreases 10.8% and steam, electricity, and process water use decreases less than 0.1%, for the optimal technologies and process utilization in response to elevated natural gas prices. Only process pathways using natural gas directly have an incentive to minimize natural gas use (from the standpoint of the objective function) and therefore change manufacturing technologies. The two major changes observed in manufacturing technologies are described below for acetaldehyde and vinyl acetate.

3.4.1.3 Acetaldehyde

As the price of methane reaches the predicted 2018 value, the model shows very few structural changes in technology pathways. As methane price increases beyond $4.80/MMBtu, however, changes in acetaldehyde, ethanol, ethylene, and vinyl acetate production methods appear. Most of these chemicals show a switch to technologies that use less natural gas/methane relative to 2012 levels in order to decrease variable cost. Acetaldehyde is the only material that switches from being produced only as a byproduct to requiring a dedicated production process, indicating its potential to become a bottleneck material. Acetaldehyde can be produced as a byproduct of vinyl acetate production from methanol and acetic acid or directly from ethylene by oxidation.

There is a potential for increased demand of acetaldehyde based on projected changes in processes that use acetaldehyde as a raw material. In the model, acetaldehyde can be used to make acetic anhydride, methomyl, peracetic acid, polyvinyl acetate, and 3-picoline. The largest of these markets are acetic anhydride and polyvinyl acetate. Acetic anhydride plants in the U.S. use the ketene/acetic acid route or methyl acetate/carbon monoxide from syngas (neither requiring acetaldehyde) and these pathways are not expected to change. Therefore, a potential reason for the expansion of acetaldehyde demand would be from polyvinyl acetate plants.

There are more than 24 operating polyvinyl acetate plants in the U.S., with three main process technologies: suspension (uses acetaldehyde), emulsion, or solution polymerization.[14] Approximately 90% of the polyvinyl acetate facilities use an emulsion technique.[15] The model indicates that the suspension polymerization method, using acetaldehyde, will become increasingly competitive with emulsion and solution polymerization as natural gas prices near 2040 levels. If more polyvinyl acetate plants begin using the suspension polymerization process, there will be an increase in demand for acetaldehyde. Only one major facility in the U.S. currently produces acetaldehyde, so there is a potential for a production capacity bottleneck. Plant locations may serve as a detriment to acetaldehyde use, as the majority of acetaldehyde is only produced in Longview, TX, while the 24 major polyvinyl acetate plants are spread around 13 states in the U.S.[14]

3.4.1.4 Vinyl Acetate

All major vinyl acetate monomer production in the U.S. uses a vapor phase ethylene process. This process remains competitive with forecasted price changes. However, if natural gas and NGL prices decrease, the current method to produce vinyl acetate in the U.S. will not be as competitive as other technologies (fluidized-bed or methanol and acetic acid). If there is a decrease in only natural gas or NGLs separately, the current vapor phase ethylene technology remains optimal.

3.4.2 Effect of Changing Natural Gas Liquids Prices

Two simulations were carried out to determine the effect of NGL price changes on the structure of the chemical manufacturing industry: a 50% increase in NGL prices from 2012 levels and a 50% decrease in NGL prices from 2012 benchmark levels. While the magnitude of NGL price increase and decrease is arbitrary for these scenarios, the changes are representative of historical NGL price movements. From the beginning of 2012 to April 2014, the NGPL composite spot price compiled by EIA varied between \$15/MMBtu and around \$10/MMBtu.[16] The NGL prices used in each scenario are shown in Table 3-2. The downstream production cost change of each material affected for these two scenarios is shown in Table 3-3. Again, the change shown for every material represents only the impact to the production cost from the NGL and subsequent raw material prices.

Table 3-2: Natural gas liquid prices used in increasing and decreasing price scenarios (in 2012 dollars).

Material	**2012 Benchmark Price**		**50% Increase in NGL Price**		**50% Decrease in NGL Price**	
	¢/lb	**¢/gal**	**¢/lb**	**¢/gal**	**¢/lb**	**¢/gal**
Ethane	13	38	20.	60.	6.5	19
Propane	22	94	33	140	11	47
n-Butane	31	150	47	230	16	78
Isobutane	36	170	54	250	18	85
n-Pentane	47	250	71	370	24	130
Isopentane	76	400	110	580	38	200

Table 3-3: Production cost changes from 2012 levels for materials affected by an increase or decrease in NGL price.

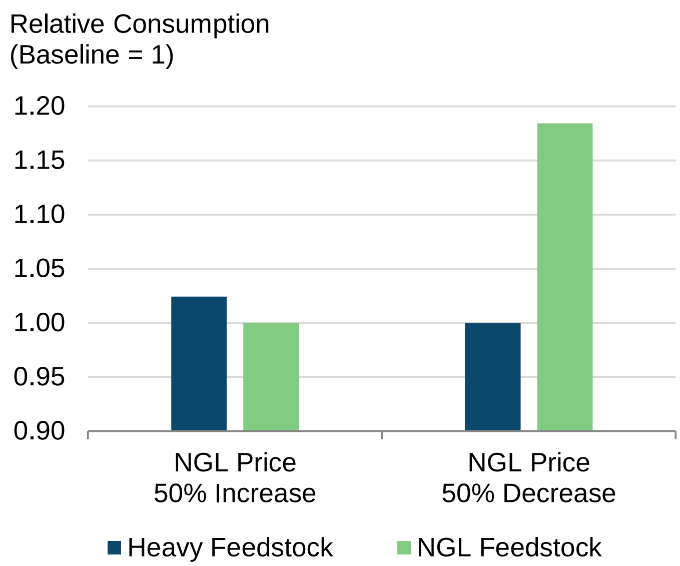
Material	Change from 2012 Production Cost (¢/lb)	
	50% Increase in NGL Price	50% Decrease in NGL Price
ABS resin	4.8	-4.0
Acetylene	8.8	-8.6
Acrylamide	18	-18
Acrylic acid (ester grade)	9.8	-9.8
Acrylic acid (glacial)	3.4	-3.3
Acrylonitrile	24	-24
Adipic acid	-3.4	0.00
Anthraquinone	0.00	5.7
Benzene	-9.6	0.00
Butadiene	0.00	21
1,4-Butandediol	2.9	-2.9
t-Butanol (gasoline grade)	15	-15
Butylated hydroxytoluene	11	-11
Copolyester ether elastomer	0.74	-0.74
EPDM rubber	5.6	-6.1
Ethyhl *t*-butyl ether	-1.1	-0.22
Ethyl acrylate	7.6	-7.6
Ethyl benzene	-3.2	0.00
Ethylene	8.2	-9.0
Ethylene dichloride	2.4	-2.6
EVOH barrier resin	6.7	-7.1
Heavy aromatics	-10.	11
1-Hexene	8.4	-9.3
Isobutylene	19	-19
Isobutylene (high purity)	20.	-20.
Kerosene jet fuel	-1.5	1.5
Maleic anhydride	-4.8	0 .00
Methyl ethyl ketone	-19	19
Methyl methacrylate	8.7	-2.8
Methyl *t*-butyl ether	-19	19
Methyl acrylate	8.7	-8.7
n-Butylacrylate	5.7	-5.7
n-Butylene	8.6	-9.4
Nitrile barrier resin	19	-17

Table 3-3, cont.

Material	Change from 2012 Production Cost (¢/lb)	
	50% Increase in NGL Price	50% Decrease in NGL Price
Polyacrylamide	17	-17
Polyacrylate latex	6.1	-6.2
Polyacrylate pellets	2.5	-2.7
Polybutadiene	0.00	20.
Polybutene-1	8.6	-9.3
Polyester unsaturated	0.88	-0.88
Polyethylene HD	8.2	-9.0
Polyethylene LD	8.2	-9.0
Polyethylene LLD	8.2	-9.0
Polyethylene terephthalate	-9.8	0.00
Polymethyl methacrylate	3.3	-3.5
Polyolefin elastomer	2.1	-2.3
Polypropylene	-0.88	0.91
Polystyrene (expandable)	3.7	-3.7
Polystyrene (general purpose)	-1.1	-2.6
Polyurethane elastomer	0.22	-0.22
Polyvinyl acetate	3.0	-3.1
Polyvinyl acetate latex	2.9	-3.0
Polyvinyl alcohol	5.6	-5.9
Polyvinyl chloride	3.7	-3.7
SAN resin	7.7	-7.7
Styrene	-1.2	-2.2
Styrene-butadiene block copolymer	1.7	3.1
Styrene-butadiene rubber	0.49	14
VDC-EA-MA copolymer	3.0	-3.1
VDC-VCM suspension copolymer	2.7	-2.7
Vinyl acetate	2.9	-3.0
Vinyl acetate-ethylene copolymer	4.0	-4.2
Vinyl chloride	3.7	-3.7
Vinylidene chloride	2.7	-2.9
p-Xylene	-24	0.00

The total volume of NGL and heavy (naphtha-range) feedstock consumption (from both raw material supply and byproduct generation) in the model industry is dependent on their relative prices. In the baseline, NGL consumption is greater than heavy feedstock consumption. As NGL prices increase, heavy feedstock consumption rises, and as NGL prices decrease, NGL consumption rises. The consumption of feedstock for each scenario (relative to the baseline) is shown in Figure 3-3.

Figure 3-3: Feedstock utilization in the two NGL price scenarios relative to consumption of each feedstock in the baseline. Heavy feedstocks are all materials derived from crude oil and NGLs are light feedstocks.



Most materials respond in the same direction as the NGL price change (if there is an increase in an NGL cost, the material's production will experience increased raw material cost and therefore an increase in overall production cost). Material cost changes that respond in the opposite direction of the NGL price change occur because either a raw material's production cost changes in the opposite direction of NGLs, or a byproduct material's production cost changes in the same direction as NGLs. For example, with an increase in NGL price, benzene experiences a decrease in production cost, so any process that uses benzene as a raw material has the potential to also show a decrease in cost, provided benzene cost dominates that technology's variable cost.

The materials that show an inconsistent production cost change between the two scenarios (e.g., changing cost when NGL prices increase but not when they decrease) are: adipic acid, anthraquinone, benzene, butadiene, ethyl *t*-butyl ether (ETBE), ethyl benzene, maleic anhydride, polybutadiene, polyethylene terephthalate, general purpose polystyrene, p-xylene, styrene, styrene-butadiene block copolymer, and styrene-butadiene rubber. The behavior of these materials is explained in Appendix A. Explanations of observed cost changes for adipic acid, benzene, butadiene, p-xylene, and propylene are presented below.

3.4.2.1 Adipic Acid

Adipic acid production cost only responds when NGL prices increase. With increasing NGL costs, the model selects a process that uses benzene as a raw material. Benzene production cost decreases in the increasing NGL cost scenario (see below for the cost movement of benzene), so the variable cost of adipic acid production decreases as NGL prices increase. A similar change is not seen when NGL costs decrease because in this scenario, benzene does not experience a change in cost, and because most of the adipic acid production in the decreasing NGL cost scenario does not use benzene as a raw material.

3.4.2.2 Benzene

As NGL prices increase, production of benzene from naphtha becomes increasingly competitive (as the C3 and C4 byproducts in the naphtha based process have an increased value in this scenario). With increasing byproduct credits, the cost of benzene production decreases. As NGL prices decrease, benzene does not experience a production cost change because production is derived from catalytic reformate, rather than from naphtha, and the catalytic reformate process does not experience a cost change in any scenario. Approximately 60% of benzene production capacity in the U.S. already uses or can use catalytic reformate, while the remaining 40% uses pyrolysis gasoline, toluene disproportionation, or similar processes.[14]

The benzene production cost change is \$0.096/lb in the NGL price increase scenario (Table 3-3). This magnitude of cost change is significant because the Platts Global Benzene Price Index shows a global market price of benzene between \$0.50 and \$0.68/lb in 2012.[17]

3.4.2.3 Butadiene

Butadiene only shows a cost change when NGL prices decrease—as NGL prices decrease, butadiene costs increase. This correctly models the movement of the butadiene market from 2008-2012: as ethane prices dropped more than 50% from 2008-2012, butadiene prices increased 9.29% over the same time period.[13] The \$0.21/lb change in butadiene production cost in the NGL decrease scenario (Table 3-3) is a large portion of the U.S. spot price, which was around \$1.35/lb at the beginning of 2012.[18]

The butadiene cost change occurs because butadiene is extracted from ethylene cracker C4 byproduct streams. Ethylene crackers in the U.S. have recently experienced a change in feedstock, and therefore a change in byproduct distribution. In 2008, naphtha was a significant component of the ethylene feed slate, but ethane-based steam crackers have since become the predominant process. As production costs for ethane-based plants have generally decreased over this time period, it is counter-intuitive that byproduct prices would rise. However, the C4 separation from ethane feedstocks generates less value, since isobutylene, n-butylene, isobutane, and n-butane have experienced a decrease in market price and yield in the new feedstock configuration. The overall industry cost is minimized by using an ethane-based steam cracker, but the cost of butadiene rises due to the reduction in other byproduct values.

Recovery of butadiene from C4 streams in the model industry is predicted to proceed by n-methyl-2-pyrrolidone extractive distillation as opposed to using dimethylformamide as the solvent, due to capital costs. Within the scope of NGL prices analyzed, extraction from a steam cracked C4 stream remains the optimal method of production. No other technology is introduced by the model (such as oxidative dehydrogenation, the TPC Oxo-D process, or a Catadiene process), as recovery of butadiene from an ethane-based plant remains cheaper than other on-purpose technologies.

Eighteen materials use butadiene as a raw material, and therefore as NGL prices decrease, and butadiene cost increases, these materials are subject to an increase in variable cost, even as NGL price is decreasing. Only four materials (anthraquinone, polybutadiene, styrene-butadiene block co-polymer, and styrene-butadiene rubber) show an increase in cost consistent with the increasing cost of butadiene as a raw material. The other 14 materials that rely on butadiene do not show this response when ethane price decreases because the impact of butadiene on the variable cost is small enough to not affect the net direction of change.

3.4.2.4 p-Xylene

Xylenes can be extracted from heavy reformate by crystallization or as a product of toluene disproportionation. Currently, the reformate pathway is cheaper per pound of p-xylene produced. This is reflected in the xylene industry in the U.S., as approximately 80% of plant capacity uses catalytic reformate feedstocks.[14] Isobutylene is a byproduct of aromatic naphtha production from olefins, so a decrease in isobutylene cost leads to an increase in aromatic naphtha cost, which is the feedstock used to produce xylenes by crystallization. If isobutylene price decreases by 18% or more (from a 2012 benchmark of 68.64 ¢/lb),[13] the model shows that use of catalytic reformate feedstocks will no longer be more competitive than toluene disproportionation.

3.4.2.5 Propylene

The model does not show a change in propylene cost when natural gas or NGL prices are altered. This is representative of the propylene industry's structure, as more than 55% of production capacity is from refining operations, while only 25% involves ethane or propane pathways (the remaining 20% of capacity can use either ethylene or refining pathways to produce propylene).[14] However, the model does show a change in polypropylene cost when methane prices increase (Table 3-1) because the selected polypropylene production process is from natural gas to methanol to propylene to polypropylene, instead of from refinery derived propylene (NGL prices affect polypropylene due to changing C4-C6 byproduct values). The model indicates that polypropylene from methanol is competitive with the refinery route from propylene. Even with natural gas prices increasing towards predicted 2040 levels, the cost of polypropylene from natural gas (methanol to propylene (MTP), to polypropylene) is lower than most other polypropylene technologies (slurry loop, circulating reactor, etc., each using propylene from cracking or refining byproduct), although significantly more cooling water and process steam is required. Polypropylene by an MTP route with the 2040 natural gas price experiences a production cost increase of $0.18/lb (Table 3-1) and is still the optimal technology (the Platts Global Polypropylene Price Index ranged between approximately $0.60 and $0.77/lb in 2012).[19]

Reflective of the need for on-purpose propylene, a number of plants have been announced in the U.S. While most of the proposed projects use a propane dehydrogenation route, BASF has begun evaluating an MTP facility on the Gulf Coast.[20] The results of this model confirm MTP's competitiveness on a production cost basis. Even with increasing natural gas prices, the model shows that MTP technology is the optimal use of all materials in the supply chain to produce polypropylene for the objective function to minimize production cost.

3.4.2.6 Utility Use

In the NGL price increase scenario, few utility consumption metrics are affected. Only inert gas use increases (0.38%) and natural gas use as a fuel increases 0.17%. In the NGL price decrease scenario, all of the utility metrics are affected except for fuel oil: use of cooling water decreases 4.6%, inert gas decreases 8.5%, and steam decreases 1.0%, while use of electricity increases 1.3%, natural gas as a fuel increases 3.3% (even though methane price was not altered), and process water increases 4.4%. More changes in utility use are observed for the NGL scenarios than in the natural gas scenario because more technology substitutions occur.

3.4.2.7 Natural Gas Liquid Composition Sensitivity Analysis

In the two NGL pricing scenarios, all NGLs had 50% price changes, however, it may be that some NGLs (e.g., ethane and propane) will experience different price changes than other NGLs (e.g., butane). For example, NGL production from the

Marcellus region is predominantly ethane and propane, so the prices of these two NGLs can change in ways that are not proportional to heavier NGLs. A sensitivity analysis was conducted by altering the ratio of changes for NGL raw material price. The results are used to explore how NGL components with different relative prices impact production cost and overall industry structure.

The first sensitivity analysis involves altering the ethane price: instead of all NGL prices increasing 50%, the ethane price increase is only 25%, while the other NGL prices increase 50%. The second analysis increases propane price 25%, while all other NGL prices increase 50%. In both of the analyses, the different ratios of NGL prices do not impact the overall process configuration in the optimal solution, but downstream material production costs do show changes that reflect the different ratios of NGL prices. Because the overall process configuration does not change, the relative NGL pricing used here does not impact processes used in chemical manufacturing. Relative availability/pricing changes of this magnitude only alter process cost and are not large enough to change the choice of technology.

3.4.3 Effects of Changing Raw Material Supplies on Intermediate and End Products

All of the modeling scenarios described so far assumed that supplies of natural gas and NGLs remain fixed at 2012 levels. The volume of NGL supply that is assumed to be available to the industry in this model is greater than the NGL supply use in any scenario, so changes to the supply constraints have limited effects on the model's solution. When the constraint on supplies of natural gas and NGLs are increased 25% above 2012 levels (while all material prices and production costs are held constant), only two main changes are observed. First, ethylene dichloride production switches from an Inovyl process to an OxyVinyls process, which uses slightly more ethylene raw material per pound ethylene dichloride and is slightly cheaper per pound product. Second, the volume of ethylene from ethane by steam cracking increases 7.9%. The changes in ethylene dichloride costs and ethylene production are also seen in the price scenarios discussed above, so, the first order effects of supply changes are not qualitatively different than the effects of price changes examined in this work.

Another feature of feedstocks to chemical manufacturing in the U.S., that is changing, is the availability of lighter crude oils (from oils co-produced with natural gas), compared to the relatively heavy crudes that currently dominate refining operations. As crude oil becomes lighter (achieved in the model by increasing the yield of lighter atmospheric distillation products and decreasing yields of gas oils and resids), the model predicts that the chemical manufacturing industry experiences an increase in cost. Aromatic naphtha is produced from light olefins, and lighter distillates are cracked to form heavy naphtha. Ethylene production from ethane by steam cracking is increased, and that ethylene is used extensively to produce linear alpha olefins. Light olefins supply is supplemented by coal to olefins processes (coal supply is not constrained). Additional transformations and production cost changes may be driven by changing needs for fuel desulfurization and other processes, but these changes were not modeled in this initial investigation.

Overall, while availability of natural gas and NGLs and quality of crude oil do impact industry structure, raw material price more than total supply availability will influence technology choices and utilization levels.

3.5 CONCLUSIONS

This systems study of the U.S. petrochemical industry provides insight into the production cost effects that value-added materials will experience as NGLs continue to replace heavier petroleum products as chemical feedstocks and methane/natural gas prices increase from current levels. Historical price movements of butadiene and polystyrene agree with the results of the model. Changes to polypropylene and aromatic supply chains have been identified by the analysis, reflecting the trend of new capacity investments.[20,21]

Recent announcements of new plants designed to capitalize on the availability of NGLs shows their expansive role in the industry. As of May 2013, 10.1 million metric tons per year of ethylene production capacity expansions have been proposed in the U.S.[22] Changes to ethylene and other supply chains will have complicated effects on downstream chemical pricing and availability, but the changes to overall energy and water use in the U.S. chemical manufacturing industry are predicted to be small. This work has begun to decipher where price, material use, energy use, and water use changes are occurring, as production from tight oil and shale formations continues to impact the U.S. chemical manufacturing industry.

3.6 References

1. American Chemistry Council, Business of Chemistry Annual Data, 2013.

2. U.S. Energy Information Administration (EIA), Annual Energy Review 2011.

3. Chang, D. Minimization of Production Cost and Chlorine Use in the Petrochemical Industry. Master's Thesis, University of California Los Angeles, Los Angeles, CA, 1996.

4. Stadtherr, M.; Rudd, D. F. Systems study of the petrochemical industry, *Chem. Eng. Sci.* 1976, 31, 1019– 1028.

5. Rudd, D. F.; Fathi-Afshar, S.; Trevino, A. A.; Stadtherr, M. A. *Petrochemical Technology Assessment*; Wiley Series in Chemical Engineering; Wiley: New York, 1981.

6. Fathi-Afshar, S.; Rudd, D. F. The economic impact of new chemical technology, *Chem. Eng. Sci.* 1981, 36, 1421– 1425.

7. Chang, D.; Allen, D. T. Minimizing chlorine use: Assessing the trade-offs between cost and chlorine reduction in chemical manufacturing, *J. Ind. Ecol.* 1997, 1, 111– 134.

8. Fathi-Afshar, S.; Yang, J.-C. Designing the optimal structure of the petrochemical industry for minimum cost and least gross toxicity of chemical production, *Chem. Eng. Sci.* 1985, 40, 781– 797.

9. Al-Sharrah, G. K.; Alatiqi, I.; Elkamel, A.; Alper, E. Planning an integrated petrochemical industry with an environmental objective, *Ind. Eng. Chem. Res.* 2001, 40, 2103– 2111.

10. Jimenez, A.; Rudd, D. F.; Meyer, R. R. A study of the development of a Mexican petrochemical industry using mixed-integer programming, *Comput. Chem. Eng.* 1982, 6, 219– 229.

11. Elia, J.; Baliban, R. C.; Floudas, C. Nationwide, regional, and statewide energy supply chain optimization for natural gas to liquid transportation fuel (GTL) systems, *Ind. Eng. Chem. Res.* 2014, 53, 5366– 5397.

12. U.S. Energy Information Administration (EIA), Annual Energy Outlook 2014.

13. IHS Chemical, Process Economics Program Yearbook, 2012.

14. IHS Chemical, Directory of Chemical Producers, March 1, 2014.

15. Cordeiro, C. F.; Petrocelli, F. P. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons: New York, 2005, 44.

16. U.S. Energy Information Administration (EIA), *Today in Energy: High Value of Liquids Drives U.S. Producers to Target Wet Natural Gas Resources*, May 8, 2014. http://www.eia.gov/todayinenergy/detail.cfm?id=16191 (accessed November 23, 2014).

17. Platts McGraw Hill Financial, Platts Global Benzene Price Index. http://www.platts.com/news-feature/2012/pgpi/benzene (accessed December 1, 2014).

18. Potter, D.; Choo, C.; Johnson, N. *Butadiene: Defying the Odds to Hit New Heights,* Platts Special Report: Petrochemicals, 2012. http://www.platts.com/IM.Platts.Content/InsightAnalysis/IndustrySolutionPapers/PetchemsButadieneWP.pdf (accessed December 1, 2014).

19. Platts McGraw Hill Financial, Platts Global Polypropylene Price Index. http://www.platts.com/news-feature/2012/pgpi/polypropylene (accessed December 1, 2014).

20. BASF, *BASF Evaluates Natural Gas-Based Investment in the United States*. https://www.basf.com/en/company/news-and-media/news-releases/2014/05/p-14-223.html (accessed March 10, 2014).

21. Oil & Gas Journal, *Tesoro plans to boost xylene recovery at US West Coast*. http://www.ogj.com/articles/2014/07/tesoro-plans-to-boost-xylene-recovery-at-us-west-coast.html (accessed March 10, 2014).

22. U.S. Energy Information Administration (EIA), Annual Energy Outlook 2013.

Chapter 4: Impact of New Manufacturing Technologies on the Chemical Industry in the United States: a Methane-to-Aromatics Case Study

Natural gas and associated liquids production in the United States has increased since 2005,[1] contributing to lower prices for domestic hydrocarbon gas liquids (ethane/ethylene, propane/propylene, butanes/butylenes, and natural gasoline). Hydrocarbon gas liquids (HGLs) are used as feedstocks to the chemical industry so their abundance, at low cost, has enabled growth in chemical manufacturing in the United States. For example, United States ethylene production is expected to increase 40% from 2014 through 2018, due to expansions at existing plants and construction of new ethane crackers.[2] Manufacturing expansions have occurred in many sectors of the chemical manufacturing industry. As of June 2015, the American Chemistry Council reports 238 announced chemical industry investment projects in the United States since the increase in natural gas and natural gas liquids production.[3]

Investments in the industry include expansions of existing technologies, such as ethane cracking, and introduction of new technologies/production routes. Improvements in process technology or lower feedstock costs may enable new technologies to become cost-competitive with existing production routes.[4] For example, as favorable feedstock economics have encouraged ethane cracking to replace naphtha cracking for olefins production, a propylene shortfall has developed, which has subsequently opened opportunities for new propylene production. Understanding how these new technologies will impact the structure of the industry can be difficult due to the complexity and interconnectedness of material flows between different sectors and end products. Using a network model of the industry and a mathematical representation of the material flows allows for a systematic analysis of potential changes in the industry when a new technology is introduced.

Network models of the chemical manufacturing industry represent production technologies as nodes connected by input and output material flows. A limited supply of feedstocks (natural gas, natural gas liquids, and crude oil) enter the network and undergo a number of manufacturing steps to meet final end product demand (plastics, fibers, fertilizers, etc.). A system of linear equations represents the chemical transformations that consume and produce different chemicals at each node. In many cases, multiple technologies have been developed to produce the same materials. Acetic acid, for example, can be produced using technologies based on ethane, ethanol, ethylene, or methanol feedstocks. These "dissimilar chemical routes" add to the complexity of the network, introducing multiple pathways for manufacturing between starting chemicals and end products.[5] Due to dissimilar chemical routes and competing technologies within the same route, there are many potential configurations of manufacturing steps that can convert raw materials into the required quantity of end products. Mathematical modeling of the network can be performed as a linear program (LP) to determine the optimal configuration of manufacturing technologies and utilization rates to satisfy end product demand given feedstock constraints and prices. The LP can be constructed using a variety of objective functions, such as maximizing total industry profit, minimizing total industry cost, minimizing raw material consumption, or minimizing various environmental metrics.[6,7,8,9]

Network model representations of the chemical industry have been utilized for a variety of applications. Rudd et al. developed a model of the 1977 United States chemical industry and used it to project a 1985 industry involving 131 chemicals and 182 processes. These projections showed what specific process pathways would need to be expanded to meet 1985 demand, how new chemical technology would fare in the 1985 industry, and how changes in energy consumption and primary feedstock availability would impact the industry structure. Rudd et al. also developed an integrated model based solely on primary feedstock and final end product prices to explore the price point at which a new feedstock and process could be competitive in the existing industry.[6] Fathi-Afshar and Rudd also utilized the 1977 Rudd et al. model to analyze how the introduction of new technologies could impact price projections, showing that chemical shadow prices from the linear programming dual problem are generally representative of the chemical's market value.[10] By utilizing the dual linear program, the model can be used to estimate the effectiveness of a new technology by comparing the shadow price of a chemical in a hypothetical environment to the market prices of chemical in the business-as-usual environment.

A mixed-integer programming model was used by Jimenez et al. to plan development of a petrochemical industry in Mexico, specifically to discover optimal domestic manufacturing substitutions for chemical imports.[11,12] Chang and Allen utilized a network model to assess the environmental impact of the chemical manufacturing system as a whole. By exploring the trade-off between total industry cost and total use of chlorine, Chang and Allen quantified the industry-wide production cost changes that would result from decreasing chlorinated intermediates in the industry. A multi-objective optimization framework was utilized to screen new technologies that could reduce chlorine use, identifying the magnitude of their impact when considered as part of the integrated industry.[13] The technology structure of the industry was also optimized for a sustainability objective function by Al-Sharrah et al., using a health index based on the National Fire Protection Association numerical ratings of chemical hazards.[9]

Another application of optimization models in the chemical industry is in long-term planning for specific investment decisions. Sahinidis et al. developed a mixed integer linear program (MILP) that optimized plant construction and expansion schedules based on forecasts of chemical prices and demand.[14] Sahinidis and Grossmann and Norton and Grossmann have expanded the original investment MILP to include flexible plants, where continuous or batch facilities can utilize a different combination of feedstocks in each time step.[15,16]

In an increasingly integrated industry, opportunities for new technologies cannot be considered in isolation. Understanding how a new technology interacts with other components of the industry is a crucial component in process development. In this work, a network model is utilized to understand the impact of new technologies on the 2012 petrochemical industry in the United States. Using a case study of a potential methane-to-aromatics (MTA) process, three components of analyzing a new technology are demonstrated. First, the maximum production cost at which the process will be selected as part of the optimal solution is calculated, including how the magnitude of utilization of the process is related to process cost. The magnitude of utilization depends on the costs of other competing technologies in addition to the requirements for raw material and product flows, so the relationship to process cost can only be observed in the context of the industry as a whole. Second, to show the extent of supply chains affected by the new process, ancillary effects are documented by observing how the optimal solution evolves and shadow prices of all chemicals change when the new process is introduced. Third, the production cost and shadow price information is used to calculate the most desirable reaction selectivity characteristics of the new process when the objective function minimizes total industry cost.

4.1 METHODS

4.1.1 Problem Statement

The model of the 2012 United States chemical manufacturing industry is fully described in previous work4 and summarized here. The network consists of 873 chemical processes (index *j*) that produce 283 different materials (index *i*). Stoichiometric and process cost data is from the IHS 2012 Process Economics Program Yearbook. The LP is represented as

$$\min \quad Total\ Cost = \sum_j C_j X_j$$

$$\text{s.t.} \quad -\sum_j a_{ij} X_j < S_i \text{ for } i \in \{\text{Primary Raw Materials}\}$$

$$\sum_j a_{ij} X_j > 0 \text{ for } i \in \{\text{Intermediate Materials}\}$$

$$\sum_j a_{ij} X_j > D_i \text{ for } i \in \{\text{Final End Products}\}$$

where C_j is the cost of process *j* in cents/pound, X_j is the production level of process *j* in pounds/year, S_i is the annual supply of chemical *i* (in pounds), D_i is the annual demand for chemical *i* (in pounds), and a_{ij} is the input-output coefficient of chemical *i* in process *j*. The input-output coefficient is the mass of chemical *i* consumed (negative coefficient) or produced (positive coefficient) in process *j* per unit mass of primary product. Fifty-three chemicals are included in the set of final end products, accounting for 42% of United States chemical industry shipments in 2012.[17] The problem was modeled using General Algebraic Modeling System (GAMS) using the BDMLP solver to find optimal values of X_j (production level of each process *j*). The baseline model consists of 886 variables and 888 constraints.

The structure of the network model developed for this work is the same as the original models developed by Stadtherr and Rudd and colleagues.[5,6,7] The current model framework did not modify the solution algorithm or problem definition. Stadtherr and Rudd included 182 technologies in their representation of the 1970 industry[7] and Chang and Allen included 428 technologies in their representation of the 1996 industry.[13] Data for technologies included in this network model have been updated and expanded to represent operations of 873 technologies in the 2012 industry in the United States. Material prices and utlity and production costs can change and have changed significantly since the original model based on the 1970 industry structure was developed. The procedure presented in this work can be applied to updated network models as material prices change.

This LP represents the general structure of the industry and does not account for individual facilities. The objective function minimizes total industry cost. While other objective functions are possible, minimizing cost was chosen because limited publically available chemical price data restricts the use of profit maximizing objective functions.

4.1.2 Supply Chain Impacts

To calculate process utilization as a function of process cost, the cost was exogenously varied in multiple scenarios. Primary and secondary impacts on industry structure are identified based on resulting changes in technology utilized and shadow prices when the new process is introduced. The dual of this primal linear program is used to calculate shadow prices of each chemical. A full description of duality is presented by Bazaraa et al.[18] and others.[19,20] In this cost minimization problem, shadow prices are the dual variables[19] and can be interpreted as the marginal cost of producing one more unit of a chemical, taking into account all necessary upstream chemicals and processes required. Shadow prices are distinct from process costs because they include costs of necessary upstream material production for all inputs required to produce a given chemical. It is important to note that the shadow prices discussed here are not internal to firms but are for the industry as a whole when they are the dual variables from the LP that represents the entire industry. This representation of shadow prices is different from some economics literature, which uses either internal firm shadow prices (which can then differ from market prices)[21] or lost opportunity cost from reducing an undesirable output.[22] In this cost minimization problem, shadow prices are representative of market values.[10,23]

A change in a chemical's shadow price between two different scenarios can then be used as one way to track how that chemical is impacted by the change in solution. Calculating shadow price changes between scenarios provides a method of quantifying ancillary supply chain effects for chemicals that are far removed from the immediate scenario being studied. By observing changes in shadow price, dependencies between two distantly connected chemicals can be quantified. For example, when an exogenous change in the benzene production route decreases the shadow price of benzene in one scenario, the shadow price of diphenyl carbonate also decreases even though diphenyl carbonate is not directly used or produced in benzene production. The relationship in shadow cost is explained by phenol, an intermediate between the two materials. Benzene can be used to make cumene and then phenol, which is then a raw material for diphenyl carbonate, so the shadow price of diphenyl carbonate follows a decrease in benzene shadow price. While the connection may be easily visualized by the network, the magnitude of the impact (a 71% decrease in benzene shadow price corresponds to an 12% change in diphenyl carbonate shadow price) is only calculated using duality. These changes in shadow price are not used as forecasts for changes in chemical prices in each scenario. While the shadow prices are representative of the magnitude of market prices, many other factors contribute to market price changes and the shadow prices used here are only to quantify supply chain connections, not forecast price changes.

4.2 Case Study

The methodology to analyze a new technology using a network model of the chemical manufacturing industry is illustrated with a case study of a methane-to-aromatics (MTA) process. This procedure can be applied to analyze any new technology that does not have wide-spread use in the current industry.

Significant work has been conducted in catalyst design for a methane-to-aromatics process. The dehydroaromatization process converts methane over a catalyst to benzene, toluene, naphthalene, and hydrogen.[24] This process can proceed without an oxidant using oxide- or zeolite-supported transition metal and bimetal catalysts.[25] Significant progress has been made in designing a system that suppresses coke formation and can maintain catalyst activity and stability,[26] resulting in a "successful" pilot-plant test of this technology.[27]

The abundance of low cost methane in the United States and promising catalyst developments show the near term potential for a cost-effective methane-to-aromatics technology. The 2012 United States chemical industry model was used to explore how this theoretical technology would fit into the existing industry and what changes would occur due to of its introduction. First, the utilization of the MTA process at different process costs and resulting industry adaptations is described. Then, the impact of aromatic selectivity on the process' role in the industry is discussed.

A number of different catalyst and system designs give different conversion rates and selectivity to end products.[28] The selectivity used for this work is from Wang, Ohnishi, and Ichikawa[29] and is shown in Table 4-1.

Table 4-1: Stoichiometric ratios used for the methane-to-aromatics process.

Material	Mass Coefficient (Methane Basis)	Mass Coefficient (Benzene Basis)	Selectivity (%) Carbon Basis
methane	-1	-2.567	
ethane	0.019	0.048	1
ethylene	0.017	0.045	1
benzene	0.389	1	48
naphthalene	0.088	0.226	11
toluene	0	0	0
p-xylene	0	0	0
m-xylene	0	0	0
o-xylene	0	0	0
coke[a]	0.248	0.637	33
hydrogen	0.208	0.535	-

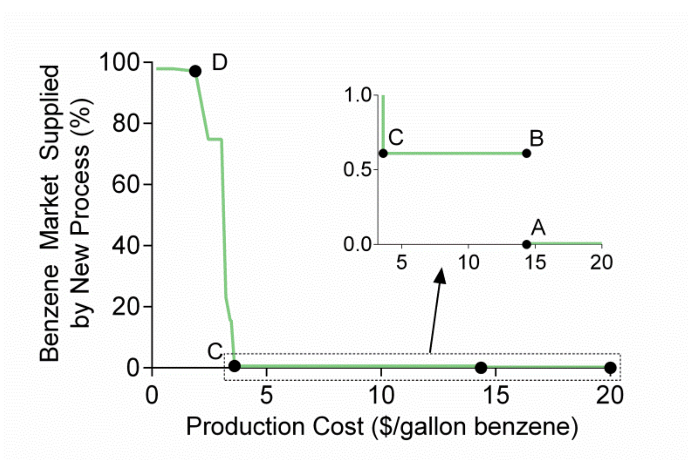
4.2.1 Production Cost

The magnitude of utilization of the new process depends on the cost of the process relative to other options for producing aromatics and required mass balances. Benzene is the primary product of the MTA process, so the data is presented on a benzene basis. As the process cost decreases, utilization of the process increases and

[a] Coke is assumed to be 95% carbon and 5% hydrogen

more benzene is produced from the new process, replacing benzene production from other routes (e.g. byproduct of toluene disproportionation, from reformate, etc.). The proportion of benzene supplied by the new process as a function of process cost is shown in Figure 4-1. At process costs of \$14.37/gallon benzene (Point A) and greater, the MTA process is not part of the optimal solution (benzene market share is shown at 0%). Between Point B and Point C, the utilization is constant and very small. Between Point C and Point D, the utilization increases very rapidly for small decreases in process cost, before plateauing again at process costs less than Point D (\$1.90/gallon benzene). Throughout all of these scenarios, as benzene market share is being consolidated by the new process, the total industry-wide amount of benzene produced does not change, the new process is simply producing more benzene while other production technologies produce less.

Figure 4-1: Benzene supplied by the methane-to-aromatics process as a function of process cost. Inset uses a different vertical axis scale to show the step change from no utilization to niche utilization of the process. Point A shows no utilization, Point B and Point C show niche utilization, and Point D shows near maximum utilization of the process.



The maximum process price for which the process is part of the optimal solution is shown at Point B ($14.36/gal benzene). With any price above $14.36/gal benzene, the process is not part of the optimal solution. This production cost is substantially higher than the 2012 United States Gulf Coast benzene price, which ranged between approximately $3.75/gal and $5.40/gal.[30] The shadow price of benzene in the baseline model (Point A) is $3.01/gal, showing relatively good agreement with the market price. Because the maximum acceptable process cost is much higher than the shadow price, it is apparent that the process was selected not for its benzene production but for its naphthalene production. Comparing the baseline Point A to when the process is first included in the optimal solution at Point B, the shadow price of naphthalene decreases, while the benzene shadow price does not change (indicating that the method of benzene production in the baseline Point A is still the marginal benzene production process, not the new MTA process).

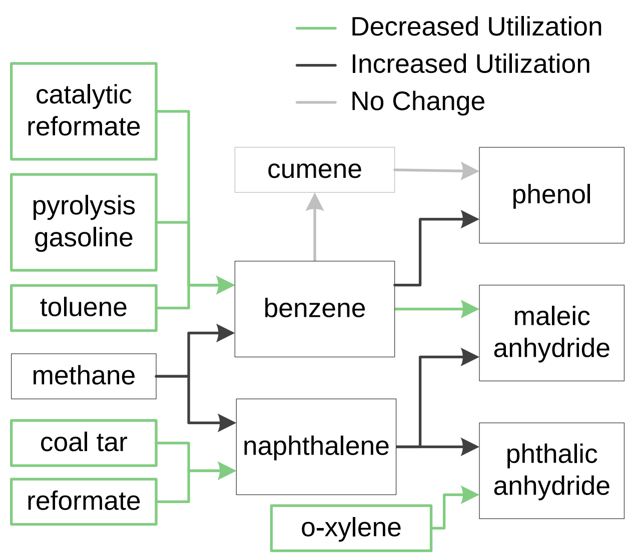
As the process cost decreases from $14.36/gal benzene to $3.60/gal (moving from Point B to Point C), the utilization of the new process does not change. At this level of production between Points B and C, all of the required naphthalene production for the entire industry is satisfied by the new process. However, it is not optimal to increase process utilization to produce excess benzene because the process cost is above the benzene shadow price (so benzene is produced more cheaply in other processes). The process' market share is unaffected by price in this range, so the process is only being utilized for its naphthalene production and benzene is treated as a byproduct. This range is referred to as the niche application of the MTA process. Below $3.60/gal process cost (Point C), even small decreases in process cost lead to large gains in benzene market share by the new process, replacing the traditional benzene production routes. As the process cost approaches $0/gal, the maximum benzene market share captured by the new process is 97.8%. The market share never reaches 100% because other processes that produce benzene as a byproduct are still necessary (xylenes production, for example) at low MTA process costs.

4.2.2 Ancillary Supply Chain Effects

Even though benzene is not the desired product from the new process between Points B and C, its introduction into the industry does impact the traditional benzene production routes and associated supply chains. With this new source of benzene there is a decrease in production of benzene from catalytic reformate, pyrolysis gasoline, and toluene.

The ancillary impacts of the new MTA process on other chemicals besides catalytic reformate, pyrolysis gasoline, and toluene are limited at Point C. However, as the utilization of the methane-to-aromatics process increases (moving towards Point D), changes in maleic anhydride, phthalic anhydride, and phenol production pathways occur. A diagram of the benzene and naphthalene production routes is shown in Figure 4-2. In the baseline at Point A, phthalic anhydride is produced from *o*-xylene. With the increased availability of naphthalene at a low cost from the new process, phthalic anhydride switches to naphthalene as the raw material, replacing the *o*-xylene route. The new phthalic anhydride route from naphthalene produces maleic anhydride as a byproduct which is not produced in the *o*-xylene route. This new source of maleic anhydride allows the traditional maleic anhydride route from benzene to decrease, despite the abundance of benzene and decrease in benzene cost towards Point D. Therefore, an increase in benzene availability may not lead to an increase in the benzene to maleic anhydride route. Instead, the resulting introduction of naphthalene to phthalic anhydride supplies sufficient maleic anhydride byproduct to allow production of maleic anhydride directly from benzene to decrease.

Figure 4-2: Naphthalene and benzene reaction routes in the model are impacted by increased utilization of a methane-to-aromatics process. The blue routes decrease utilization as the black routes increase, while grey routes show no utilization change in any scenario.



Now that less benzene is used for maleic anhydride, more benzene is available for use in phenol production. Currently in the U.S., phenol is produced almost entirely from cumene. With the new MTA process, however, an increase in abundant, low cost benzene enables introduction of a direct benzene-to-phenol technology. In the model, benzene directly to phenol (single step hydroxylation) is represented by two different process configurations of Solutia Inc.'s AlphOx technology. The single step hydroxylation process is discussed by Notte[31] and the two configurations are reported by IHS.[32] The major difference between the two configurations is the amount of benzene required. As additional benzene becomes available at low cost, phenol production switches to an AlphOx route that directly uses benzene. The AlphOx technology was previously explored in a pilot plant by Solutia, but never fully commercialized in a large-scale use. Results of the simulation show that a new MTA process may favorably impact the economics of the AlphOx technology.

The introduction of the MTA process has two major impacts. First, when naphthalene completely replaces *o*-xylene as the raw material for phthalic anhydride production, the resulting maleic anhydride byproduct decreases the need for benzene to maleic anhydride process, even with low cost benzene available. Second, the additional low cost benzene facilitates a switch to a different single step hydroxylation technology. While more benzene is used for phenol production overall, the direct benzene route does not take phenol market share from the other raw materials (cumene and toluene), even as the benzene cost and shadow price approach $0/gallon.

Besides the technology shifts caused by the new process, a change in benzene production cost introduces cost effects on other chemicals, even if their production technologies did not change. When the process is first introduced at Point B, coke, naphthalene, anthraquinone, and syndiotactic polystyrene show a decrease in shadow price. By Point D, when 97.8% of benzene is produced by the new process, 83 chemicals show a change in shadow price. The list of shadow price changes from Point C to Point D is shown in Table 4-2, showing the full extent of materials impacted by changes in benzene production technology.

Table 4-2: Change in chemical shadow prices as utilization of the methane-to-aromatics process increases from 0.67% to 97.8% of the benzene market (Point C to Point D).

Chemical	**Change in Shadow Price (%)**
naphthalene	-1.0E+02
perchloroethylene	-1.0E+02
toluene	-1.0E+02
n-butyl acetate	-1.0E+02
reformate, heart cut	-88
anthraquinone	-86
cyclohexane	-74
benzene	-71
n-heptane	-64
chlorobenzene	-58
cumene	-52
o-xylene	-52
ethylbenzene	-28
phthalic anhydride	-25
phenol	-23
maleic anhydride	-22
styrene	-22
cyclohexanone	-21
nitrobenzene	-21
nylon salt, 63% solution	-21
Cyclohexanol	-19
polystyrene, general purpose	-19
bisphenol a, PC grade	-19
o-dichlorobenzene	-18
polystyrene, high impact	-15
adipic acid	-14
polystyrene, anionic	-13
aniline	-12

Table 4-2, cont.

Chemical	Change in Shadow Price (%)
diphenyl carbonate	-12
polystyrene, expandable	-11
polyester, unsaturated	-11
catechol	-9.2
benzoic acid	-8.7
SAN resin	-8.5
methylene diphenylene isocyanate	-8.4
polycarbonate	-8.4
ABS resin	-7.6
epoxy, solid DGEBPA and BPA	-7.0
ammonium sulfate	-6.9
hydroquinone	-6.7
styrene-butadiene block copolymer	-6.5
acetone	-6.2
petroleum resin, C5 aliphatic	-5.3
diphenyl isophthalate	-5.0
propylene oxide	-4.9
nylon-6,6 chips	-3.5
elastomer, polyurethane	-2.5
acetic anhydride	-2.3
methyl isobutyl ketone	-1.9
styrene-butadiene rubber	-1.7
propylene glycol ethers	-1.1
polyacrylate pellets	-1.0
nitric acid, dilute	-0.27
peracetic acid	-0.25
polybutadiene	-0.12
polybutene-1	-9.3E-2
acrylic acid, ester grade	-7.0E-2
isobutylene, high purity	-6.7E-2

Table 4-2, cont.

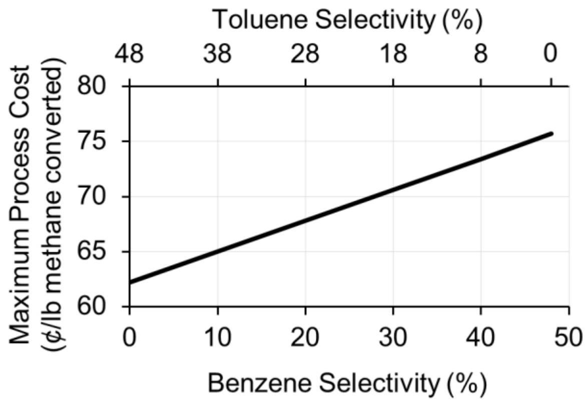
Chemical	**Change in Shadow Price (%)**
epoxy, liquid DGEBPA	-4.1E-2
methyl acrylate	-3.8E-2
ethyl acrylate	-3.4E-2
carbofuran	-2.9E-2
t-butanol, gasoline grade	-2.6E-2
butylated hydroxytoluene	-1.7E-2
n-butyl acrylate	-1.5E-2
epoxy, solid TGBAPPB	-1.3E-2
caustic soda beads	-6.1E-3
nitrile barrier resin	-5.2E-3
polymethyl methacrylate	-3.5E-3
polyacrylate latex	-3.4E-3
VDC-EA-MA copolymer	-1.6E-3
vinyl acetate-ethylene copolymer	6.6E-4
polyvinyl acetate	7.9E-4
acrylic acid, glacial	0.25
t-butanol	1.3
hydrogen peroxide	2.8
refinery gas	2.9
butadiene raffinate	8.5
methyl ethyl ketone	10.
polyethylene terephthalate	11
sec-butanol	11
terephthalic acid	19
p-xylene	65

Even though many materials are impacted as the new process becomes the marginal benzene producer, most of the impacts on shadow prices are small in magnitude. The largest decreases in shadow prices can be explained by either a decrease in demand or lower benzene and naphthalene feedstock costs (anthraquinone, cyclohexane, chlorobenzene, and cumene). As the benzene process becomes cheaper, the cost of producing toluene also decreases because toluene is no longer produced as a byproduct of the old benzene production processes, but is extracted from heavy reformate.

4.2.3 Aromatic Selectivity

For all of the previous analysis, the process has an aromatic selectivity of 48% benzene, 11% naphthalene, and 0% toluene. To understand the impact of aromatic selectivity on maximum process cost, the distribution between benzene and toluene coproducts was studied. As less benzene and more toluene is produced, the maximum allowable process cost was calculated, shown in Figure 4-3. For this scenario, the selectivity to naphthalene was held constant at 11% and the benzene selectivity was decreased from 48% to 0%, while the toluene selectivity was increased from 0% to 48%. This scenario shows where Point B in Figure 4-1 would be if toluene selectivity was above zero. Note that the process cost is now in units of cents/pound methane converted because the mass of methane converted is constant, whereas the mass of benzene produced by the process is not constant so cannot be the basis for cost comparisons.

Figure 4-3: The maximum process cost of the methane-to-aromatics process as a function of aromatic selectivity of benzene and toluene coproducts.



A higher maximum process cost implies that the products are of more value to the industry, because the process will be integrated despite higher costs. The hypothetical MTA process should therefore strive to produce as much benzene as possible, as the highest allowable process cost occurs when benzene selectivity is greater than toluene. Ignoring the niche naphthalene market, the results of this analysis show that toluene is a less valuable product than benzene from an MTA process. In this instance, the distribution of desired products matches their relative prices (the benzene market price is usually higher than the toluene market price), but using the model ranks the distribution in terms of shadow prices, taking into account the entire industry structure.

4.3 Conclusions

A network model of the 2012 United States petrochemical industry has been used to show the impact of a new chemical manufacturing technology on the structure of the industry. Through a case study, the analysis of a new technology is broken down into three components: how utilization depends on process cost, direct and ancillary supply chain effects, and which chemicals should be the preferred products of a new process. For a methane-to-aromatics process, the initial acceptance as part of the optimal solution occurs for the niche naphthalene market and only begins capturing meaningful benzene market share at process costs less than $3.60/gallon benzene. Ancillary effects of high utilization of this new process include changes to demand or manufacturing technologies for phthalic anhydride, maleic anhydride, and phenol. Eighty chemicals experience changes in shadow prices, even though their production technologies do not change. Of the other potential aromatics that could be produced from this process based on catalyst and system design, benzene should be targeted before toluene.

As the chemical manufacturing industry in the United States continues to adapt to an abundance of low cost domestic feedstocks, many changes are expected in technology utilization and production routes. These changes in technology will impact the overall structure of the industry in ways that are difficult to quantify because of dissimilar production routes and complex material flows between processes. The developed network model of the 2012 United States petrochemical industry enables a straightforward analysis of expected chemical supply chain transformations when a new technology is introduced.

4.4 References

1. U.S. Energy Information Administration (EIA), *Monthly Energy Review,* September 2015.
2. U.S. Energy Information Administration (EIA), *Today in Energy: Growing U.S. HGL production spurs petrochemical industry investment.* January 29, 2015, http://www.eia.gov/todayinenergy/detail.cfm?id=19771 (accessed Oct 9, 2015).
3. American Chemistry Council, *U.S. Chemical Investment Linked to Shale Gas: $145 Billion and Counting*, June 2015. http://www.americanchemistry.com/Policy/Energy/Shale-Gas/Fact-Sheet-US-Chemical-Investment-Linked-to-Shale-Gas-145B-and-Counting.pdf (accessed Oct 9, 2015).
4. DeRosa, S. E.; Allen, D. T. Impact of natural gas and natural gas liquids supplies on the United States chemical manufacturing industry: production cost effects and identification of bottleneck intermediates. *ACS Sustainable Chem. Eng.* 2015, *3* (3), 451-459.
5. Stadtherr, M. A. A Systems Study of the Petrochemical Industry. Ph.D. Dissertation, The University of Wisconsin-Madison, Madison, WI, 1976.
6. Rudd, D. F.; Fathi-Afshar, S.; Trevino, A. A.; Stadtherr, M. A. *Petrochemical Technology Assessment;* Wiley-Interscience: New York, 1981.
7. Stadtherr, M. A.; Rudd, D. F. Resource use by the petrochemical industry. *Chem. Eng. Sci.* 1978, *33* (7), 923-933.
8. Sokic, M.; Stevancevic, D. The optimal structure of the system of the petrochemical industry. *Chem. Eng. Sci.* 1983, *38* (2), 265-273.
9. Al-Sharrah, G. K.; Alatiqi, A.; Elkamel, A.; Alper E. Planning an integrated petrochemical industry with an environmental objective. *Ind. Eng. Chem. Res.* 2001**,** *40*, 2103-2111.
10. Fathi-Afshar, S.; Rudd, D. F. The economic impact of new chemical technology. *Chem. Eng. Sci.* 1981, *36,* 1421-1425.
11. Jimenez, A.; Rudd, D. F.; Meyer, R. R. A study of the development of a Mexican petrochemical industry using mixed-integer programming. *Comp. Chem. Eng.* 1982, *6* (3), 219-229.
12. Jimenez, A.; Rudd, D. F. Use of a recursive mixed-integer programming model to detect an optimal integration sequence for the Mexican petrochemical industry. *Comp. Chem. Eng.* 1987, *11* (3), 291-301.
13. Chang, D.; Allen, D. T. Minimizing chlorine use: assessing the trade-offs between cost and chlorine reduction in chemical manufacturing. *J. Ind. Ecol.* 1997, *1* (2), 11-34.

14. Sahinidis, N. V.; Grossmann, I. E.; Fornari, R. E.; Chathrathi, M. Optimization model for long range planning in the chemical industry. *Comp. Chem. Eng.* 1989, 13, 1049-1063.

15. Sahinidis, N. V.; Grossmann, I. E.; Multiperiod investment model for processing networks with dedicated and flexible plants. *Ind. Eng. Chem. Res.* 1991, 30, 1165-1171.

16. Norton, L. C.; Grossmann, I. E.; Strategic planning model for complete process flexibility. *Ind. Eng. Chem. Res.* 1994, 33, 68-76.

17. American Chemistry Council, *Business of Chemistry Annual Data*, 2013.

18. Bazaraa, M. S., Jarvis, J. J.; Sherali, H. D. *Linear programming and network flows*; Wiley: Hoboken, NJ, 2011.

19. Farris, M. C.; Mangasarian, O. L; Wright, S. J. *Linear Programming with MATLAB*; MOS-SIAM Series on Optimization; Society for Industrial and Applied Mathematics and Mathematical Programming Society: Philadelphia, PA, 2007.

20. Vanderbei, R. *Linear Programming: Foundations and Extensions*; Springer: New York, 2014.

21. Atkinson, S. E.; Primont, D. Stochastic estimation of firm technology, inefficiency, and productivity growth using shadow cost and distance functions. *J. Econometrics* 2002, *108* (2), 203-225.

22. Lee, S-c; Oh, D-h; Lee, J-d. A new approach to measuring shadow price: Reconciling engineering and economic perspectives. *Energ. Econ.* 2014, *46*, 66-77.

23. Atkinson S. E.; Halvorsen, R. Parametric efficiency tests, economies of scale, and input demand in U.S. electric power generation. *Int. Econ. Rev*. 1984, *25* (3), 647-662.

24. Holmen, A. Direct conversion of methane to fuels and chemicals. *Catal. Today* 2009, *142*, 2-8.

25. Xu, Y.; Bao, X.; Lin, L. Direct conversion of methane under nonoxidative conditions. *J. Catal.* 2003, *216*, 386-395.

26. Ohnishi, R.; Liu, S.; Dong, Q.; Wang, L.; Ichikawa, M. Catalytic dehydrocondensation of methane with CO and CO_2 toward benzene and naphthalene on Mo/HZSM-5 and Fe/Co-modified MO/HZSM-5. *J. Catal.* 1999, *182*, 92-103.

27. Cui, Y.; Xu, Y.; Lu J.; Suzuki, Y.; Zhang, Z-G. The effect of zeolite particle size on the activity of Mo/HZSM-5 in non-oxidative methane dehydroaromatization. *Appl. Catal., A* 2011, *393*, 348-358.

28. Xu, Y.; Lin, L. Recent advances in methane dehydro-aromatization over transition metal ion-modified zeolite catalysts under non-oxidative conditions. *Appl. Catal., A* 1999, *188*, 53-67.

29. Wang, L.; Ohnishi, R.; Ichikawa, M. Selective dehydroaromatization of methane toward benzene on Re/HZSM-5 catalysts and effects of CO/CO_2 addition. *J. Catal.* 2000, *190*, 276-283.

30. Fallas, B. *$5/gal benzene: Here to stay, or recurring but shortlived fad?* Platts, February 6, 2014. http://blogs.platts.com/2014/02/06/high-benzene/ (accessed Oct 2, 2015).

31. Notte, P. The AlphOx process or the one-step hydroxylation of benzene into phenol by nitrous oxide. Understanding and tuning the ZSM-5 catalyst activities. *Top. Catal.* 2000, *13* (4), 387-394.

32. IHS Chemical, Process Economics Program Yearbook, 2012.

Chapter 5: Opportunities for Chemical Manufacturing in the San Juan Basin[a]

The increase in oil and gas production in the United States since 2005 has enabled renewed investment in domestic chemical manufacturing. Relatively low energy and feedstock costs and access to abundant raw materials (natural gas, natural gas liquids, and petroleum) have increased opportunities for U.S.-based manufacturing.[1,2,3] Most primary chemical production in the U.S. has historically occurred in the Gulf Coast region because of proximity to petroleum feedstocks from refineries. A recent surge in natural gas and natural gas liquids production in other regions of the U.S., however, has introduced new feedstock supplies that have enabled manufacturing expansions in other regions. During 2014 and 2015, on a percentage basis, all regions of the U.S. experienced faster growth in chemical production than the Gulf Coast region.[4]

Expanding manufacturing in locations besides the Gulf Coast faces challenges but may also benefit from feedstock and location advantages. A lack of transportation infrastructure may hinder the ability to distribute products, especially given the potential increase in distance from other chemical manufacturing operations which may be customers. Also, if the manufacturing process requires co-raw materials that are not produced locally, raw materials may have to be transported from the Gulf Coast or other location to the manufacturing site, potentially increasing cost. However, some end products can be sold directly to consumers (e.g. fertilizers) and may benefit from being produced in distributed regions. Access to local feedstocks may also provide a benefit for regional production. For example, the methane price and availability in one region may

[a] The author wishes to thank Sue Downes and Rick Lentz at PRISM Analytics Corporation for their assistance in the study design and use of the GABLES Agent-based framework and the PRISM Engine™

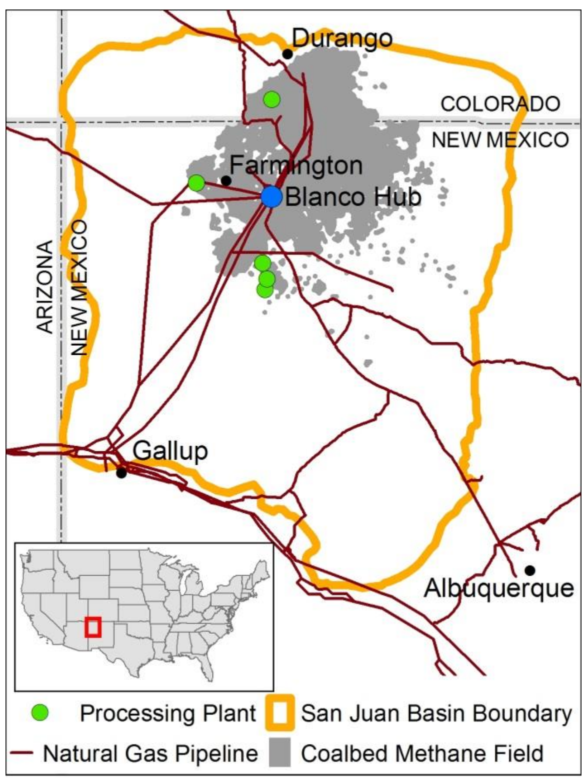
make methane-to-chemicals competitive with traditional petroleum-based routes in other regions.

To analyze the competitiveness of an emerging methane-to-chemicals market, the San Juan Basin in northwestern New Mexico and southwestern Colorado (the Four Corners region) is used as a case study. Natural gas production in northwestern New Mexico in 2014 totaled 430 billion cubic feet (bcf) from oil and gas wells and 281 bcf from coalseam wells (approximately 2% of U.S. natural gas withdrawals).[5] There are five natural gas processing plants in the San Juan Basin, all located near the Blanco Hub. Natural gas infrastructure in the region is shown in Figure 5-1. On average during the first ten months of 2015, the Blanco Hub natural gas spot price was 16 ¢/MMBtu (6%) below the Henry Hub price.[6] The large volume of production at discounted prices makes San Juan Basin natural gas an attractive raw material for local manufacturing.

The production of three different chemicals from natural gas was studied: urea, propylene, and polypropylene (PP). These three chemicals were chosen based on potential for profitability and their market characteristics (Appendix C). Urea is produced throughout the United States with natural gas as a primary feedstock and is sold to both wholesale and retail consumers across the country. Propylene is only used as an intermediate and only sold to chemical plants, so the potential customer base will be smaller. However, propylene production from methane in the Four Corners would provide a feedstock cost advantage not shared with any other current producers in the United States. Polypropylene, from methane-derived propylene, would offer a feedstock advantage compared to other domestic manufacturers and offer a wider potential customer base because of sales to fabricators and processors throughout the country. By comparing the competitiveness of these three different types of chemicals, the broad characteristics of optimal chemical production in the Four Corners can be characterized.

An agent-based model of the 2013 U.S. market for each of the three chemicals was developed to simulate trade flows between buyers and sellers, including imports and exports. A hypothetical plant in the Four Corners is included in the 2013 model to show how that plant would compete in the market based on historical operations. The agent-based models enable calculation of possible market share for a plant in the Four Corners, taking into account buyer/seller locations, transportation constraints (infrastructure), and competing firms' production costs. The potential for a new urea, propylene, or polypropylene plant in the Four Corners is estimated, using metrics such as market share and production cost necessary to remain competitive with existing firms in the 2013 market.

Figure 5-1: San Juan Basin and natural gas infrastructure in the Four Corners.[7,8,9]



5.1 AGENT-BASED MODELING AND SIMULATION

Agent-based models of the chemical industry represent the behavior of individual plants (enterprise-firms) and allow markets to emerge from interactions between enterprises. Agents are autonomous firms that are capable of determining their own optimal course of action based on events occurring in the modeled market.[10] Each enterprise-firm is composed of sub-agents that manage each task at a chemical plant, such as buying raw materials, managing manufacturing operations, and planning inventory and sales.[11] All components of the chemical value chain are modeled to show the resulting full-system effects of an enterprise's sub-agent's actions. Agents interact with one another through data sharing – inquiring about commodity prices/availability and then buying/selling commodities. Agent-based models do not necessarily show globally optimal material flows in a supply chain, but instead show flows and trends that emerge based on individual firm's actions. North and Macal[12] or Ehlen et al.[13] provide detailed reviews of agent-based modeling and simulation.

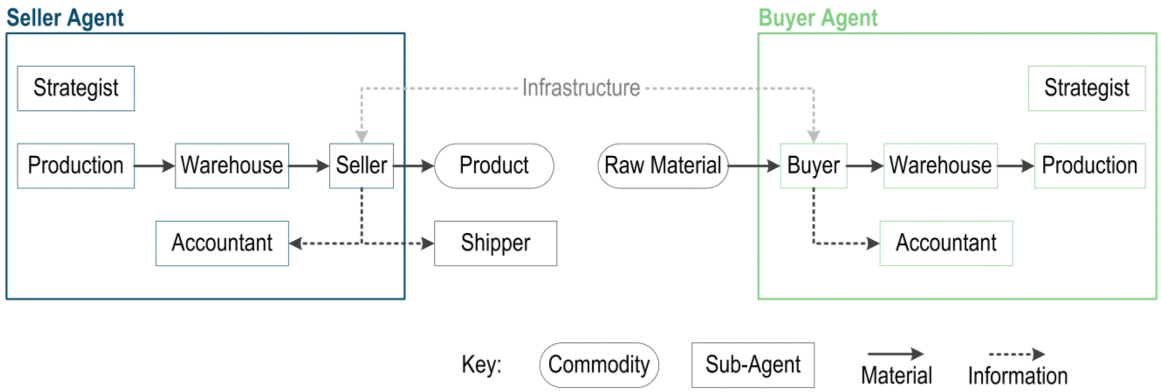
Many components of supply chain systems have been modeled using an agent-based framework. Julka et al. developed a framework for "modeling, monitoring, and management of supply chains."[14] Garcia-Flores and Wang constructed an agent-based model to simulate dynamic behavior of cooperating agents along a single supply chain.[15] The specific operation of a warehouse system was modeled by Ito and Abadi.[16] Models of refinery supply chains have also been used to determine optimal business processes and configurations in one specific plant.[17,18] Sha and Srinivasan developed an agent-based model to determine optimal tank car fleets in chemical supply chains.[19]

The U.S. Department of Homeland Security National Infrastructure Simulation and Analysis Center (NISAC) developed the NISAC Agent-Based Laboratory for Economics (N-ABLE) to conduct economic analysis of "homeland security-related disruptive events."[20] Ehlen et al. used the N-ABLE framework with a chemical data model to simulate thousands of chemical plants and related firms in the U.S. N-ABLE has been used to simulate the impact of disruptive events (both natural and man-made disasters) on the chemical industry. This framework effectively represents plant-level operations and the system-wide behaviors of the entire U.S. chemical industry.[13,21]

5.2 METHODS

An agent-based model of the 2013 U.S. market was created for each of the three chemicals in this work (urea, propylene, and polypropylene). The models were built on the Global Agent-Based Library for Economic Systems (GABLES) agent-based framework and the PRISM Engine™ from PRISM Analytics Corporation.[22] The chemical market consists of sellers that produce the chemical and buyers that consume the chemical. A schematic of the sub-agent structure used in this work is shown in Figure 5-2 and described in Appendix D. A baseline run for each chemical market simulated one year of market operation. The 2013 simulation was then repeated with a new plant in the Four Corners region that produces each chemical. The behavior of the markets with and without the Four Corners plant for one year was studied to determine (1) the potential domestic and export market captured by the new plant and (2) the relationship between production cost and market share. The 2013 market for each chemical is modeled both with and without the hypothetical Four Corners plant to determine the characteristics that a new plant would require to be competitive in the 2013 market for each chemical.

Figure 5-2: Agent configuration for the market structure used in this work.



For each modeled market, supply includes domestic manufacturers and country-level imports. Demand includes domestic chemical plant demand, consumer demand by county, and country-level exports. The data sources and methods for each chemical market model are described in Appendix D. Commodity transportation occurs by truck, rail, or waterway. Shipment mode is determined based on proximity to truck, rail, or waterway networks, shipment volume, shipment cost, and time requirements. The transportation network is intermodal. For initial market share calculations, commodity sales prices are based on historical prices, not estimated plant production costs. Production costs contribute to plant economics which affect agent behavior but are not directly related to sales prices. For subsequent detailed production cost analysis, the markets are simulated with commodity sales prices in each transaction determined by production and transportation costs, not historical market prices.

5.2.1 Model Limitations

The models represent markets made up of buyers and sellers but do not represent entire supply chains. In this model, feedstocks impact unit production cost but feedstock availability from upstream suppliers is not modeled. The sourcing of raw materials is an important component of competitiveness that must be addressed when making investment decisions. The results of this model, therefore, are used only to determine potential product market share for a new plant and not to compare using natural gas a raw material in the Four Corners to competitor's supply chains.

In the urea model, only fertilizer demand is included, not demand for resins, livestock feed, or environmental applications. Fertilizer use accounted for 90% of urea consumption in 2013.[23] Also, many ammonia plants have multiple fertilizer trains and switch production as needed to maximize profit. This flexibility is not included in the model.

For the propylene model, no distinction is made between purity grades (refinery, chemical, and polymer). It is assumed that concentrator products are the same grade as steam crackers and PDH units. This limits the impact of refinery propylene production and distinctions between concentrator and refinery production that would be important if using the model for forecasting investment decisions.

The production costs for all sellers are approximated based on IHS data that represent average industry costs as a function of capacity but do not represent specific plants (which may have design or feedstock factors that could change the calculated production cost).[24] It is assumed that import unit costs are constant and no differentiation is given to costs for import shipments of different volumes from the same country. Since the model represents historical shipments, this represents average import costs, but distinctions in contract sizes and prices will be necessary if used for forecasting scenarios.

The spatial distribution of demand for urea and polypropylene (PP) is assumed based on employees in North American Industry Classification System (NAICS) categories in each county and does not represent specific wholesale consumers. This approximation may not accurately reflect the exact material consumed in each county. For example, locations of PP fabricators and processors are not included directly but are approximated based on counties where processing any type of plastic occurs. Some of these counties might not process PP specifically, so the number of counties that demand PP may be overestimated. Therefore, the calculation of potential market share a new plant could capture represents the general regions and total magnitude that can be achieved, but resolution to the county level does not represent specific consumers.

The scenarios used in this work are representations of 2013 markets and not projections of future scenarios. To determine the optimal chemicals to produce in the Four Corners for new investment, the data must incorporate future projections of market performance, including production capacity, demand growth, and raw material prices.

5.3 Results

The 2013 U.S. market for each chemical is simulated as a baseline without a Four Corners plant and then with a Four Corners plant. Domestic sales and exports from Four Corners in the simulated market are reported, along with market changes attributed to the introduction of the new plant.

Two sensitivity studies were conducted for each market: transport mode and competitor production costs. The initial scenarios assume that the Four Corners plant is built near Farmington, NM which is not connected to the North American rail network. Each market was also simulated with the plant location moved to Gallup, NM (approximately 100 miles south) so that the Four Corners plant then has direct access to rail transportation. Because the production costs of all plants are estimated, a number of studies are also run to determine the sensitivity of Four Corners' operation and sales volume to competitor's production costs. The production costs of the three largest plants in each market are varied by 10% and the simulations are rerun. Results of the analysis and sensitivity studies for the three chemicals are given below.

5.3.1 Urea

The hypothetical Four Corners urea plant has a capacity of 630,000 MT/yr. When the 2013 urea market is simulated, all of the available Four Corners capacity is utilized, with 616,800 MT/yr of domestic sales and 13,200 MT/yr of exports. The magnitude of Four Corners sales to each county is shown in Figure 5-3. The Four Corners plant sells urea throughout almost the entire western half of the U.S, including sales in Texas, Oklahoma, and Nebraska where there are competing urea producers. Local sales in the Four Corners states total 70,800 MT/yr, but the largest market is California with total sales of 447,900 MT/yr.

Out of 407 counties with purchases from the Four Corners plant, most counties have more than one urea supplier throughout the year. The Four Corners plant captures 100% of the market in 22 counties (17 in California, two in Idaho, two in Arizona, and one in Colorado). The market share in each county captured by the Four Corners plant is shown in Figure 5-4.

The Four Corners plant also supplies exports of 13,200 MT/yr total to three locations: Australia (1,300 MT/yr), Japan (1,600 MT/yr), and British Columbia, Canada (10,300 Mt/yr). U.S. exports in the simulated market are shown in Figure 5-5. Four Corners exports do not completely replace all other U.S. exports to those three countries, but capture 69%, 73%, and 73% of the exports to Australia, Japan, and British Columbia, respectively.

Figure 5-3: U.S. county urea purchases from the Four Corners plant in the simulated 2013 market.

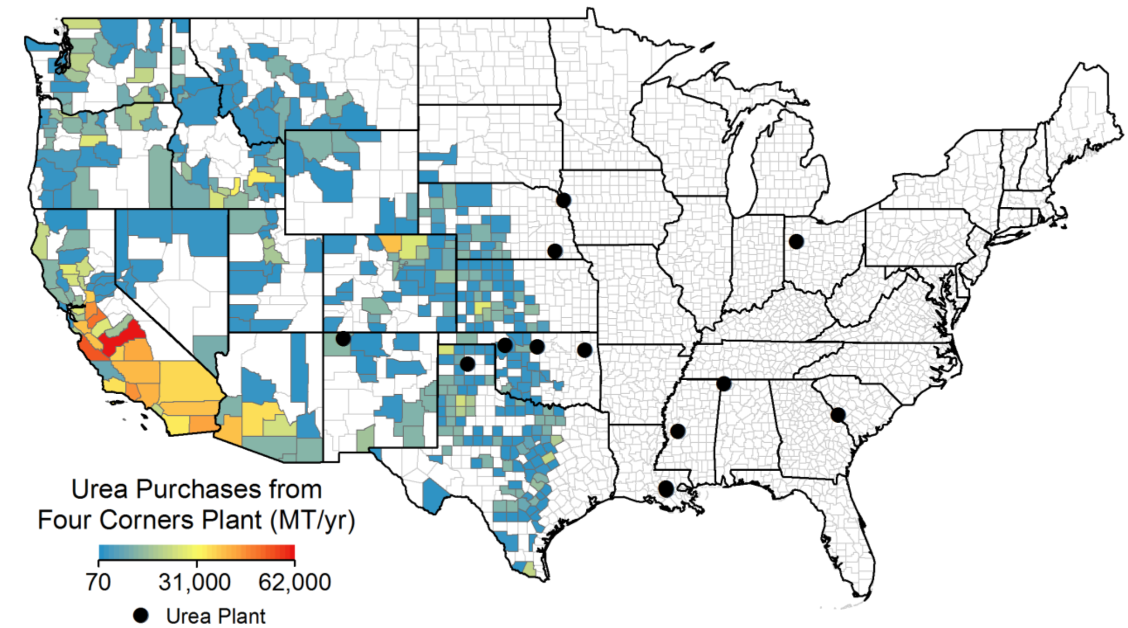


Figure 5-4: U.S. county market share captured by the Four Corners plant in the simulated 2013 urea market.

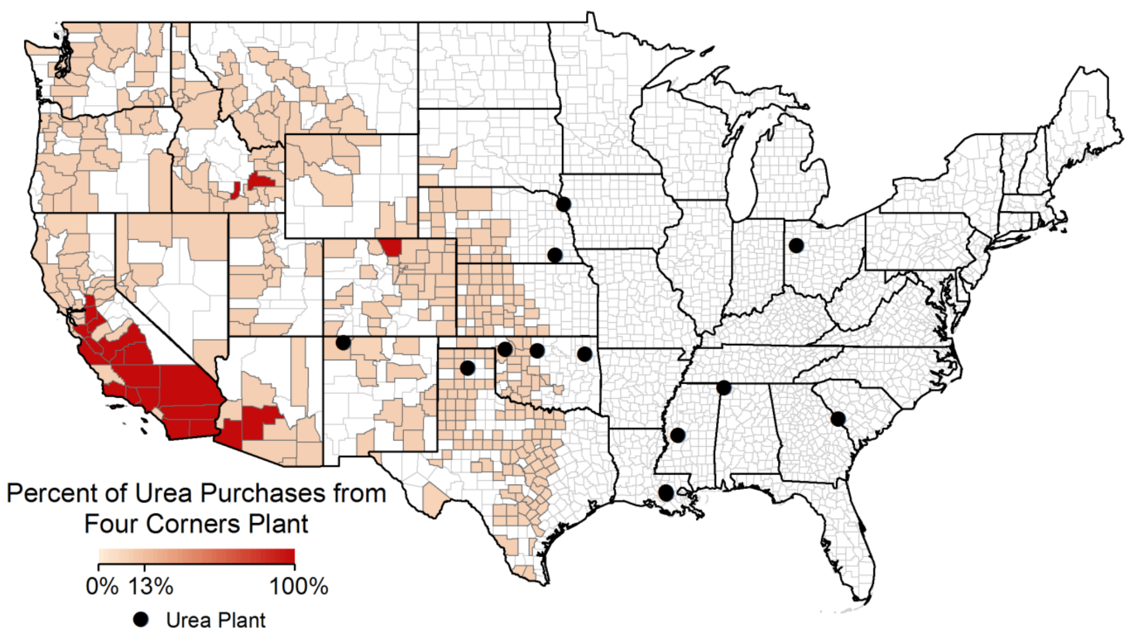
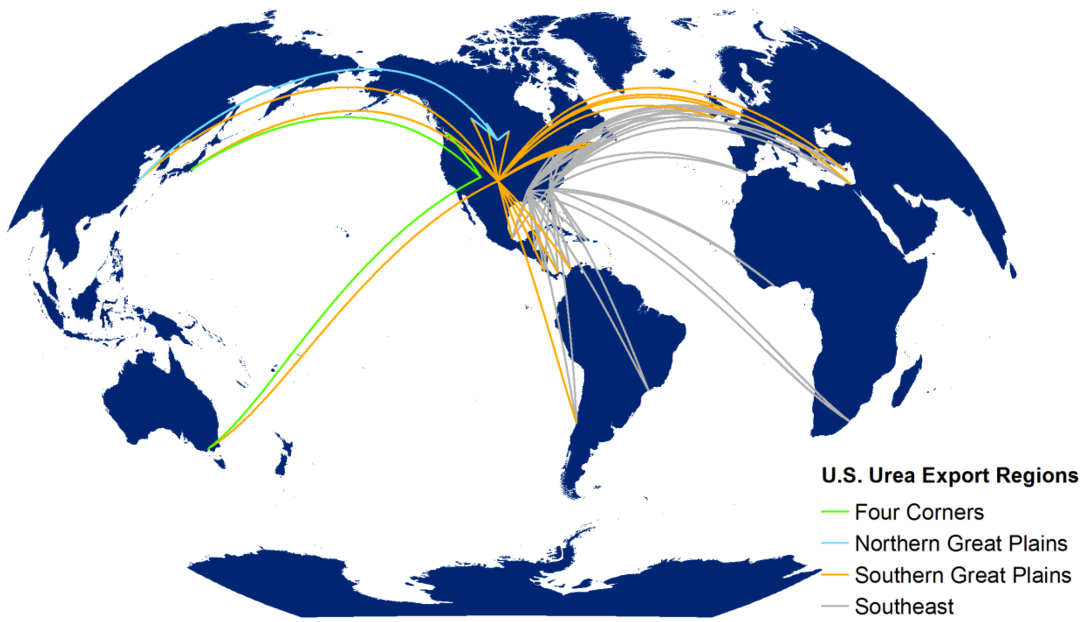


Figure 5-5: U.S. urea exports by region in the simulated 2013 market.

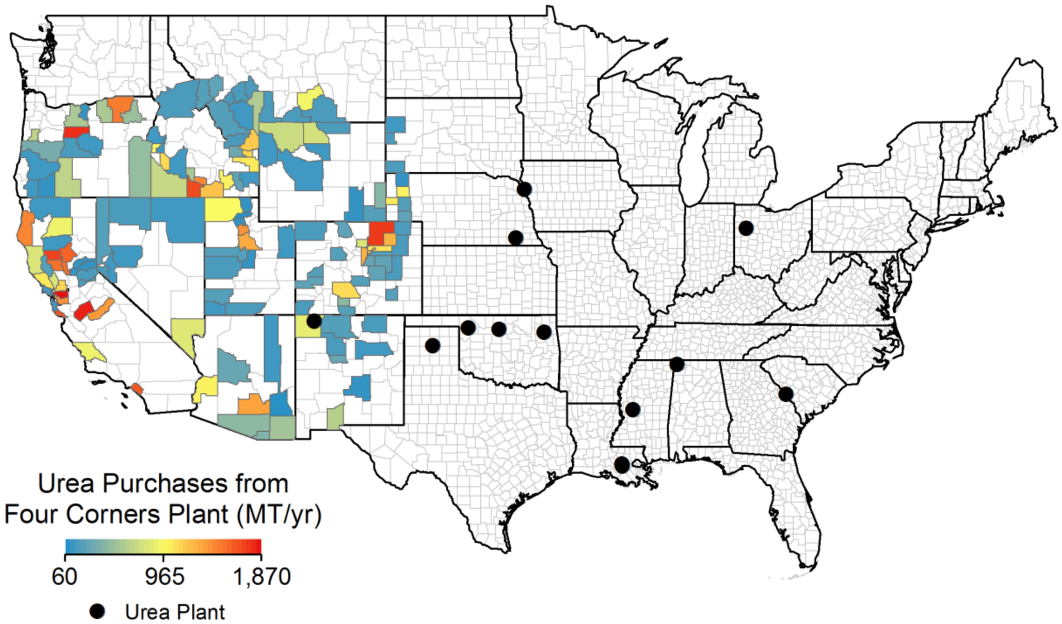


When the plant is located on the rail network (location moved to Gallup, NM), there are very small changes in sales leading to an average sales price that is 0.1% lower than when located near Farmington, NM. This change in plant location has a very small impact on location of sales. Sales to portions of the Texas market near the Gulf Coast are only feasible when production originates on the rail network (Goliad County, TX and Nueces County, TX). However, many other counties in Texas are accessible with the plant location in Farmington with 2013 prices. No change is observed in total sales from the Four Corners plant during sensitivity studies of production costs for CF Industries Holdings, Inc. Donaldsonville, LA; Koch Nitrogen Co., LLC Enid, OK; and PCS Nitrogen, Inc. Augusta, GA.

5.3.1.1 Urea Production Cost

To model the impact of production cost, the 2013 urea market is simulated again with sales price determined by production cost at each plant, not the historical market prices. The maximum production cost that the Four Corners urea plant can have and maintain sales is $422/MT. At this production cost, Four Corners can sell 53,300 MT/yr to 151 counties with no exports. The average sales price achieved by the plant is $470/MT, the highest price of any plant in the simulation. Differences in sales prices are driven by transportation costs and what the buying agent is willing to pay based on the availability and cost of the next most competitive seller. The counties with sales in this production cost scenario are shown in Figure 5-6. In this scenario, the Four Corners plant has a 10.2% profit margin (the lowest of the domestic producers), which includes transport costs. This higher production cost removes the possibility of sales in Texas, Oklahoma, or eastern Kansas, where competition from existing producers is high. Sales in the California market are limited in this scenario because Canadian imports and Koch Nitrogen Enid, OK supplies are cheaper, even with greater transportation costs from those locations.

Figure 5-6: U.S. county urea purchases from the Four Corners plant when the Four Corners production cost is \$422/MT and sales price is determined by plant production costs.



5.3.2 Propylene

The Four Corners propylene plant has a capacity of 514,000 MT/yr. When the 2013 propylene market is simulated, the available Four Corners capacity is not fully utilized, with only 186,000 MT/yr of domestic sales (all to the INEOS polymers plant in Carson, CA) and 1,180 MT/yr of total exports to Australia (190 MT/yr), Canada (780 MT/yr), and China (210 MT/yr). The domestic trade pattern when the Four Corners plant is introduced is shown in Figure 5-7.

In the baseline, the INEOS Carson, CA plant is supplied by Canadian imports (86,170 MT), Eastman Chemical Longview (53,310 MT), Formosa Point Comfort (27,170 kMT), PetroLogistics Houston (acquired by Flint Hills Resources in 2014) (13,780 MT), and Chevron Phillips Chemical Sweeny (5,560 MT). When the Four Corners plant is introduced, it replaces all other supplies to the INEOS Carson plant. In the baseline, exports to Australia are supplied by Chevron Phillips Chemical Cedar Bayou, Chevron Phillips Chemical Sweeny, Formosa Point Comfort, INEOS Chocolate Bayou, and PetroLogistics Houston; exports to Canada are supplied by Eastman Chemical Longview and Enterprise Products Partners Mont Belvieu; exports to China are supplied by Eastman Chemical Longview, Enterprise Products Partners Mont Blevieu, and PetroLogistics Houston. When the Four Corners plant is introduced, it replaces all exports to Australia, Canada, and China. U.S. propylene exports in the simulated market are shown in Figure 5-8.

Figure 5-7: Comparison of propylene trade flows with and without the Four Corners plant in the simulated 2013 market.

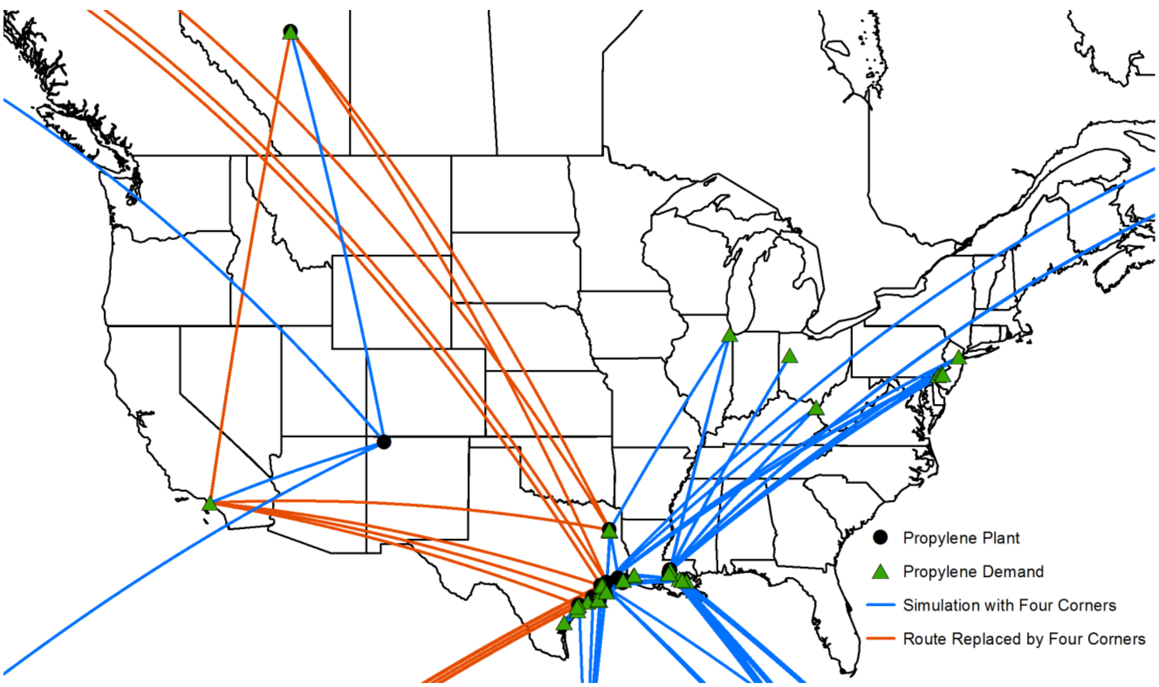
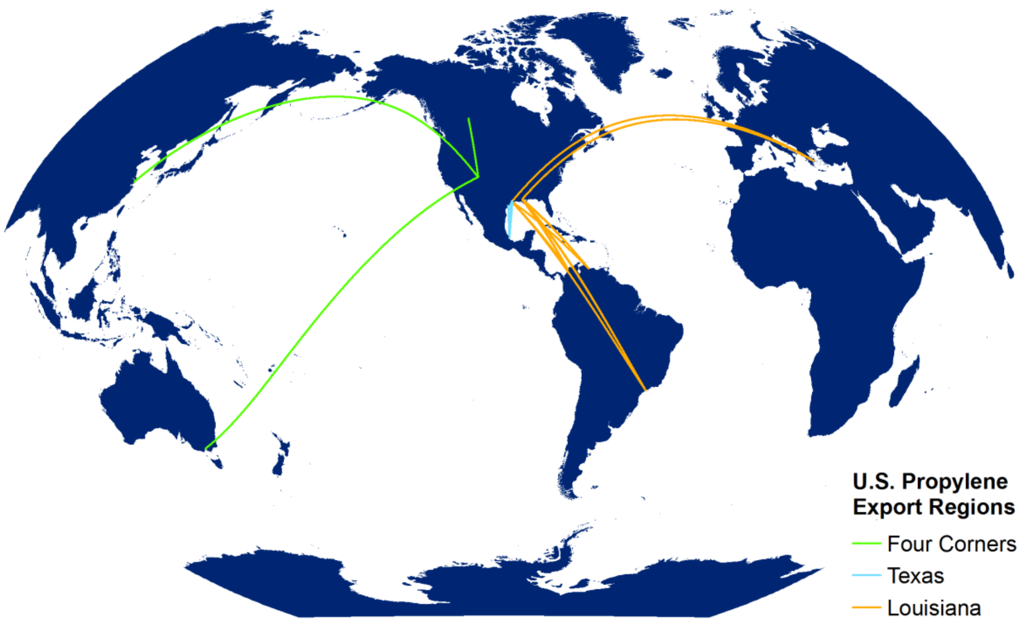


Figure 5-8: U.S. propylene exports by region in the simulated 2013 market.



When the plant location is moved to Gallup, NM, there is no change in the quantity of propylene sold by the Four Corners plant. Even with improved rail transportation connections, the Four Corners plant cannot compete in the Gulf Coast propylene market.

No change is observed in total sales from the Four Corners plant during sensitivity studies of production costs at Chevron Phillips Chemical Sweeny, Dow Chemical Plaquemine, and Dow Chemical Taft. Small variations in sales around the Gulf Coast occur in these sensitivity scenarios. The largest change involves a reduction in sales from BASF Corporation Port Arthur and Enterprise Products Partners Mont Belvieu and a corresponding increase in sales from Chevron Phillips Chemical Port Arthur. The changes in firm performance in the sensitivity studies occur only along the Gulf Coast among the region's marginal producers. In all sensitivity scenarios, sales from the Four Corners plant do not change.

5.3.2.1 Propylene Production Cost

To model the impact of production cost, the 2013 propylene market is simulated again with sales price determined by production cost at each plant, not the historical market prices. The maximum production cost that the Four Corners propylene plant can have and maintain sales is $1,347/MT. At this production cost, Four Corners can sell 95,300 MT/yr to the INEOS Carson, CA plant and 100 MT/yr in exports to China. The average sales price achieved by the plant is $1,496/MT, the highest price of any plant in the simulation. Estimated production cost from local natural gas, would need to be less than $1,347/MT, but cost reductions can only increase sales to a maximum of 186,000 MT/yr.

5.3.3 Polypropylene

The Four Corners polypropylene plant has a capacity of 500,000 MT/yr. When the 2013 PP market is simulated, all of the available Four Corners capacity is utilized, with 413,600 MT/yr of domestic sales and 86,400 MT/yr of exports. The magnitude of domestic Four Corners sales to each county is shown in Figure 5-9. The Four Corners plant sells PP throughout most of the western U.S. and parts of the Midwest. Most sales occur in California (175,350 MT/yr), despite the presence of the INEOS polymers plant in Carson, California. Local sales to the Four Corners states are 80,050 MT/yr. Significant sales occur in the northwestern U.S. (57,200 MT/yr). A small quantity of sales occur in west Texas (13,130 MT/yr) with no sales near the Gulf Coast because of competition with existing PP plants. Of the Four Corners PP sales to 241 counties, 70 counties purchase more than half of their total demand from Four Corners. However, no county is solely dependent on purchases from Four Corners, as shown in Figure 5-10.

The Four Corners plant exports 86,400 MT/yr to 16 countries in the simulated market, shown in Figure 5-11. The largest trade partners are China (23,980 MT/yr), Alberta, Canada (12,020 MT/yr), and Manitoba, Canada (9,390 MT/yr), although Four Corners sales only account for 38%, 68%, and 68% of exports supplied to those locations respectively. No export destination is solely supplied by Four Corners. The Four Corners plant competes with INEOS Carson, CA, Flint Hills Longview, TX, Total LaPorte, TX, and Phillips Linden, NJ PP plants for exports to China and Canada, with most competition from Total LaPorte because of its large capacity even though Total LaPorte's unit production cost is not the lowest available.

When the plant is moved to Gallup, NM, there is less than a 0.01% change in total sales. No change is observed in total sales from the Four Corners plant during sensitivity studies of production costs at Total LaPorte, ExxonMobil Baytown, and LyondellBasell Bayport.

Figure 5-9: U.S. county polypropylene purchases from the Four Corners plant in the simulated 2013 market.

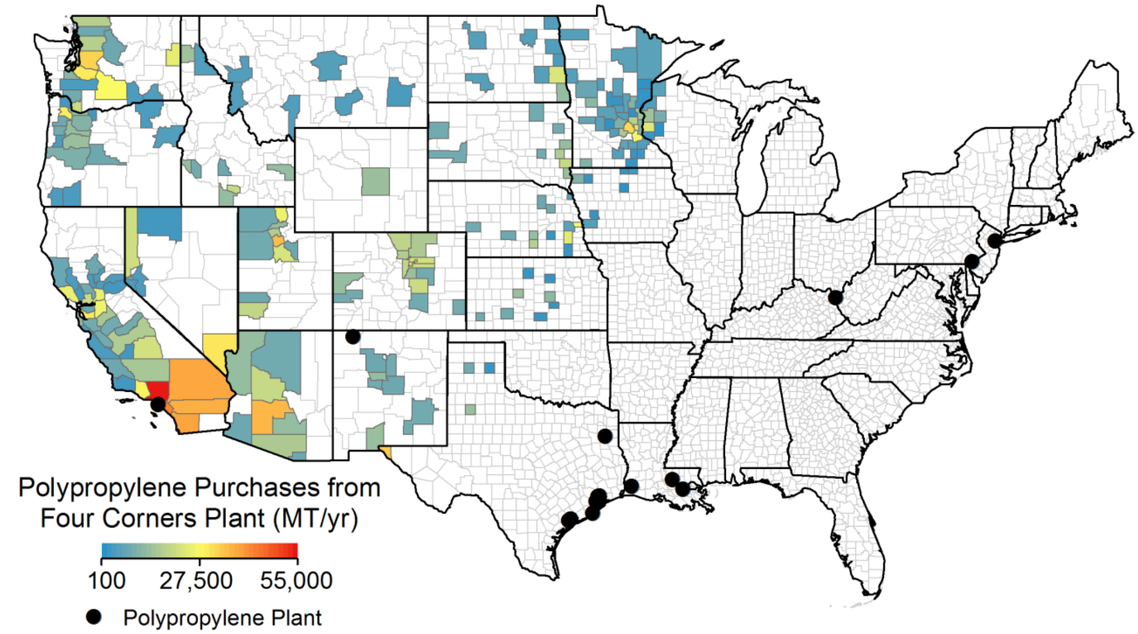


Figure 5-10: County market share captured by the Four Corners plant in the simulated 2013 market.

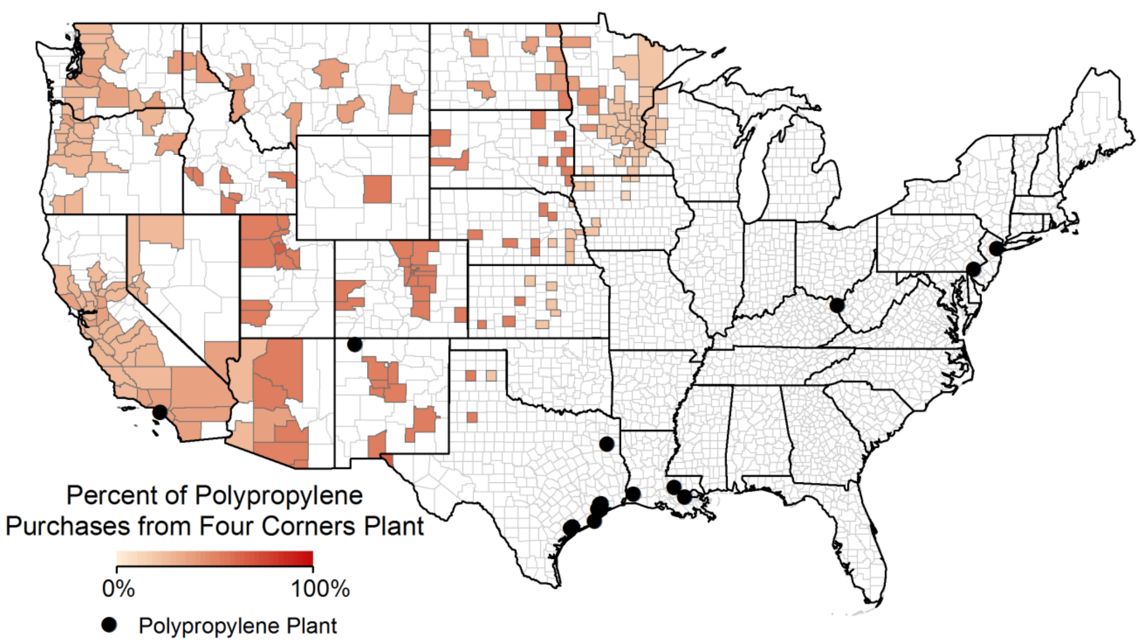
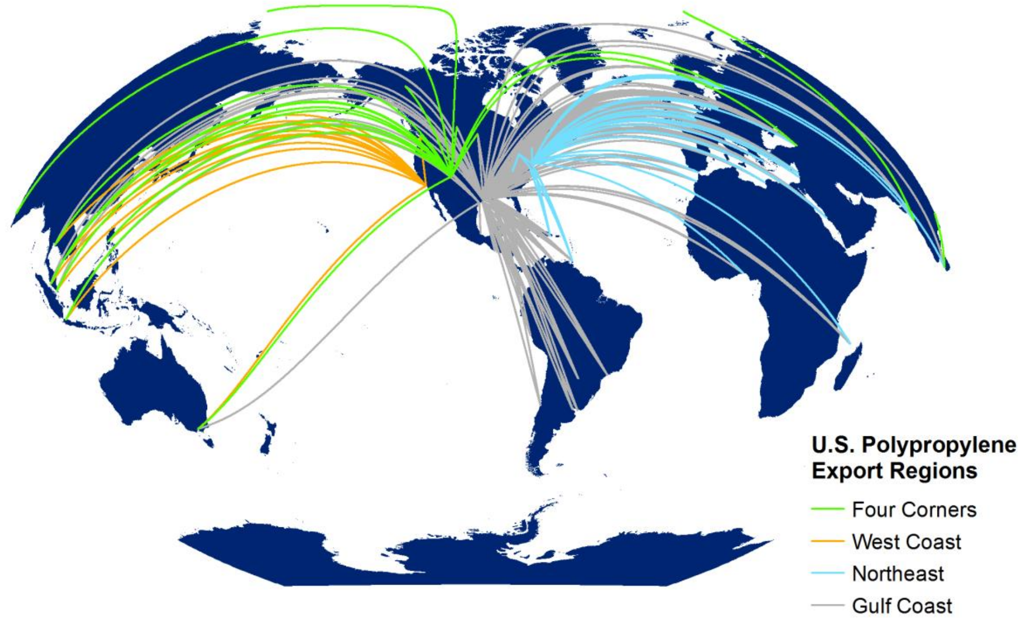


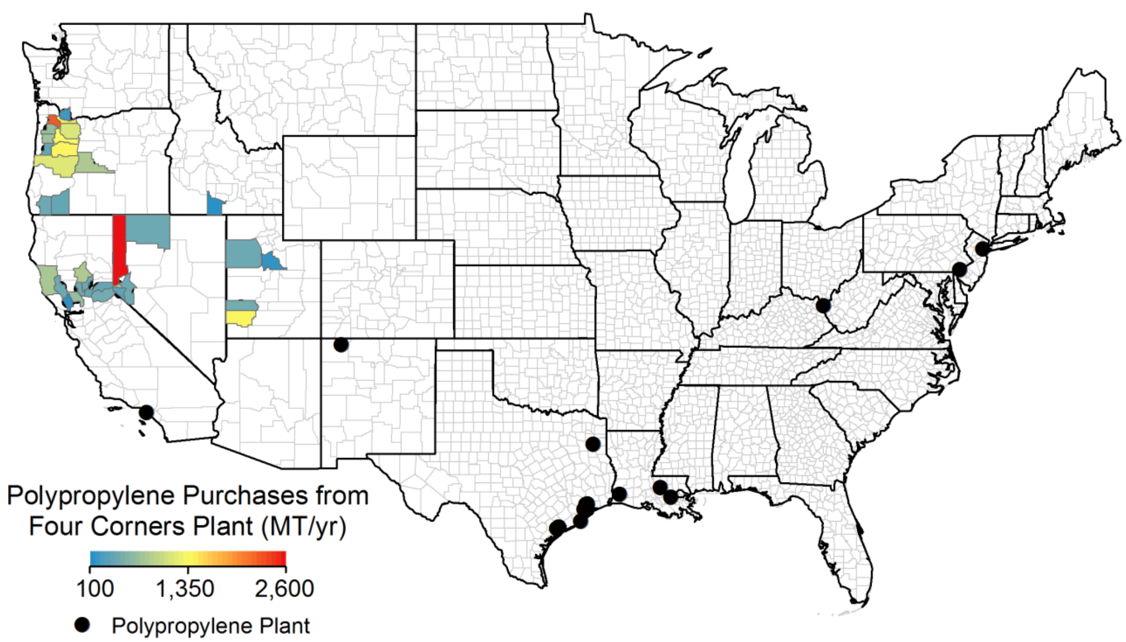
Figure 5-11: U.S. polypropylene exports by region in the simulated 2013 market.



5.3.3.1 Polypropylene Production Cost

To model the impact of production cost, the 2013 PP market is simulated again with sales price determined by production cost at each plant, not the historical market prices. The maximum production cost that the Four Corners PP plant can have and maintain sales is \$1,415/MT. At this production cost, Four Corners can sell 18,600 MT/yr to 32 counties and export 1,300 MT/yr to Indonesia and the Philippines. Domestic sales are shown in Figure 5-12. The average sales price achieved by the plant is \$1,572/MT, the highest price of any plant in the simulation. Differences in sales prices are driven by transportation costs and what the buying agent is willing to pay based on the availability and cost of the next most competitive seller. At this high production cost, sales are very limited and only possible to counties near the west coast, as any counties farther east can purchase cheaper PP from the Gulf Coast producers. Sales to the southern California market are not possible because of competition from INEOS Carson, CA. Production cost reductions from $1,572/MT would dramatically increase market share up to 500,000 MT/yr in the scenarios studied. It is estimated that PP production from methane would cost below $800/MT, indicating the possibility of a substantial profit margin based on 2013 PP market prices even with limited transportation infrastructure in the Four Corners region.

Figure 5-12: U.S. county polypropylene purchases from the Four Corners plant when Four Corners production cost is $1,415/MT and sales price is determined by plant production cost.



5.4 Discussion

A world-scale urea plant in the Four Corners operating in 2013 has the potential to sell up to 616,800 MT/yr domestically and 13,200 MT/yr in exports to Australia, Japan, and British Columbia, Canada for fertilizer use. In the Four Corners region, around 25,000 MT/yr of additional urea demand may exist at the San Juan Generating Station and Four Corners Power Plant for use in air pollution control technologies (selective catalytic reduction of nitrogen oxides). The amount of urea required by these power plants at the 2013 prices would be about 6% of 2013 fuel costs. Results of this model indicate that a urea plant in the Four Corners has sufficient local, regional, and export demand to enable world-scale operation instead of only supplying small quantities to local power plants. The highest production cost that can sustain sales, based on model predictions, is $442/MT, which limits total sales to 53,300 MT/yr.

A propylene plant in the Four Corners can supply the INEOS Carson, CA polymers plant (186,000 MT/yr) and all U.S. exports to Australia, western Canada, and China (1,180 MT/yr), but cannot competitively supply propylene to any other part of the country. Even with improved rail transportation connections, the model predicts that the Four Corners plant cannot compete in the Gulf Coast propylene market. With a production cost increased to $1,347/MT, sales to the INEOS Carson, CA plant are cut nearly in half, as INEOS is also supplied by Eastman Longview and Formosa Point Comfort, TX.

A world-scale polypropylene plant in the Four Corners could be fully utilized, with 413,600 MT/yr of domestic sales and 86,400 MT/yr of exports to China and Canada, using 2013 market prices and a production cost of $1,388/MT. An increase in production cost to $1,415/MT, however, severely limits the potential for sales, indicating that the feedstock advantage from using low cost methane is very important for potential market share.

5.5 Conclusions

Of the three chemicals studied, urea and polypropylene plants in the Four Corners fully utilize potential capacity, while propylene production in the Four Corners can only supply one domestic customer (INEOS Carson, CA). While INEOS Carson has experienced trouble acquiring feedstocks and might benefit from an additional feedstock source,[25] Four Corners propylene production would have no other domestic customers and the export market is relatively small compared to end product chemicals. Production cost or transportation network improvements to eliminate competition from existing propylene producers in the Gulf Coast are not enough to expand Four Corners' propylene customer base.

In general, the addition of a rail transport option for product shipment from the Four Corners does not have a large impact on potential customers or total sales assuming 2013 market prices. However, future price changes can affect this conclusion.

Based on the results of this study, chemical production in the Four Corners should focus on final end products instead of intermediates. Even with rail transport from the region, intermediate demand in the Gulf Coast cannot be served by Four Corners production. Final end products to target for development should have demand distributed throughout the U.S. as the Four Corners plant has the potential to capture a significant portion of the western U.S. and Pacific export markets.

5.6 REFERENCES

1. U.S. Energy Information Administration (EIA), Annual Energy Outlook 2015.

2. Siirola, J. The impact of shale gas in the chemical industry, *AIChE J.* 2014, 60 (*3*).

3. Swift, T. K.; Moore, M. G. Shale gas brightens outlook for U.S. chemicals, *Chemical Engineering Progress*, January 2013.

4. American Chemistry Council, *Year-End 2015 Chemical Industry Situation and Outlook*, December 2015, http://www.americanchemistry.com/Jobs/EconomicStatistics/Year-End-2015-Situation-and-Outlook.pdf (accessed January 8, 2016).

5. State of New Mexico Oil Conservation Division, *Statewide Natural Gas and Oil Production Summary Including Produced Water and Injection by Month*, January 7, 2016, https://wwwapps.emnrd.state.nm.us/ocd/ocdpermitting//Reporting/Production/ExpandedProductionInjectionSummaryReport.aspx (accessed January 7, 2016).

6. GO-TECH New Mexico Price Sheet http://octane.nmt.edu/gotech/Marketplace/year_prices.aspx?year=2015 (accessed January 12, 2016).

7. U.S. Geological Survey (USGS), *U.S. Coalbed Methane Field Boundaries (2007) in CO & NM*, http://my.usgs.gov/eerma/data/index/4f501131e4b022a71b94a911?q=&facetType=Shapefile (accessed January 12, 2016).

8. U.S. Energy Information Administration (EIA), *Layer Information for Interactive States Maps* https://www.eia.gov/maps/layer_info-m.cfm (accessed January 12, 2016).

9. U.S. Geological Survey (USGS), *National Oil and Gas Assessment - San Juan Basin*, http://energy.usgs.gov/OilGas/AssessmentsData/NationalOilGasAssessment/USBasinSummaries.aspx?provcode=5022 (accessed January 12, 2016).

10. Wooldridge, M.; Jennings, N. R. Intelligent agents: theory and practice, *The Knowledge Engineering Review*, 1995, 10, 115-152.

11. Vugrin, E. D.; Camphouse, R. C.; Downes, P. S.; Ehlen, M. A.; Warren, D. E. Measurement of System Resilience: Application to Chemical Supply Chains, *Proceedings of the 2009 SIAM Conference on 'Mathematics for Industry'*, 2010.

12. North, M. J.; Macal, C. M. *Managing Business Complexity: Discovering Strategic Solutions with Agent-Based Modeling and Simulation*; Oxford University Press: New York, 2007.

13. Ehlen, M. A.; Sun, A. C.; Pepple, M. A.; Eidson, E. D.; Jones, B. S. Chemical supply chain modeling for analysis of homeland security events, *Comp. Chem. Eng.* 2014, 60, 102-111.

14. Julka, N.; Srinivasan, R.; Karimi, I. Agent-based supply chain management – 1: framework, *Comp. Chem. Eng.* 2002, 26, 1755-1769.

15. Garcia-Flores, R.; Wang, X. Z. A multi-agent system for chemical supply chain simulation and management support, *OR Spectrum*, 2002, 24, 343-370.

16. Ito, T.; Mousavi Jahan Abadi, S. M. Agent-based material handling and inventory planning in warehouse, *Journal of Intelligent Manufacturing*, 2002, 13, 201-210.

17. Srinivasan, R.; Bansal, M.; Karimi, I. A. A multi-agent approach to supply chain management in the chemical industry. In B. Chaib-draa and J. Muller (Eds.), *Multiagent Based Supply Chain Management* (p 419-450). Springer: Berlin, 2006.

18. Julka, N.; Karimi, I.; Srinivasan, R. Agent-based supply chain management: Framework and a refinery application. *Comp. Chem. Eng.* 2002, 26, 1755-1769.

19. Sha, M.; Srinivasan, R. Fleet sizing in chemical supply chains using agent-based simulation, *Comp. Chem. Eng.* 2016, 84, 180-198.

20. Ehlen, M. *Economics Definitions, Methods, Models, and Analysis Procedures for Homeland Security Applications*, Sandia National Laboratories SAND2010-4315, Prepared for The Science and Technology Directorate, U.S. Department of Homeland Security Chemical Sector and Resilience Project, January 29, 2010.

21. Vugrin, E. D.; Warren, D. E.; Ehlen, M. A. A resilience assessment framework for infrastructure and economic systems: quantitative and qualitative resilience analysis of petrochemical supply chains to a hurricane, *Process Safety Progress*, 2011, 30 (*3*).

22. PRISM Analytics Corporation, http://www.prismanalytics.net/PRISM_Analytics_Corporation/Home.html (accessed January 13, 2016).

23. IHS Chemical, *Chemical Economics Handbook: Urea, Abstract*, January 2014, https://www.ihs.com/products/urea-chemical-economics-handbook.html (accessed January 21, 2016).

24. IHS Chemical, Process Economics Program Yearbook, 2012.

25. Kelley, L. INEOS declares PP force majeure on feedstock issue, *ICIS News*, December 2, 2015 http://www.icis.com/resources/news/2015/12/02/9949705/ineos-declares-pp-force-majeure-on-feedstock-issue/ (accessed January 20, 2016).

Chapter 6: Development of a Comprehensive Natural Gas Liquids Industry Model

Between 2009 and 2015, production of natural gas liquids (NGLs) in the United States has increased by more than 50%.[1] As NGL production has increased there have been many changes to the industry. Hydrocarbon gas liquid (HGL) production from refineries has remained relatively constant since 2005, while production from wet natural gas has expanded.[2] While PADD 3 is still the dominant producing region (due primarily to the Permian and Eagle Ford Basins), there has been a large growth in production from PADDs 1 and 2. In less than four years (January 2012 – May 2015), PADD 1 NGL production increased nearly 10 fold.[3] Along with significant changes in NGL production, NGL price dynamics have been altered dramatically over the past five years. Before 2012, NGL composite prices closely tracked crude oil prices on a BTU basis. Since 2012, NGL composite prices have decreased to fall between crude oil and natural gas spot prices.[4]

As the industry adapts to these changes, significant infrastructure expansions have occurred. The shifting competitiveness of U.S. NGL production has enabled opportunities for new exports to global markets. Chemical demand for NGLs, already the largest consumption sector, has accelerated with investments in retrofits for feedstock substitutions and greenfield projects. With impacts in residential heating, transportation fuels, international markets, and every major domestic chemical sector, it is vital to understand the extent of changes occurring within the industry and the resulting impacts on system operations. An integrated model spanning from NGL extraction through olefin chemical consumption allows for analysis of potential changes, identifying environmental impacts, new vulnerabilities and optimal strategies for mitigation, and outcomes for consumers.

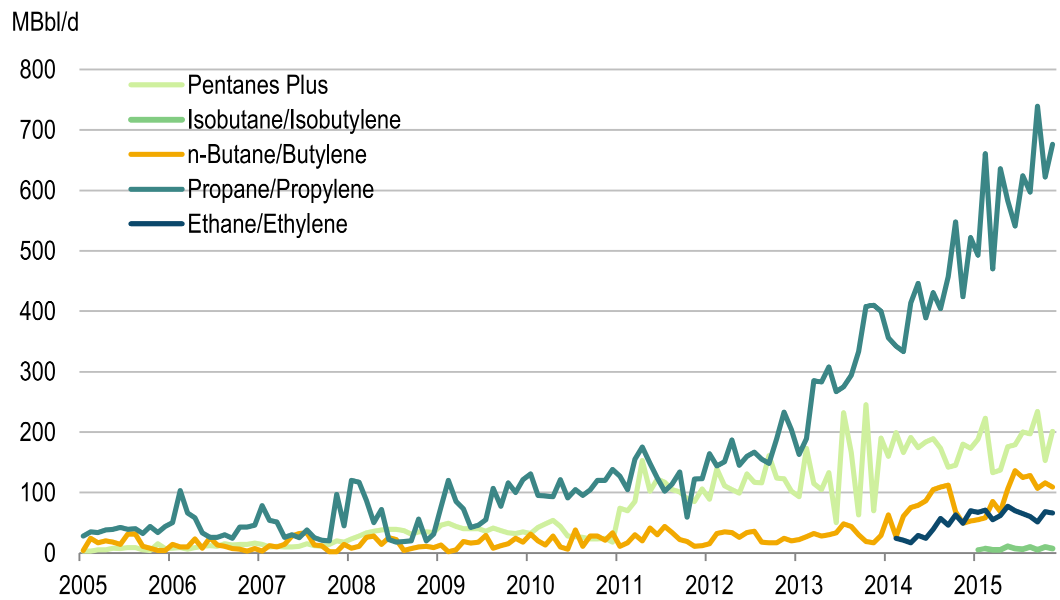
6.1 Motivations for Model

In January 2014, President Obama issued a Presidential Memorandum "directing the administration to conduct a Quadrennial Energy Review (QER)."[5] The QER launched a comprehensive review of domestic energy services designed to "identify the threats, risks, and opportunities for U.S. energy and climate security."[5] The first installment of the QER was released in April 2015, examining transmission, storage, and distribution infrastructure.[6] Through modeling and analysis conducted for the QER, specific areas undergoing transformation in the NGL industry have been identified that warrant further in-depth study. The issues discussed below are the driving factors for developing a comprehensive model of the NGL industry.

6.1.1 Exports

The NGL market is balanced using storage and exports. With increasing levels of NGL production, and a comparatively small amount of available storage, a large portion of production is exported if local demand is not sufficient or accessible. Because of these constraints and favorable international price spreads, hydrocarbon gas liquid (HGL – C2-C5 alkanes and alkenes) exports have increased significantly since 2010, with the largest increase in propane/propylene exports (Figure 6-1). The EIA data does not differentiate between the alkane and alkene component of export volumes.

Figure 6-1: Monthly U.S. exports of hydrocarbon gas liquids, January 2005 – November 2015.[7]



To accommodate the large demand for exports based on pricing arbitrage, 17 export facilities have been expanded or built in the last few years. More than 900 thousand barrels per day (MBbl/d) of design capacity has been added in 2013, 2014, and 2015, with an additional 760 MBbl/d projected to be operational by 2018.[8]

Typically, small quantities of ethane have been transported in pressure vessels originally designed for ethylene and LPG transport. Extremely low ethane prices however, encouraged the development first of pipeline exports to Canada from the Bakken and Marcellus/Utica basins and more recently refrigerated export terminals in the Gulf Coast and Pennsylvania. Responding to increased refrigerated ethane export capacity, a dedicated ethane fleet of very large ethane carriers (VLEC) is being developed. The global ethane carrier fleet capacity is expected to reach nearly 1,400,000 cubic meters by the end of 2017. This new fleet is expected to traverse six major routes from the U.S. to Sweden, the United Kingdom, the west cost of India, and the Far East.[9]

The timing of seaborne ethane shipments and deployment of VLECs is dependent on U.S. ethane price advantages which may diminish as additional domestic demand comes online, as discussed below.

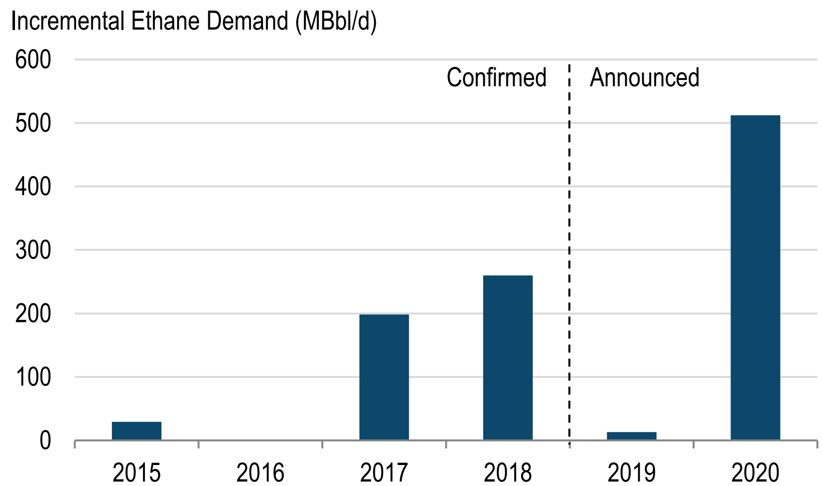
6.1.2 Natural Gas Liquids Supply/Demand Balances

6.1.2.1 Ethane

The two primary uses of ethane are as a feedstock for ethylene production by steam cracking and as natural gas through ethane rejection. See Section 6.3.5 for a full description of ethane rejection and implications for model development.

Steam cracker expansions and new builds currently underway will add 490 MBbl/d of ethane demand along the Gulf Coast by 2018 – a 60% increase in petrochemical ethane demand since 2013. An additional 440 MBbl/d of ethane demand has been announced but development has not yet started (Figure 6-2).[8] The increase in domestic ethane demand coinciding with export capacity (bound by take or pay contracts) will likely impact prices, which could incentivize extraction in marginal supply regions (Bakken, then northern Rockies, followed by Marcellus/Utica as of 2015).[8]

Figure 6-2: Annual additional ethane demand for ethylene production, 2015 – 2020, based on announced capacity additions as of June 2015.[8]



6.1.2.2 Propane

In general, propane demand for domestic petrochemicals is expected to remain constant through 2020. The only exception is propane demand for on-purpose propylene production in propane dehydrogenation (PDH) units. The only currently operating PDH unit is Flint Hills Resources on the Houston Ship Channel, with propane demand of 30 MBbl/d. Five more PDH plants are expected to come online by 2017, increasing propane demand for PDH units to 190 MBbl/d by the end of 2017.[10]

6.1.2.3 Butanes

Projected domestic demand for butane is expected to contract through at least 2018[10] and exports have not experienced the same growth seen with propane. n-Butane is primarily used as a gasoline blendstock, although in highly seasonally varying quantities due to Reid vapor pressure (RVP) specifications. Isobutane is used as a feedstock for refinery alkylate production. As gasoline demand has decreased, both n-butane and isobutane have seen a significant decrease in demand. The lack of market growth can impact butane prices and negatively affect fractionation spreads that drive liquids extraction. Increased butane exports or emergence of a larger domestic chemical market for butanes is required to maintain beneficial n-butane prices. Edmonton butane spot prices have been consistently above Conway/Mont Belvieu prices throughout 2013 and 2014, which was not the case in 2012.

Since isobutane is now a relatively cheap alkylate feedstock, there is potential for the share of alkylate produced from isobutane to increase, although with decreasing gasoline demand overall in the U.S., the growth is not likely to be sufficient to significantly alter a supply/demand balance. Merchant isomerization is expected to be cut in half from 2014 to 2018 since isobutane gas plant production is sufficient to supply domestic demand.

6.1.3 Pipeline Infrastructure

NGL pipelines across the U.S. are being expanded or developed to efficiently transport new production to fractionation and demand locations. 1.8 MMBbl/d of NGL pipeline capacity was constructed in 2012 and 2013, with more than 2 MMBbl/d of NGL pipeline capacity built or under development between 2014 and 2018.[11] Most capacity additions are directed to flow towards Mont Belvieu. Significant take-away capacity from Marcellus/Utica and the Bakken is important because providing take-away capacity from stranded or semi-stranded regions may incentivize liquids extraction or fractionation. This will also impact the attractiveness of localized manufacturing – if ethane, for example, is easily and cheaply transported to the Gulf Coast, it is not as necessary to build local chemical demand.

6.1.4 Vulnerabilities

As part of both the national liquid fuels and natural gas systems, natural gas liquid infrastructure is vulnerable to natural and human threats, including hurricanes, earthquakes, tsunamis, tornadoes, heat waves and drought, derechos, wildfires, flooding, and severe winter weather. Threats vary by region depending on:

- Types of natural disasters common to the region
- Amount of vulnerable infrastructure within the region
- Dependency on imports into the region
- Level of demand in the region.

A systematic assessment of threats to various components of energy infrastructure was conducted as part of the QER. Probability and severity of damage to NGL-related infrastructure for select hurricane, earthquake, and tornado scenarios is shown in Table 6-1, Table 6-2, and Table 6-3, respectively. The predominant threat in terms of severity of damage is loss of electrical power to all systems in most natural disaster scenarios. The NGL industry relies on electrical power to operate pumping stations and underground storage operations. A major scenario not yet fully understood is the effect of regional disruptions to natural gas plant NGL supply on delivery to consumers throughout the country. The large number of processing plants increases overall resiliency, but long-distance transport between regions relies on a limited number of NGL pipeline corridors to connect supply to demand regions (i.e., Marcellus to Gulf Coast is essentially connected by one pipeline corridor and Jones Act requirements limit the prevalence of ship transport).

Table 6-1: Probability and severity of hurricane damage to select NGL-related infrastructure.[12]

Infrastructure	**Hurricane Cat 1-2**		**Hurricane Cat 3-5**	
	Probability of Damage	Severity of Damage	Probability of Damage	Severity of Damage
Electrical Power	Med-High	Major	High	Catastrophic
Pipelines	Low-Med	Interrupting	Med-High	Major
Ports	Med-High	Major	High	Catastrophic
Natural Gas Plants	Med	Significant	Med-High	Major
Propane Tanks	Low	Minor	Low	Minor
Underground Storage	Low	Minor	Low	Minor

Table 6-2: Probability and severity of earthquake damage to select NGL-related infrastructure.[12]

Infrastructure	**Magnitude < 5.0**		**Magnitude > 5.0**	
	Probability of Damage	Severity of Damage	Probability of Damage	Severity of Damage
Electrical Power	Med	Significant	High	Catastrophic
Pipelines	Low-Med	Interrupting	Med-High	Major
Ports	Low	Minor	Med-High	Major
Natural Gas Plants	Low	Minor	Med	Significant
Propane Tanks	Low	Minor	Med	Significant
Underground Storage	Low	Minor	Low-Med	Interrupting

Table 6-3: Probability and severity of EF2-5 tornado damage to select NGL-related infrastructure.[12]

Infrastructure	**EF2-3 Tornado**		**EF4-5 Tornado**	
	Probability of Damage	Severity of Damage	Probability of Damage	Severity of Damage
Electrical Power	Med-High	Major	High	Catastrophic
Pipelines	Low-Med	Interrupting	Med	Significant
Ports	Low-Med	Minor	Low	Minor
Natural Gas Plants	Med	Significant	Med	Significant
Propane Tanks	Low-Med	Interrupting	Low-Med	Interrupting
Underground Storage	Low	Minor	Low	Minor

The analysis shows that in general, direct NGL infrastructure (propane tanks, underground storage) is resilient to most natural disasters and will only face minor damage with low probability. However, the interdependent infrastructure components such as electrical power, pipelines, and ports have the most probability and severity of damage.

6.1.4.1 Regional Vulnerability[13]

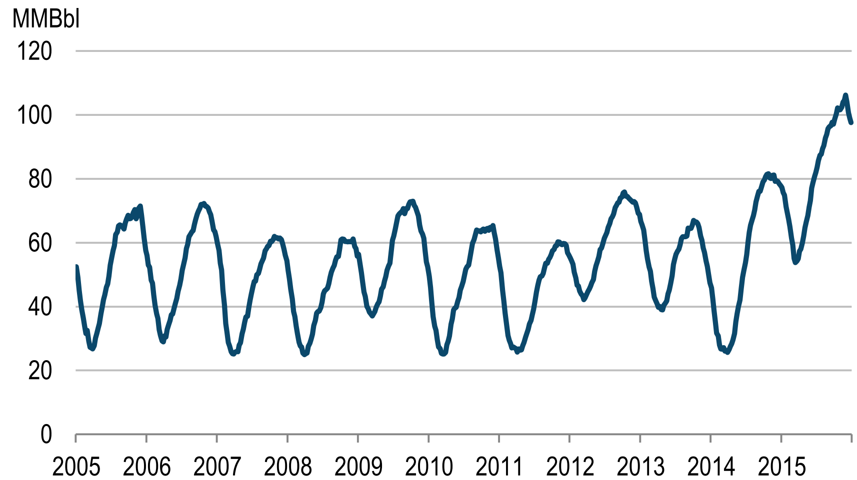
Until recently, PADD 1a sourced propane from PADD 2 and PADD 3, with minimal demand for other NGLs. Supplies can be acquired using the Enterprise and TEPPCO pipeline systems or by waterway from PADD 1B, 1C, or 3. Waterway transport could require weeks to deliver supplies to consumers, based on availability of Jones Act vessels. Significant storage capacity exists in Rhode Island and New Hampshire with typically about 6-8 days of stocks available during non-peak demand, a minimum amount required based on distribution infrastructure. Sufficient propane storage exists in PADD

1B and typically 15 days of stocks are held in PADD 1C, providing adequate time for infrastructure repairs after a disruption.

The primary NGL hub in the Midwest (Conway, KS) offers multiple supply sources and typically has more than 120 days of stocks. Resiliency is improved by the presence of a second propane hub at Medford, OK. The reversal of the Kinder Morgan Cochin Pipeline in 2014 reduced swing propane supply to the Midwest, limiting access to storage capacity in the Midwest to rail and truck transportation. The total amount of propane supplied will not be impacted, as U.S. production is sufficient in general to meet demand, but during periods of high demand, the lack of peak transportation capacity can reduce supply reliability and may increase the cost of propane in the region.[14] PADD 2 West historically has low propane stocks (averaging 1-2 days of demand), and transport into the region is reliant on truck and rail shipments from Kansas and Oklahoma.

Propane stocks in PADDs 3, 4, and 5 are usually sufficient for short term disruptions. However, fundamental shifts in petrochemical and export demand may change incentives for storage. This currently does not appear to be an issue as total U.S. propane/propylene stocks have increased in the last two years (Figure 6-3), but significant petrochemical demand will come online over the next few years which may alter incentives for propane stock build-up.

Figure 6-3: U.S. weekly ending stocks of propane/propylene, 2005 – 2015.[15]



The QER recommended developing a comprehensive analytical framework to assess energy infrastructure "resilience, reliability, and asset security."[16] A consistent method for NGL sector resilience is needed to address this recommendation. An NGL model can also provide guidance for how to increase energy and chemical supply following a disruption. For example, state or federal authority can be used to regionally prioritize pipeline shipments, such as FERC's actions for propane during the 2013-2014 winter shortages. The impact and efficacy of such actions can be understood and planned for using a model.

6.1.5 North American Integration

Significant energy trade occurs within North America. U.S. energy trade with Canada was valued at $140 billion in 2013 and trade with Mexico was valued at $65 billion in 2012. Coordinating development of a robust energy system between all three countries will improve efficiency and increase resilience. Mexico's recent energy sector reforms provide an opportunity for increased trade with the U.S. To facilitate expansion and a more robust system, the QER specifically recommends to "increase the integration of energy data among the United States, Canada, and Mexico" and to "undertake comparative and joint energy system modeling, planning, and forecasting."[17]

6.1.5.1 Propane Markets in Mexico

Deregulation of the liquefied petroleum gas (LPG) market in Mexico will remove retail price caps and allow companies besides Pemex to import LPG. LPG production in Mexico has dropped from 225 MBbl/d in 2004 to 150 MBbl/d in 2015.[18,19] Domestic sales of LPG in 2015 were 277.8 MBbl/d and 105 MBbl/d were imported.[20,21] The large potential for imports to Mexico coincides with growing U.S. exports. Currently, LPG is being transported from the U.S. to Mexico by pipeline, rail, truck, and ship (the largest volume of trade occurs by ship).[22] There is potential for development of an underground salt cavern storage facility in Pajaritos, which would enable regular delivery of LPG by ship.[22] High freight rates have prompted deliveries of new very large gas carriers (VLGCs) which may reduce shipping costs from the U.S. Gulf Coast to Pajaritos, but the lowest cost long term delivery method for U.S. LPG to Mexico is by pipeline.[23] A planned joint venture between Pemex affiliate PMI and NuStar Energy would deliver LPG from Mont Belvieu and Corpus Christi to Nuevo Laredo and Burgos-Reynosa, Mexico.[24] Opportunities for additional trans-border pipelines need to be identified and evaluated to comply with National Interest Determinations as required by the presidential permitting process. Modeling the interconnected LPG system could contribute to the Determination. Advanced market opportunities may exist that use U.S. exports in conjunction with internal LPG pipelines in Mexico. For example, the proposed Transoceanic Corridor Project would enable receipt of LPG or other hydrocarbons from ports on the Gulf Coast, transport by pipeline 186 miles across Mexico to the Pacific, and then exports to Pacific markets, bypassing the Panama Canal.[25,26]

6.2 Modeling Approaches

The combination of chemical transformations, choices of processing techniques, and physically constrained flows (pipelines and rail with congestion and flow limits) is difficult to accurately model with one system. Previous work has modeled propane supply/demand balances at the PADD level[27] and RBAC Inc. has constructed a market-clearing model of the NGL industry by optimizing material flows in a piecewise linear program.[28] Agent-based modeling is unique because of the ability to accurately represent market operations while optimizing internal firm performance, where internal profit maximization is not necessarily the same result that occurs when industry-wide objective functions are used.

Preliminary work to construct an agent-based model of the U.S. NGL industry was conducted at the National Infrastructure Simulation and Analysis Center (NISAC) at Sandia National Laboratories using the NISAC Agent-Based Laboratory for Economics (N-ABLE™).[a] For an overview of N-ABLE's functionality see Chapter 2. Agent behavior needs to be defined for each component of the NGL industry based on operational decisions that are unique to NGL firms. Section 6.3 describes components of the industry and how to formulate their behaviors.

[a] The author would like to thank Mark Pepple, John Masciantoni, Mark Ehlen, Eric Eidson, and Lori Parrott at Sandia National Laboratories for their assistance with N-ABLE.

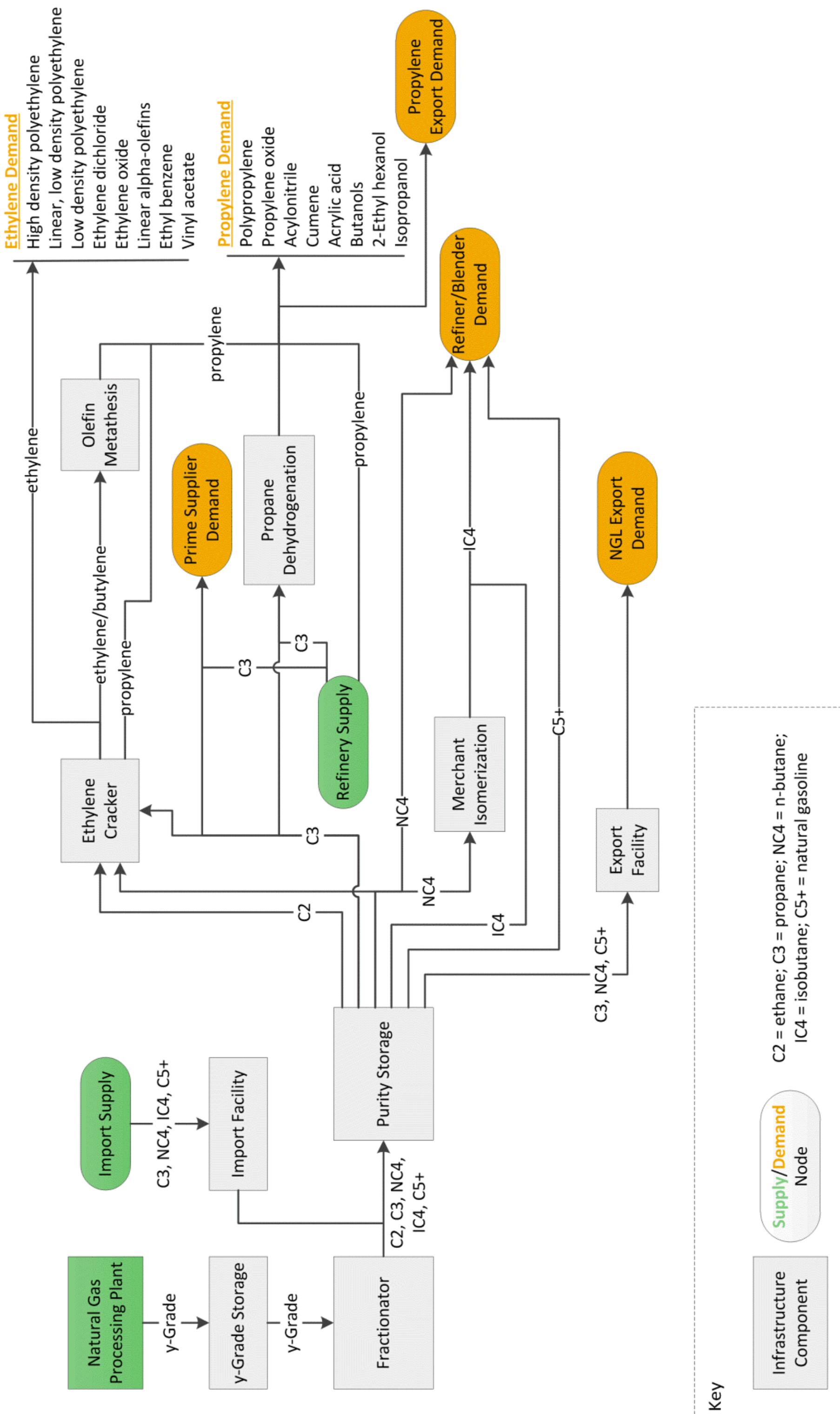
6.3 Components of a Model

The model represents production sources of NGLs (domestic and imports), midstream infrastructure, residential and export consumption of purity NGLs, primary chemical uses of NGLs, and demand points for C2 and C3 olefins produced from NGLs and refineries. An outline of the components to be included in the model is shown in Figure 6-4, followed by details of select components.

NGL field supply begins at natural gas processing plants, with approximated quantity and composition produced at each gas plant calculated using data from EIA. Import supply is directly connected to import infrastructure. Midstream infrastructure includes storage, fractionation, isomerization, ethylene crackers, and on-purpose propylene plants. Refineries produce propane/propylene and consume n-butane, isobutane, and natural gasoline.

Direct chemical, consumer, and export consumption of NGLs is included for a baseline year. Location of propylene and ethylene production is included, along with their primary chemical demand locations.

Figure 6-4: Overview of NGL industry components to be included in the model.



6.3.1 Natural Gas Liquids Supply

Natural gas liquids are supplied from natural gas processing plants, imports, and refineries. Supply from processing plants (y-grade, a raw mix of all NGL components) is approximated based on nameplate capacity of the plant and the magnitude of y-grade production/average y-grade composition for the EIA refining district in which the plant is located. Import supplies are grouped into global regions. Supply from refineries is approximated based on size of the refinery and the magnitude of net C3 production in each EIA refining district.

6.3.2 Midstream Infrastructure

6.3.2.1 Purity and Y-Grade Storage

Using the N-ABLE framework, it is difficult to design enterprise-firms that only store materials. Plants must operate using a manufacturing technology, but a storage technology with no material transformations means that there is no incentive for the enterprise to exchange goods with anyone but itself once inventories are full. For storage facilities that handle multiple purity products, the storage location can usually be used for different products at different times. Therefore, allocating capacity to each potential commodity and incorporating turnover costs and timeframes is a complicated optimization problem that each storage firm must run continuously. The major difficulty is that future prices are unknown. Production decisions are made on daily time steps and storage facilities have no inherent knowledge of when commodity prices might rise which would ordinarily give them an incentive to hold supply until prices rise (i.e. propane demand is stored during low demand times in anticipation of higher prices during the winter).

Local propane storage (marketers and distributers) plays an important role in connecting national storage hubs to local demand. If propane marketers and distributors are not included in the model, propane demand will be satisfied faster than in reality, because state-wide demand can be satisfied directly from wholesalers, without having to wait for inventory to pass through retailers. If propane demand is represented at the state level, propane distribution details within the state may be ignored. A more rigorous understanding of propane distribution with spatially resolved demand to the county or city level requires development of marketer and distributor agents.

6.3.2.2 Fractionators and Butane Isomerization

Fractionators can typically receive y-grade NGL of any composition. Each batch that is fractionated will provide a different distribution of products based on exact composition of the feed. A fractionator's buying agent must optimize the feedslate purchased based on a desired product distribution that maximizes profit. Capacity is usually reported in volume of input processed, whereas the default capacity constraint in N-ABLE is capacity for production of the main product.

When calculating fractionation yield for each region's raw mix using EIA data for Natural Gas Plant Field Production,[1] it is necessary to correct the reported butane amounts. EIA's calculation for NGL field production from natural gas plants also includes merchant butane isomerization operations. Since this model will incorporate merchant isomerization units as separate agents, the field production of NGLs must be corrected from EIA's data to show true field production based on capacity and operating rate of units in each region for which the fractionation yield is calculated.

No public data is available for refinery isomerization unit input, so only merchant isomerization plants are included. Refinery-based isomerization unit demand for n-butane is included in aggregate refinery/blender demand for C4s and is treated as an end consumption node.

6.3.3 Hydrocarbon Gas Liquids Consumption

Ethane is used almost entirely for ethylene production,[29] so ethylene crackers are the only chemical demand for ethane included in the model. Cracking yields vary by feedstock, so each potential combination of feedstocks is given its own technology for agents to produce.

In the model, ethylene demand includes facilities that produce high density polyethylene (HDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE), ethylene dichloride (EDC), ethylene oxide, linear alpha-olefins (LAO), ethyl benzene, and vinyl acetate (VAM). The ethylene consumed by these processes represents 96.8% of total ethylene consumption in the U.S. in 2014.[30]

Chemical demand for propane is almost entirely for ethylene and propylene production,[31] so those are the only two chemical uses for propane in this model. The main products manufactured from propylene are polypropylene (PP), propylene oxide, acrylonitrile, cumene, acrylic acid, butanols, 2-ethyl hexanol, and isopropanol. These eight products represent 91.4% of propylene chemical consumption.[32]

6.3.4 Transportation

The transport network is composed of y-grade NGL pipelines, purity NGL pipelines, olefin pipelines, inland waterways, rail, truck, and tanker routes. Transportation modes are assigned to each enterprise based on reasonable distance to infrastructure. Pipeline corridors are created to approximate pipeline laterals where data is not available. PADD 1 ethane take-away capacity such as the ATEX pipeline is important to include for scenarios of ethane exports.

6.3.5 Ethane Rejection

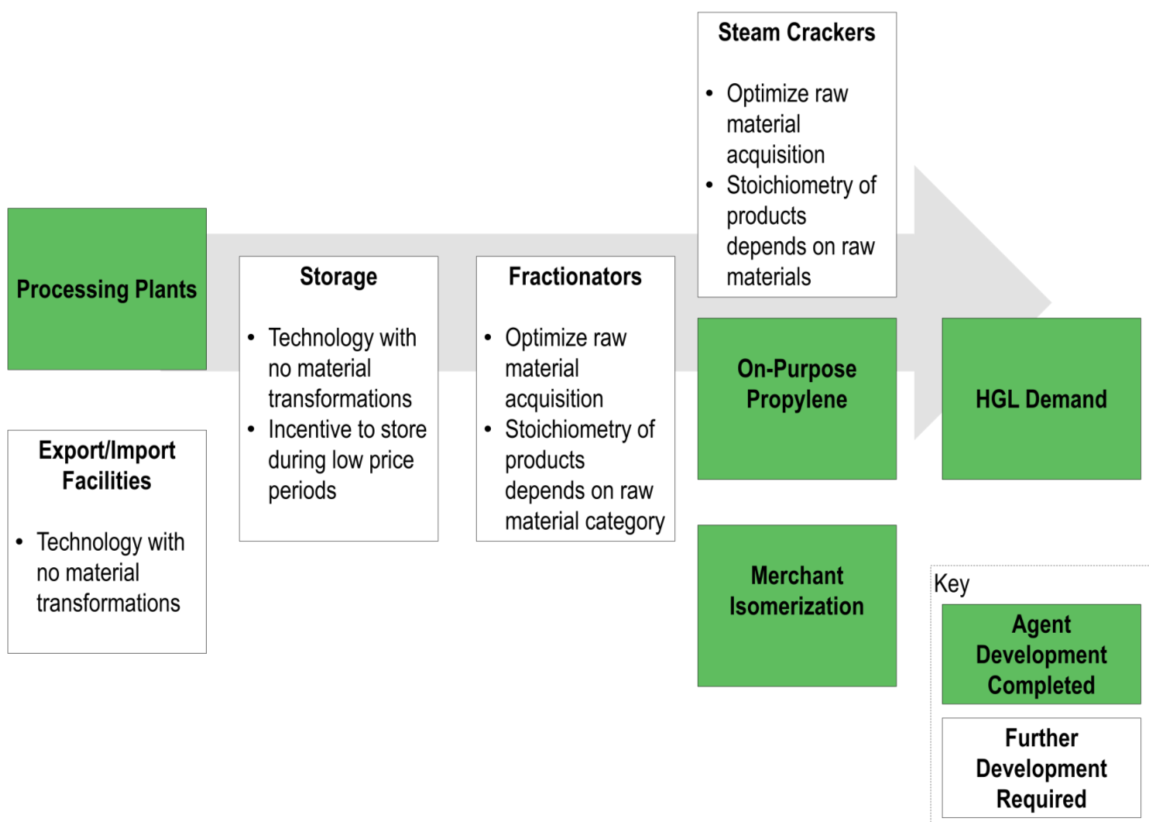
Natural gas processing plants extract liquids from a wet natural gas stream based on processing economics and desired dry natural gas properties. The amount of ethane removed can vary based on processing plant operations. Ethane rejection occurs when some ethane is not extracted as a liquid and is instead left in the natural gas stream. Estimates can vary widely, but in 2014 approximately 20% of ethane produced was rejected and sold as natural gas.[33] The role that ethane rejection plays in supply of natural gas and ethane for exports and petrochemicals is complicated and not well understood by traditional modeling approaches. Contract structures for extraction and fractionation complicate decisions made by producers which are not captured by models of optimal material flow. By approaching the problem from an enterprise-firm's operational standpoint, extraction economics for each processing plant can be explicitly modeled, leading to bottom-up calculations of ethane rejection behaviors that contribute to broader market trends.

To accurately model the decision-making behind an enterprise's decision to reject ethane, processing plants must be given control over the C2 composition of the y-grade they produce. To predict ethane rejection the total mass of *potential* y-grade production for each plant must be matched with *actual* y-grade production (which assumes some ethane may not be produced). Any difference between the potential and actual production is rejected ethane. The accuracy of estimates for potential y-grade production will be difficult to validate.

6.4 Conclusions

Many factors in the NGL industry necessitate development of a comprehensive model to understand connections from y-grade production to the wide range of end uses for each NGL component. Development of an agent-based model of the NGL industry will be able to accurately reflect operational decisions by firms that are not typical of traditional refineries or chemical plants. Specific agent behavior needs to be designed for storage, fractionation, and steam cracker operations. The current stage of development of agent categories is shown in Figure 6-5. The model can be used to fulfill the Administration's recommendations presented in the QER and understand the extent of changes occurring within the industry and the resulting impacts on system operations and market development in the United States.

Figure 6-5: Key steps required to complete a working prototype model of the NGL industry.



6.5 References

1. U.S. Energy Information Administration (EIA), *U.S. Natural Gas Plant Field Production*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbblpd_m.htm (accessed August 24, 2015).
2. U.S. Energy Information Administration (EIA), *Hydrocarbon Gas Liquids (HGL): Recent Market Trends and Issues*, November 2014, http://www.eia.gov/analysis/hgl/pdf/hgl.pdf (accessed August 25, 2015).
3. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Monthly-Thousand Barrels per Day*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_r10_mbblpd_m.htm (accessed September 30, 2015).
4. U.S. Energy Information Administration (EIA), *Today in Energy: High value of liquids drives U.S. producers to target wet natural gas resources.* May 8, 2014, http://www.eia.gov/todayinenergy/detail.cfm?id=16191 (accessed August 25, 2015).
5. The White House, Office of the Press Secretary, *Presidential Memorandum – Establishing a Quadrennial Energy Review*, https://www.whitehouse.gov/the-press-office/2014/01/09/presidential-memorandum-establishing-quadrennial-energy-review (accessed February 25, 2016).
6. U.S. Department of Energy, The Quadrennial Energy Review (QER). http://energy.gov/epsa/quadrennial-energy-review-qer (accessed February 22, 2016).
7. U.S. Energy Information Administration (EIA), *Exports (Monthly-Thousand Barrels per Day)*, http://www.eia.gov/dnav/pet/pet_move_exp_dc_NUS-Z00_mbblpd_m.htm (accessed August 25, 2015).
8. RBN Energy, *It's Not Supposed to Be That Way – Part 1.* Drill Down Report, June 2015.
9. Poten & Partners Ltd., *U.S. Ethane Export – Activity, Challenges and Outlook.* Platts 4th NGLs Conference, September 2014.
10. Van Hull, K. *NGLs and Gas – Pricing, Supply and Demand: An Overview of Current Conditions*, RBN Energy, 8th Annual Midstream Summit, February 19, 2014.
11. RBN Energy, Midstream Infrastructure Database Interface, accessed February 22, 2016.
12. INTEK, Inc. *United States Fuel Resiliency Part II: U.S. Fuels Supply Infrastructure Vulnerability to Natural and Physical Threats*, prepared for Office of Energy Policy and Systems Analysis, U.S. Department of Energy, September 2014.
13. INTEK, Inc. *United States Fuel Resiliency Part III: U.S. Fuels Supply Infrastructure Vulnerabilities and Resiliency*, prepared for Office of Energy Policy and Systems Analysis, U.S. Department of Energy, September 2014.

14. ICF International, *Impact of the Cochin Pipeline Reversal on Consumer Propane Markets in the Midwest*, August 2014, presented by Propane Education & Research Council.

15. U.S. Energy Information Administration (EIA), *Weekly Supply Estimates, Stocks – Propane/Propylene*, https://www.eia.gov/dnav/pet/pet_sum_sndw_a_EPLLPZ_sae_mbbl_w.htm (accessed February 23, 2016).

16. U.S. Department of Energy, The Quadrennial Energy Review (QER). Page 2-38, http://energy.gov/epsa/quadrennial-energy-review-qer (accessed February 22, 2016).

17. U.S. Department of Energy, The Quadrennial Energy Review (QER). Page 6-13, http://energy.gov/epsa/quadrennial-energy-review-qer (accessed February 22, 2016).

18. Pemex, *Statistical Yearbook 2014*, http://www.pemex.com/en/investors/publications/Anuario%20Estadstico%20Archivos/2014_full.pdf (accessed February 22, 2016).

19. Pemex, *Proceso de gas y fraccionamiento de liquidos*, http://www.pemex.com/ri/Publicaciones/Indicadores%20Petroleros/eprocesogas_esp.pdf (accessed February 22, 2016).

20. Pemex, *Volumen de las ventas internas de productos petroliferos y gas natural*, http://www.pemex.com/ri/Publicaciones/Indicadores%20Petroleros/evolumenventas_esp.pdf (accessed February 22, 2016).

21. Pemex, *Volumen de las importaciones de productos petroliferos, gas natural y petroquimicos*, http://www.pemex.com/ri/Publicaciones/Indicadores%20Petroleros/eimporpetro_esp.pdf (accessed February 22, 2016).

22. Carr, H. *Enciende Mi Fuego (Light My Fire) – Moving U.S. LPG to Mexican Consumers*, RBN Energy, August 27, 2015.

23. Fielden, S. *Enciende Mi Fuego (Light My Fire) – LPG Pipelines To and Through Mexico*. RBN Energy, September 29, 2015.

24. Vaughan, V. NuStar, Pemex Plan pipeline project to Northern Mexico, *FuelFix*, October 15, 2014 http://fuelfix.com/blog/2014/10/15/nustar-pemex-plan-pipeline-project-to-northern-mexico/ (accessed February 22, 2016).

25. Sibaja, A. M. *A turning point: defining the future of midstream and downstream activities.* PEMEX Investor Day London, October 29, 2014. http://www.pemex.com/ri/herramientas/pemexday/PemexDay/4_PEMEX%20Day%20London_IT_2014.pdf (accessed February 22, 2016).

26. Carr, H. *Enciende Mi Fuego (Light My Fire) – Opening Up Mexico's LPG Market*, RBN Energy, October 27, 2015.

27. RBN Energy, *Next to You: A Transformation in Propane Markets*, Drill Down Report, October 6, 2015.

28. Brooks, R. Modeling the North American Market for Natural Gas Liquids. *United States Association for Energy Economics Dialogue*, 2013, 21 (*3*).

29. IHS Chemical, *Chemical Economics Handbook: Ethane*, May 2015.

30. IHS Chemical, *Chemical Economics Handbook: Ethylene*.

31. IHS Chemical, *Chemical Economics Handbook: Propane*, October 2012.

32. IHS Chemical, *Chemical Economics Handbook: Propylene.*

33. RBN Energy, *Tailgate Blues: NGL Markets and Natural Gas Processing Economics*, Drill Down Report, August 2014.

Chapter 7: Conclusions and Recommendations

Production of natural gas and natural gas liquids (NGLs) in the United States has increased dramatically since 2005. As raw materials for chemical production, the increased availability, at low cost, of these materials has the potential to influence the structure of the U.S. chemical manufacturing industry. The introduction of new technologies based on these light feedstocks will have complicated effects across many supply chains. The increase in NGL exports has also changed NGL availability for consumers and added an additional layer of complexity for domestic manufacturers.

In this work, two modeling techniques have been used to quantify adaptations in the structure of the industry and identify new possibilities for manufacturing. A network model of the 2012 U.S. chemical manufacturing industry was built to represent material flows between technologies. The network model was used to explore production cost changes, consequences of introducing new technologies, and life-cycle assessments. Agent-based models were developed to represent individual plants and provide a more detailed understanding of market operations for specific commodities.

The network model of the 2012 chemical manufacturing industry represents 873 technologies and 283 different chemicals. A novel solution algorithm was developed to calculate production cost impacts due to feedstock supply and price changes. Many materials, ranging from ammonia and other large volume chemicals to specialty plastics and resins, are impacted by changes in natural gas and NGL price. Throughout a variety of simulations, it was found that:

- The production costs for 32 chemicals are affected by a change in natural gas price, both as a utility and as a raw material.

- The production costs for 65 chemicals are affected by a change in NGL prices.
- As the industry structure adapts to changes in natural gas and NGL price, acetaldehyde is a potential bottleneck intermediate.
- Production cost changes are not uniform across supply chains, are not linearly related to raw material price fluctuations, and are not symmetric with increasing and decreasing raw material prices.
- Raw material price more than total supply availability will influence the structure of the industry.
- Changes to overall energy and water use in the industry are predicted to be small based on the pricing scenarios in this work.

Due to the interconnected material flows throughout many parts of the chemical manufacturing industry, introducing new technologies can potentially change the use of many related processes throughout the entire system. The network model was used to analyze the effect of new technologies on the industry's structure. As a case study, a new methane-to-aromatics process with selectivity of 48% benzene, 11% naphthalene, and 0% toluene was introduced to the industry. For this methane-to-aromatics process:

- The initial acceptance of the new process as part of the optimal solution occurs for the niche naphthalene market and only begins capturing benzene market share at process costs less than $3.60/gallon benzene.
- Ancillary effects of this new process include changes to demand or manufacturing technologies for phthalic anhydride, maleic anhydride, and phenol. Eighty chemicals experience changes in shadow prices when the new process is introduced, even though their production technologies do not change.

- Of the potential aromatics that could be produced from this process based on catalyst and system design, benzene should be targeted before toluene.

The network model was also applied to a consequential life cycle assessment of utility use in the chemical industry. The model is able to quantify physical flows of indirectly affected processes as ethylene cracker feedstocks shift:

- Thirty eight processes and 30 main products change utilization levels and technologies as ethylene feedstocks shift from heavy to light. The variations in ancillary processes lead to changes in industry-wide energy and water use that are different than utility changes in only the ethylene process.
- Using the model for a consequential life cycle assessment accounts for more utility changes than are apparent when conducting an attributional life cycle assessment.

Access to abundant, low cost raw materials in new locations of the county may enable manufacturing in greenfield areas. As the manufacturing system in the U.S. moves towards a more distributed structure, an important first step is evaluating the potential for chemical production in new basins. A framework was developed to select optimal materials for manufacture in the San Juan Basin (Four Corners) and agent-based models were used to determine potential competitiveness and target markets. Major findings for the San Juan Basin in New Mexico include:

- Chemical production should focus on final end products instead of intermediates.
- Of the three chemicals studied, urea and polypropylene plants in the Four Corners have the potential to fully utilize world-scale capacity, while

propylene production in the Four Corners can only supply one domestic customer.

- The addition of rail transport for product shipment from the Four Corners to Gallup, NM does not have a large impact on potential customers or total sales assuming 2013 market prices.
- The use of methane as a feedstock for polypropylene production provides considerable price advantage compared to domestic competitors and allows for potential sales throughout the western U.S. and the Pacific export market.

Many factors in the NGL industry necessitate development of a comprehensive model to understand connections from y-grade production to the wide range of end uses for each NGL component. An integrated agent-based model of the NGL industry can be used to:

- Understand the interplay between increased exports, increasing chemical demand, and consumer uses of NGLs.
- Assess the resiliency of the NGL industry to natural and human threats, including the impact of NGL supply disruptions on chemical manufacturing.
- Direct efficient development of cross-border infrastructure as the LPG industry in Mexico evolves.

Recommendations for modeling the NGL industry include:

- Once a completed model of the NGL industry is established, perform sensitivity analyses to determine which segments of the model need the highest degrees of accuracy.

- To the extent allowed by data, and over time scales consistent with the industry's ability to transform processing plants, do a performance evaluation of model predictions to determine what features the model is able to capture.
- Integrate the U.S. model with world models of natural gas and NGLs to assess the potential importance of exports and imports, including the role of ethane rejection in natural gas supplies and exports. Begin by integrating the model with LPG infrastructure in Mexico.

The two techniques presented in this work to model the chemical industry provide complimentary approaches to understand impacts of the industry's evolution. The network model was used to analyze technology development and to quantify trends in the industry based on material flows throughout supply chains. Agent-based modeling was used to simulate individual chemical markets and to determine the viability of emerging markets. The analyses completed in this work have begun to identify critical developments during this period of unprecedented expansion of the chemical manufacturing industry in the United States.

Appendix A: Chemical Industry Model Methodology

Supporting Information for Chapter 3

A.1 Chemicals Included in the Model

Mass balances are computed for 884 materials that are involved in 873 processes utilizing 283 unique products. The unique products from each process are shown in Table A-1; 141 of those unique products are identified as final end products and their demand values for the baseline model year, 2012, are presented in Table A-3. The processes chosen to include in the model are selected out of those available from the IHS 2012 Process Economics Program Yearbook.

Table A-1: Chemicals included in the model.

1,4-Butanediol	Methyl acrylate
1-Octene	Methyl chloride
2-Ethyl hexanol	Methyl ethyl ketone
3-Picoline	Methyl formate
ABS resin	Methyl isobutyl ketone
Acetaldehyde	Methyl methacrylate
Acetic acid	Methyl t-butyl ether
Acetic anhydride	Methylene diphenylene isocyanate
Acetone	Methylene diphenylene isocyanate, hydrogenated
Acetylene	Methylene diphenyleneisocyanate and PMPPI
Acrolein	Monoammonium phosphate
Acrylamide	Naphtha
Acrylic acid copolymer, superabsorbent	Naphtha, heavy
Acrylic acid ester grade	Naphtha, light
Acrylic acid glacial	n-Butane

Table A-1, cont.

Acrylonitrile	n-Butanol
Adipic acid	n-Butylacrylate
Alachlor	n-Butylamine
Allyl alcohol	n-Butylene
Allyl chloride	n-Butyraldehyde
Ammonia	Nitric acid 60%
Ammonium nitrate fertilizer	Nitric acid, conc
Aniline	Nitrile barrier resin
Anthraquinone	Nitrobenzene
Benomyl	Nitrogen
Benzene	n-Methyl-2-pyrrolidone
Benzoic acid	n-Pentane
Biodiesel	Nylon salt, 63% soln
Biosynfuel	Nylon salt, solid
Bisphenol A	Nylon-1,1 chips
Bisphenol A pc grade	Nylon-4,6
Butadiene	Nylon-6 chips
Butylated hydroxytoluene	Nylon-6 melt
Caprolactam	Nylon-6,12 chips
Carbofuran	Nylon-6,6 chips
Carbon black	Nylon-6,6 resin
Carbon dioxide	Oxygen
Carbon disulfide	PBT pellets
Carbon monoxide	PBT pellets (30% glass filled)
Carbon tetrachloride	PBT pellets (IV=0.85)
Caustic soda 50%	PBT pellets (IV>1.1)
Chlorine	Peracetic acid
Chlorobenzene	Permethrin
Chloroprene	PET pellets (30% glass filled)
Coke	PET pellets (IV=0.6)
Crude oil, light	PET pellets (IV=0.7)
Cumene	PET pellets (IV=0.8)
Cyanamide 50% soln	PET pellets (IV=1.04, SP grade)

Table A-1, cont.

Cyclohexane	PET pellets, glycol modified
Cyclohexanol	Petroleum resin, C5 aliphatic
Cyclohexanone	Petroleum resin, DCPD
Cyclohexanone oxime	Phenmedipham
Diammonium phosphate	Phenol
Diesel	Phosgene
Dimethyl carbonate	Phosphoric acid
Dimethyl ether	Phosphoric acid, wet
Dimethyl sulfoxide	Phosphorus pentasulfide
Dimethyl terephthalate	Phthalic anhydride
Dimethylformamide	Polyacrylamide (MW10M)
Dinitrotoluene	Polyacrylamide (MW20M)
Diphenyl carbonate	Polyacrylamide (MW7-15M)
Diphenyl isophthalate	Polyacrylamide (MW7M)
Diphenyl terephthalate	Polyacrylate latex
Diphenylamine	Polyacrylate pellets
Elastomer, fluorocarbon	Polyacrylate resin
Elastomer, copolyester ether	Polyacrylate resin, superabsorbent
Elastomer, epichlorohydrin	Polybutadiene
Elastomer, polyamide	Polybutene-1
Elastomer, polyolefin	Polycarbonate
Elastomer, polyurethane	Polycarbonate, polyester
EPDM rubber	Polyester, unsaturated
Epichlorohydrin	Polyethylene HD
Epoxy, HMW, DGEBPA & BPA	Polyethylene HDBM
Epoxy, liquid, DGEBPA	Polyethylene LD
Epoxy, liquid, TGMDA	Polyethylene LLD
Epoxy, novolac resin, ECN	Polyethylene LLD, BM
Epoxy, novolac resin, EPN	Polyethylene terephthalate
Epoxy, solid, DGEBPA & BPA	Polyethylene very LD
Epoxy, solid, TGBAPPB	Polymethylmethacrylate
Epoxy, solid, TGETPE	Polypropylene
Epoxy, solid, TGPAP	Polypropylene block copolymer

Table A-1, cont.

Ethane	Polypropylene copolymer
Ethanol	Polypropylene ICP
Ethyl acetate	Polypropylene, syndiotactic
Ethyl acrylate	Polystyrene, anionic
Ethyl benzene	Polystyrene, expandable
Ethyl t-butyl ether	Polystyrene, general purpose
Ethylene	Polystyrene, high impact
Ethylene carbonate	Polystyrene, syndiotactic
Ethylene dichloride	Polytetrafluoroethylene
Ethylene glycol	Polyurethane foam board
Ethylene glycol butyl ethers	Polyurethane foam slab
Ethylene glycol ethyl ethers	Polyurethane rim
Ethylene glycol t-butyl ether	Polyvinyl acetate
Ethylene oxide	Polyvinyl acetate latex
Ethylene vinyl alcohol	Polyvinyl alcohol
Ethylene/MA acid ionomer	Polyvinyl chloride
Ethylene/methyl acrylate	Polyvinyl chloride dispersion
Ethylene/VA copolymer	Polyvinyl chloride, chlorinated
Ethylene-norbornene copolymer	Propane
Ethylene-propylene copolymer	Propylene
EVOH barrier resin	Propylene carbonate
Fenvalerate	Propylene glycol
Fluorided silica alumina	Propylene glycol ethers
Formaldehyde	Propylene oxide
Formic acid 85%	Propylene polymer grade
Gas oil, atmospheric	Pseudocumene
Gasoline	p-Xylene
Gasoline alkylate	SAN resin
Gasoline isomerate	SEC-butanol
Gasoline octane propylene dimate	Sodium chlorate
Glycerin	Sodium chlorite
Glyphosate IPA salt	Styrene
Heavy aromatics	Styrene-butadiene block copolymer

Table A-1, cont.

Hexamethylenediamine	Styrene-butadiene block copolymer, star block
Hexene-1	Styrene-butadiene rubber
Hydrogen	Sulfur
Hydrogen cyanide	Sulfuric acid
Hydrogen peroxide	Synthesis gas (2:1)
Hydroquinone	Synthesis gas (3:1)
Hydroxylammonium sulfate	t-Amyl methyl ether
Isobutane	t-Butanol, gasoline grade
Isobutanol	Terephthalic acid
Isobutylene	Terephthaloyl chloride
Isobutylene, high purity	Tetrahydrofuran
Isooctane	Toluene
Isopentane	Toluene diisocyanate
Isophthalic acid	TPU-ABS blends
Isoprene	TPU-PC blends
Isopropanol	Trifluralin
Isopropanol amines	Urea, agricultural grade
Isopropyl chloride	Urea-formaldehyde
Kerosene	Urea-formaldehyde syrup
Kerosene, jet fuel	VDC/EA/MA copolymer
Malathion	VDC/VCM suspension copolymer
Maleic anhydride	Vinyl acetate
Mancozeb	Vinyl acetate/ethylene copolymer
Melamine	Vinyl chloride
Methacrylate-butadiene-styrene	Vinyl chloride/acetate
Methane	Vinylidene chloride
Methanol	Xanthan gum
Methomyl	

A.2 SUPPLY DATA

Supply data is only necessary for the three primary raw material categories (natural gas, natural gas liquids, and crude oil).

A.2.1 Natural Gas

Industrial natural gas consumption was 7,223,834,975 thousand cubic feet in 2012.[1] Using a density of 0.042001 lb/cubic foot,[2] the supply of natural gas was 303 × 10^9 lb in 2012. The distribution of components in natural gas is 93.07% methane, 3.21% ethane, 0.59% propane (higher hydrocarbons and non-hydrocarbons are ignored in the mass balance).[3]

A.2.2 Natural Gas Liquids

Natural gas plant liquid data from EIA gives total production in 2012 for NGL constituents in barrels and was converted to pounds.[4] The 2012 distribution of components in NGLs are shown in Table A-2.

Table A-2: 2012 NGL component distribution.

Product	Barrels in 2012	10^6 Pounds in 2012	Percent Composition
Ethane	356,592,000	44,496	30.43%
Propane	260,704,000	46,426	31.75%
N-Butane	65,555,000	13,420	9.18%
Isobutane	82,453,000	16,269	11.12%
N-Pentane	58,001,000	12,816	8.76%
Isopentane	58,001,000	12,816	8.76%
Total		**146,243**	**100.00%**

A.2.3 Crude Oil

Total crude oil refinery input for all U.S. refineries in 2012 was 5,489,516 thousand barrels,[5] with a weighted average API Gravity of 31.0.[6] This API Gravity gives a density of 7.267 lb/gal which leads to 1,675 × 10^9 lb crude oil supply in 2012. The crude yield is approximated for the baseline year (2012) using EIA refinery yield data.[7]

A.3 Demand Data

Comprehensive production data for all synthetic chemicals is not available in standard publications. Some current production figures were obtained from the American Chemistry Council (ACC) Business of Chemistry annual data[8] and from Chemical & Engineering News.[9] For chemicals not included in those publications, production levels from previous years were scaled to 2012 levels using industrial production indices (ACC Business of Chemistry from Federal Reserve Board indices) using the following formula:

$$Production_{2012} = \left(\frac{Production_{2001}}{Index_{2001}/100} \right) \cdot \frac{Index_{2012}}{100}$$

where $Production_i$ is the production level in year i, and $Index_j$ is the production index in year j. The methodology used to determine demand for each chemical is shown in Table A-3. Chemicals are only included as a constraint in the model if a value for 2012 production is available.

Table A-3: Demand data and source for final end products. Sources are listed below the table.

Product Name	2012 Production (lb)	Source
ABS resin	1,158,280,502	a
Acrolein	ND	
Alachlor	ND	
Ammonia	29,541,908,000	b
Ammonium nitrate fertilizer	11,865,138,100	a
Anthraquinone	10,000,000	c
Benomyl	ND	
Biodiesel	6,914,207,000	d
Carbofuran	1,000,000	c
Acrylic acid copolymer, SAP	ND	
Diammonium Phosphate	18,707,518,119	a
Diesel	379,696,258,895	e
Dimethyl Ether	ND	
Diphenyl isophthalate	617,937,853	f
Diphenyl terephthalate	ND	
Diphenylamine	ND	
Copolyester-ether elastomer	121,081,081	g
Epichlorohydrin elastomer	ND	
Fluorocarbon elastomer	ND	
Polyamide elastomer	ND	
Polyolefin Elastomer	298,523,490	g
EPDM rubber	549,521,830	g
Epoxy novolac resin, ECN	545,000,000	h
Epoxy novolac resin, EPN		
Epoxy, HMW, DGEBPA & BPA		
Epoxy, liquid DGEBPA		
Epoxy, liquid TGMDA		
Epoxy, solid DGEBPA & BPA		
Epoxy, solid TGBAPPB		
Epoxy, solid TGETPE		
Epoxy, solid TGPAP		
Ethylene glycol butyl ethers	ND	
Ethylene glycol ethyl ethers	ND	
Ethylene glycol t-butyl ether	ND	
Ethylene vinyl alcohol	ND	

Table A-3, cont.

Product Name	2012 Production (lb)	Source
Ethylene-norbornene copolymer	ND	
Ethylene-propylene copolymer	ND	
Ethylene/MA acid ionomer	ND	
Ethylene/Methyl acrylate	ND	
Ethylene/VA copolymer	ND	
EVOH barrier resin	625,317,568	g
Fenvalerate	ND	
Gasoline	851,967,463	e
Isooctane	ND	
Kerosene, jet fuel	152,636,045,898	e
Polyethylene, LD	6,885,028,260	i
Polyethylene, LLD	13,443,772,760	i
Malathion	ND	
Mancozeb	ND	
Methylene diphenylene isocyanate & PMPPI	ND	
Melamine	ND	
Polymethylmethacrylate	345,167,785	g
Methacrylate-butadiene-styrene	ND	
Methomyl	ND	
Methylene diphenylene isocyanate, hydrogenated	ND	
Methylene diphenylene isocyanate	1,813,540,091	a
Monoammonium phosphate	10,299,984,640	j
Methyl t-butyl ether	23,883,851,444	a
Nitrile barrier resin	625,317,568	g
Nylon 6 chips		
Nylon 11 chips		
Nylon 4,6		
Nylon 6 melt		
Nylon 6,12	1,238,996,440	j
Nylon 6,6 resin		
Nylon 6,6 chips		
Nylon salt (63% soln)		
Nylon salt, solid		
Permethrin	ND	
Phenmedipham	ND	
PET pellets, glycol modified	ND	

Table A-3, cont.

Product Name	2012 Production (lb)	Source
Polyacrylamide (MW: 10M)	186,577,181	g
Polyacrylamide (MW: 20M)		
Polyacrylamide (MW: 7-15M)		
Polyacrylamide (MW: 7M)		
Polyacrylate latex	204,906,445	g
Polyacrylate pellets	754,428,274	g
Polyacrylate resin	ND	
Polyacrylate resin, SAP	ND	
Polybutadiene	1,288,313,550	a
Polybutene-1	699,664,430	g
PBT pellets (IV=0.85)	3,042,142,163	a
PBT pellets (IV>1.1)		
PBT pellets		
PBT pellets (30% GF)		
Polycarbonate	1,474,002,281	a
Polycarbonate, polyester	ND	
Polyester, unsaturated	2,652,157,860	j
PET pellets (IV=0.6)	3,042,142,163	a
PET pellets (30% GF)		
PET pellets (IV=0.7)		
PET pellets (IV=0.8)		
PET pellets (IV=1.04), SP grade		
Polyethylene terephthalate		
Polyethylene, HD	17,738,372,520	i
Polyethylene, HD BM	ND	
Polyethylene, LLD BM	ND	
Polyethylene, very LD	ND	
Polypropylene block copolymer	ND	
Polypropylene	16,327,415,720	i
Polypropylene copolymer	ND	
Polypropylene ICP	ND	
Polypropylene, syndiotactic	ND	
Polystyrene, anionic	5,897,358,500	i
Polystyrene, GP		
Polystyrene, HI		
Polystyrene, syndiotactic		

Table A-3, cont.

Product Name	2012 Production (lb)	Source
Polystyrene, EXP	879,000,000	k
Polytetrafluoroethylene	ND	
Polyvinyl acetate	69,966,443	g
Polyvinyl acetate latex	536,409,396	g
Polylvinyl alcohol	223,892,617	g
Polyvinyl chloride	13,988,313,900	i
Polyvinyl chloride dispersion		
Polyvinyl chloride, chlorinated	ND	
Pseudocumene	ND	
SEC-butanol	ND	
SAN resin	177,081,081	g
Styrene-butadiene block copolymer	457,114,094	g
Styrene-butadiene block copolymer, star		
Styrene-butadiene rubber	1,836,147,816	a
t-Amyl methyl ether	ND	
TPU/ABS blends	ND	
TPU/PC blends	ND	
Trifluralin	ND	
Urea, agricultural grade	5,456,434,500	j
Urea-formaldehyde	2,736,634,265	a
Urea-formaldehyde syrup	1,893,758,389	g
Vinyl acetate/ethylene copolymer	1,156,778,523	g
Vinyl chloride/acetate copolymer	718,322,148	g
VDC/EA/MA copolymer	317,181,208	g
VDC/VCM suspension copolymer	475,771,812	g
Xanthan gum	ND	
Polyurethane foam slab	2,520,068,415	a
Elastomer, polyurethane		
Polyurethane foam board		
Polyurethane rim		

ND: No Data; (a) 2001 production data[8] extrapolated to 2012; (b) 2012 production value;[10] (c) 2012 approximate production value;[11] (d) 2012 production value,[12] using the density of diesel for conversion to pounds; (e) 2012 net production;[13] (f) data for baseline year[11] scaled to 2012 using the ACC Production Index;[8] (g) 1996 production data[14] scaled to 2012 using the ACC Production Index;[8] (h) 2012 production value;[15] (i) 2012 production value;[8] (j) 2012 production value;[9] (k) 2012 production value[16]

A.4 Cost Calculations/Solution Procedure

Total process cost is a composite of three individual costs:

$$Total\ Cost/lb\ = Capital\ Cost/lb + Operating\ Cost/lb + Variable\ Cost/lb$$

Capital cost (per pound of product) depends on the scale of the plant, which in turn depends on the required annual amount of production. In this work, capital cost is not considered a function of process utilization. Capital costs for each process are from the 2012 IHS Process Economics Program Yearbook.

A.4.1 Operating Cost

Operating cost is determined from the capital cost according to estimates from the 2012 IHS Process Economics Program Yearbook. The methodology employed by the IHS estimates is summarized in Table A-4.

Table A-4: Methodology used to estimate operating costs in the 2012 IHS Process Economics Program Yearbook. Ranges represent variation by process type.

Operating Cost Category	Methodology Employed by IHS
Maintenance Materials	Depending on process type, 1.5-6% of battery limits, with a 60-40 split between materials and labor.
Maintenance Labor	
Operating Supplies	10-20% of Operating Labor cost
Operating Labor	Estimated based on the equipment included in the plant. The labor rate uses the national average rates in industrial chemical plants.
Control Laboratory	20-35% of Operating Labor cost
Plant Overhead	60-120% of Operating Labor + Control Laboratory + Maintenance Labor
Taxes and Insurance	Costs for fixed assets and local taxes, not including income taxes or royalties
Depreciation	10%/yr of fixed capital
General and Administrative, Sales, and Research	5-30% of sales value of the product

A.4.2 Variable Cost

Variable cost is composed of raw material cost, byproduct credits, and utility costs. Representing variable cost as a function of the materials involved, and holding utility costs constant gives:

$$C_j = Capital + Operating + Utility + \sum_{i \cap j} -a_{i,j} \cdot B_i$$

where C_j is the cost of process j per pound primary product, with $j = \{P1, P2, \ldots, P1373\}$, $a_{i,j}$ is the input-output coefficient of chemical i in process j, and B_i is the cost of chemical i. If $a_{i,j}$ is negative, then the chemical is an input material and its purchase increases C_j, if $a_{i,j}$ is positive, then the chemical is a byproduct and its sale or use decreases C_j. Changes in the production cost of i from the primary process producing i impact the byproduct value in this process, j.

A.4.3 Solution Methodology

Because of the way cost data is obtained from IHS, the cost of each chemical, B_i, is not directly included in the model. Instead, an entire process is represented with a "baseline" cost, without specifying individual material costs. The cost equation must instead deal with changes in process and chemical cost:

$$C_j = C_{j,o} + \sum_{i \cap j} -a_{i,j} \cdot \Delta B_i$$

$$\Delta B_i = B_i - B_{i,o} = \Delta C_{j,selected\ to\ produce\ i}$$

So cost is equal to the baseline cost plus the change in all input/output material costs. The change in each material cost, B, is defined as the change in cost of the process used to produce that material. Now, cost is no longer a scalar parameter because it must be calculated, while ΔB_i is calculated based on the processes that produce it.

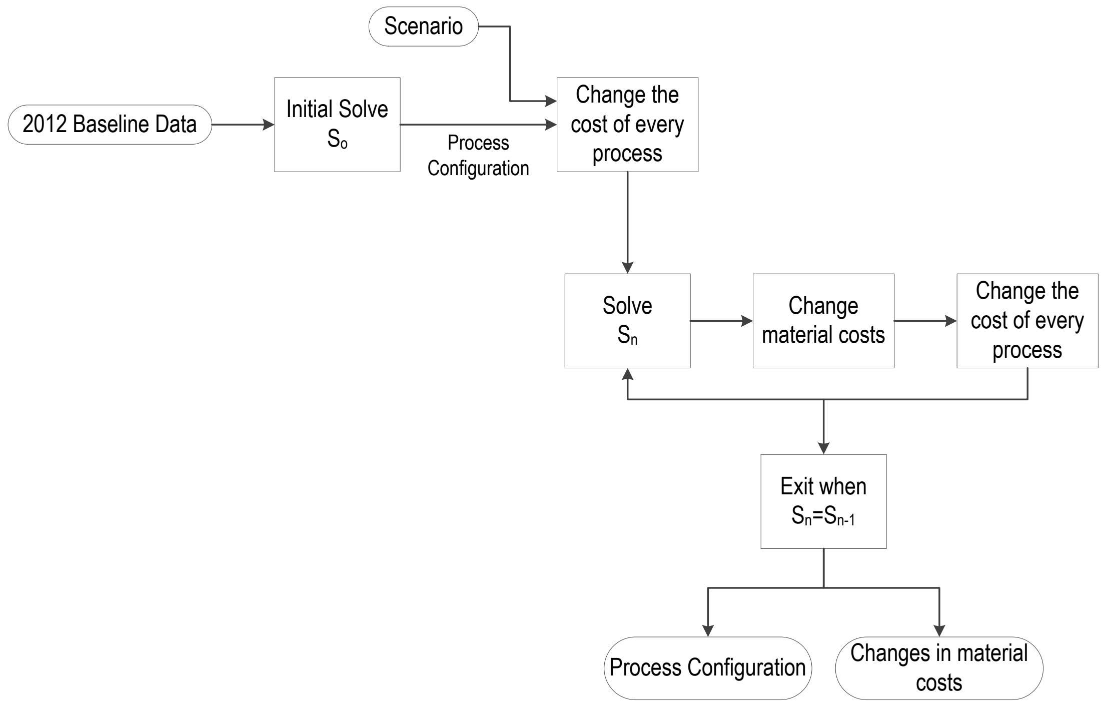
B_i is not easily defined based on the number of processes that can produce any given chemical. The market price of a chemical is partly set by cost of a process that produces that chemical. So a change in process cost could lead to a change in price. However, multiple processes exist in the model to produce most chemicals (for example, 28 processes in the model produce ethylene as the main product). So, the cost change of one single process will not always lead to a market price change for each chemical. The model must first identify the main product for every process and then choose which of those processes will affect the price of a given primary product. This is accomplished by setting initial values of B to enable an initial solve. The processes selected by the initial solve are used to determine the value of B. Subsequent solve iterations allow each solution to re-evaluate which processes were chosen and determine if the value of each chemical should be altered. The value of B must be chosen based on which process was chosen for the solution (has a non-zero value). In this algorithm, the process that produces the largest volume of each material dictates the final market price for that material.

As an example of the solution procedure, consider the two processes available to make ethyl acetate: Process 1 is the direct addition of ethylene and acetic acid, and Process 2 is via ethanol dehydrogenation. The main product of both of these processes is ethyl acetate, so any change in cost of these two processes (ΔC_1 or ΔC_2) can be translated to a change in the production cost of ethyl acetate, $B_{ethyl\ acetate}$. On an initial solve, Process 1 is chosen as the only route to make ethyl acetate (because it is cheaper per pound of product, $C_1 < C_2$) and no costs have been altered, so $\Delta B_{ethyl\ acetate} = \Delta C_1 = 0$. If the cost of ethylene, $B_{ethylene}$, is raised so that $\Delta B_{ethylene} = x$, the cost of every process is recalculated, and any process that uses ethylene has a variable cost that will change. In this case, the cost of Process 1 increases because ethylene is a raw material in the process and the cost of Process 2 does not change because ethylene is not used in the process ($\Delta C_1 = -a_{ethylene,Process\ 1} \cdot x = 0.36 \cdot x,$ and $\Delta C_2 = 0$). The model is solved again, with the new values of $C_1 = C_{1,o} + \Delta C_1 = C_{1,o} + 0.36x$ and $C_2 = C_{2,o} + \Delta C_2 = C_{2,o}$. If C_1 is chosen again by the new solve, the price of the main product of C_1 will then be increased by ΔC_1, so $\Delta B_{ethyl\ acetate} = \Delta C_1$. If C_2 is chosen, the price of the main product of C_2 will be increased by ΔC_2, so $\Delta B_{ethyl\ acetate} = \Delta C_2 = 0$. If C_1 and C_2 are chosen in some combination, the process that produces the most ethyl acetate is used to calculate $\Delta B_{ethyl\ acetate}$.

If C_1 is chosen, ethyl acetate cost is increased by ΔC_1. When ethyl acetate costs change, the cost of every process in the rest of the model is recalculated if ethyl acetate contributes to variable cost. The same set of calculations is carried out for any of those affected processes, to propagate the ethyl acetate cost change through all processes, and the main products of those affected processes will experience a cost change. The loop of calculating process cost changes followed by material cost changes is iterated multiple times to ensure that the chosen processes are continually updated as the optimization solution evolves. A variety of control structures are embedded in the program code to ensure that no cyclic cost calculations are introduced.

The solution procedure is iterative in order to propagate intermediate cost changes completely throughout supply chains. To minimize a bias towards the initial solution, every step of the solution loop involves a complete new solution for the industry, reflecting the extent of price propagation at that step. The loop exit condition ensures all materials have had an opportunity to experience a price or technology change and the optimal industry configuration remains unchanged from the previous solution (Figure A-1).

Figure A-1: Solution procedure for the network model with material cost propagation.



A.5 THE EFFECT OF CHANGING NATURAL GAS PRICES TO THE 2018 VALUE

As natural gas prices rise to the EIA Annual Energy Outlook projected 2018 value ($4.80/MMBtu, in 2012 dollars) from a representative 2012 price of $3.80/MMBtu, affected materials show production cost increases less than 5 cents per pound above 2012 levels, as shown in Table A-5.

Table A-5: Magnitude of production cost changes from 2012 values when methane price increases from a representative 2012 level ($3.80/MMBtu) to a projected 2018 value ($4.80/MMBtu, in 2012 dollars).

Material	Effect of Natural Gas as a Utility (¢/lb)	Effect of Methane as a Raw Material (¢/lb)	Total Impact (¢/lb)
Intermediates			
Acetylene	0.06	4.3	4.36
Acrylamide	0.00	0.51	0.51
Acrylic acid (glacial)	0.00	3.1	3.1
Acrylonitrile	0.00	0.68	0.68
Adipic acid	0.00	0.20	0.20
Ammonia	0.3	0.82	1.12
1,4-Butanediol	0.00	1.4	1.4
Carbon dioxide	0.00	0.27	0.27
Carbon monoxide	0.00	2.5	2.5
Diphenyl carbonate	0.00	0.06	0.06
Methyl methacrylate	0.00	0.54	0.54
Nitric acid (60%)	0.00	0.32	0.32
Synthesis gas (2:1)	0.04	1.5	1.54
Synthesis gas (3:1)	0.00	2.1	2.1
Tetrahydrofuran	0.00	-0.04	-0.04
Final End Products			
ABS resin	0.04	0.10	0.14
Ammonium nitrate fertilizer	0.00	0.48	0.48
Copolyester ether elastomer	0.32	0.04	0.36
Diammonium phosphate	0.02	0.23	0.25
Kerosene jet fuel	0.23	1.0	1.23
Methylene diphenylene isocyanate	0.00	1.1	1.1
Monoamonium phosphate	0.00	0.14	0.14
Nitrile barrier resin	0.00	0.48	0.48
Nylon 6,6 chips	0.00	0.13	0.13
Polyacrylamide	0.00	0.49	0.49
Polyacrylate latex	0.00	0.18	0.18

Table A-5, cont.

Material	Effect of Natural Gas as a Utility (¢/lb)	Effect of Methane as a Raw Material (¢/lb)	Total Impact (¢/lb)
Polyacrylate pellets	0.00	0.48	0.48
Polycarbonate	0.07	0.23	0.30
Polymethyl methacrylate	0.00	0.48	0.48
Polypropylene	0.00	5.0	5.0
Polystyrene (general purpose)	0.38	-0.4	-0.02
Polyurethane elastomer	0.00	0.44	0.44
SAN resin	0.04	0.13	0.17
Urea (agricultural grade)	0.00	0.85	0.85
VDC-EA-MA Copolymer	0.00	0.02	0.02

A.6 Expanded Discussion of Natural Gas Liquids Scenario Results

The materials that show an inconsistent production cost change between the two NGL scenarios (e.g., changing cost when NGL prices increase but not when they decrease) are: adipic acid, anthraquinone, benzene, butadiene, ethyl *t*-butyl ether (ETBE), ethyl benzene, maleic anhydride, polybutadiene, polyethylene terephthalate, general purpose polystyrene, p-xylene, styrene, styrene-butadiene block copolymer, and styrene-butadiene rubber. The behavior of these materials is explained below.

A.6.1 Adipic Acid

Adipic acid production cost only responds when NGL prices increase. With increasing NGL costs, the model selects a process that uses benzene as a raw material. Benzene production cost decreases in the increasing NGL cost scenario (see below for the cost movement of benzene), so the variable cost of adipic acid production decreases as NGL prices increase. A similar change is not seen when NGL costs decrease because in this scenario, benzene does not experience a change in cost, and because most of the adipic acid production in the decreasing NGL cost scenario does not use benzene as a raw material.

A.6.2 Anthraquinone

Anthraquinone only shows a cost response when NGL prices decrease. Anthraquinone production relies on butadiene as a raw material, and butadiene costs only change in the NGL price decrease scenario, leading to an increase in anthraquinone production cost (see below for the cost movement of butadiene).

A.6.3 Benzene

As NGL prices increase, production of benzene from naphtha becomes increasingly competitive (as the C3 and C4 byproducts in the naphtha based process have an increased value in this scenario). With increasing byproduct credits, the cost of benzene production decreases. As NGL prices decrease, benzene does not experience a production cost change because production is derived from catalytic reformate, rather than from naphtha, and the catalytic reformate process does not experience a cost change in any scenario. Approximately 60% of benzene production capacity in the U.S. already uses or can use catalytic reformate, while the remaining 40% uses pyrolysis gasoline, toluene disproportionation, or similar processes.[17]

The benzene production cost change is \$.096/lb in the NGL price increase scenario (Table 3-3). This magnitude of cost change is significant because the Platts Global Benzene Price Index shows a global market price of benzene between \$0.50 and \$0.59/lb in 2012.[18]

A.6.4 Butadiene

Butadiene only shows a cost change when NGL prices decrease—as NGL prices decrease, butadiene costs increases. This correctly models the movement of the butadiene market from 2008-2012: as ethane prices dropped more than 50% from 2008-2012, butadiene prices increased 9.29% over the same time period.[19] The $0.21/lb change in butadiene production cost in the NGL decrease scenario (Table 3-3) is a large portion of the U.S. spot price, which was around $1.35/lb at the beginning of 2012.[20]

The butadiene cost change occurs because butadiene is extracted from ethylene cracker C4 byproduct streams. Ethylene crackers in the U.S. have recently experienced a change in feedstock, and therefore a change in byproduct distribution. In 2008, naphtha was a significant component of the ethylene feed slate, but ethane-based steam crackers have since become the predominant process. As production costs for ethane-based plants have generally decreased over this time period, it is counter-intuitive that byproduct prices would rise. However, the C4 separation from ethane feedstocks generates less value, since isobutylene, n-butylene, isobutane, and n-butane have experienced a decrease in market price and are less plentiful in the new feedstock configuration. The overall industry cost is minimized by using an ethane-based steam cracker, but the cost of butadiene rises due to the reduction in other byproduct values.

Recovery of butadiene from C4 streams in the model industry is predicted to proceed by n-methyl-2-pyrrolidone extractive distillation as opposed to using dimethylformamide as the solvent, due to capital costs. Within the scope of NGL prices analyzed, extraction from a steam cracked C4 stream remains the optimal method of production. No other technology is introduced by the model (such as oxidative dehydrogenation, the TPC Oxo-D process, or a Catadiene process), as recovery of butadiene from an ethane-based plant remains cheaper than other on-purpose technologies.

Eighteen materials use butadiene as a raw material, and therefore as NGL prices decrease, and butadiene cost increases, these materials are subject to an increase in variable cost, even as NGL price is decreasing. Only four materials (anthraquinone, polybutadiene, styrene-butadiene block co-polymer, and styrene-butadiene rubber) show an increase in cost consistent with the increasing cost of butadiene as a raw material. The other 14 materials that rely on butadiene do not show this response when ethane price decreases because the impact of butadiene on the variable cost is small enough to not affect the net direction of change.

A.6.5 Ethyl *t*-Butyl Ether

ETBE cost is very dependent on the magnitude of the price difference between butanes (byproduct of the process) and butylenes (raw material for the process). As NGL prices increase, ETBE production costs decrease because of a large butanes byproduct credit. As NGL prices decrease, ETBE production costs still decrease (with less magnitude) because the butylenes raw material cost decrease is greater than the loss of byproduct credit.

A.6.6 Styrene and Polystyrene (General Purpose)

Both styrene and polystyrene production costs decrease whether NGL prices increase or decrease, indicating that the magnitude change in benzene cost impacts the styrene or polystyrene production cost more than ethane.

A.6.7 Styrene-Butadiene Block Co-Polymer or Rubber

Styrene-butadiene rubber and block co-polymer production costs are driven more by butadiene costs than butylated hydroxytoluene and styrene, because the net effect of a butadiene cost increase outweighs a decrease in butylated hydroxytoluene cost.

A.6.8 *p*-Xylene

Xylenes can be extracted from heavy reformate by crystallization or as a product of toluene disproportionation. Currently, the reformate pathway is cheaper per pound of p-xylene produced. This is reflected in the xylene industry in the U.S., as approximately 80% of plant capacity uses catalytic reformate feedstocks.[17] Isobutylene is a byproduct of aromatic naphtha production from olefins, so a decrease in isobutylene cost leads to an increase in aromatic naphtha cost, which is the feedstock used to produce xylenes by crystallization. If isobutylene price decreases by 18% or more (from a 2012 benchmark of 68.64 ¢/lb),[19] the model shows that use of catalytic reformate feedstocks will no longer be more competitive than toluene disproportionation.

A.6.9 Ethyl Benzene, Maleic Anhydride, Polybutadiene, Polyethylene Terephthalate

Ethyl benzene and maleic anhydride production costs follow benzene costs, and polybutadiene only follows butadiene costs, so those materials only respond in one of the scenarios. Polyethylene terephthalate follows only p-xylene cost changes, which explains why it also only responds in the scenario where p-xylene costs change.

A.6.10 Butene-1

The model shows that as NGL prices decrease, butene-1 from ethylene oligomerization becomes increasingly more competitive compared to distillation from raffinate-2 streams (MTBE plant raffinate). Competitiveness depends primarily on ethylene, as ethylene prices must stay below 59.61 ¢/lb ($1314/tonne), all else constant, for butene-1 from ethylene oligomerization to be cheaper per pound of product than distillation from raffinate-2 streams. Forty-nine percent of current butene-1 capacity uses the ethylene route.[17]

A.6.11 Propylene

The model does not show a change in propylene cost when natural gas or NGL prices are altered. This is representative of the propylene industry's structure, as more than 55% of production capacity is from refining operations, while only 25% involves ethane or propane pathways (the remaining 20% of capacity can use either ethylene or refining pathways to produce propylene).[17] However, the model does show a change in polypropylene cost when methane prices increase (Table 3-1) because the selected polypropylene production process is from natural gas to methanol to propylene to polypropylene, instead of from refinery derived propylene (NGL prices affect polypropylene due to changing C4-C6 byproduct values). The model indicates that polypropylene from methanol is competitive with the refinery route from propylene. Even with natural gas prices increasing towards predicted 2040 levels, the cost of polypropylene from natural gas (methanol to propylene (MTP), to polypropylene) is lower than most other polypropylene technologies (slurry loop, circulating reactor, etc., each using propylene from cracking or refining byproduct), although significantly more cooling water and process steam is required. Polypropylene by an MTP route with the 2040 natural gas price experiences a production cost increase of $0.18/lb (Table 3-1) and is still the optimal technology(the Platts Global Polypropylene Price Index ranged between approximately $0.60 and $0.77/lb in 2012.[21]

Reflective of the need for on-purpose propylene, a number of plants have been announced in the U.S. While most of the announced projects use a propane dehydrogenation route, BASF has begun evaluating an MTP facility on the Gulf Coast.[22] The results of this model confirm MTP's competitiveness on a production cost basis. Even with increasing natural gas prices, the model predicts that MTP technology is the optimal use of all materials in the supply chain to produce polypropylene for the objective function to minimize production cost.

A.7 References

1. U.S. Energy Information Administration (EIA), *Natural Gas Annual Respondent Query System*. http://www.eia.gov/cfapps/ngqs/ngqs.cfm?f_report=RP1&f_sortby=&f_items=&f_year_start=&f_year_end=&f_show_compid=&f_fullscreen=.
2. National Energy Technology Laboratory, *Life Cycle Greenhouse Gas Inventory of Natural Gas Extraction , Delivery and Electricity Production*, DOE/NETL-2011-1522, 2011.
3. American Petroleum Institute, *Compendium of greenhouse gas emissions methodologies for the oil and natural gas industry*, 2009.
4. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production,* http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_m.htm.
5. U.S. Energy Information Administration (EIA), *Refinery & Blender Net Input*, http://www.eia.gov/dnav/pet/pet_pnp_inpt_dc_nus_mbbl_a.htm.
6. U.S. Energy Information Administration (EIA), *Crude Oil Input Qualities,* http://www.eia.gov/dnav/pet/pet_pnp_crq_dcu_nus_m.htm.
7. U.S. Energy Information Administration (EIA), *Refinery Yield*, http://www.eia.gov/dnav/pet/pet_pnp_pct_dc_nus_pct_a.htm.
8. American Chemistry Council, Business of Chemistry Annual Data, 2013.
9. Lackluster year for chemical output. *Chem. Eng. News*. 2013, 91 (*40*), http://cen.acs.org/content/dam/cen/91/26/FF_Production_2013.pdf.
10. US ammonia demand will be robust. *ICIS News*, December 26, 2012, http://www.icis.com/resources/news/2012/12/26/9625085/outlook-13-us-ammonia-demand-will-be-robust/ (accessed May 29, 2014).
11. Toxicology Data Network. http://toxnet.nlm.nih.gov/index.html.
12. U.S. Energy Information Administration (EIA), *Monthly Biodiesel Production Report*, http://www.eia.gov/biofuels/biodiesel/production/.
13. U.S. Energy Information Administration (EIA), *Weekly Refiner & Blender Net Production*, http://www.eia.gov/dnav/pet/pet_pnp_wprodrb_a_epm0f_YPT_mbblpd_w.htm.
14. Chang, D. Minimization of Production Cost and Chlorine Use in the Petrochemical Industry. Master's Thesis, University of California Los Angeles, Los Angeles, CA, 1996.
15. American Chemistry Council, *U.S. Resin Production & Sales*, http://www.americanchemistry.com/Jobs/EconomicStatistics/Plastics-Statistics/Production-and-Sales-Data-by-Resin.pdf (accessed May 29, 2014).

16. American Chemistry Council, *U.S. resins industry strengthens in 2013,* http://www.americanchemistry.com/jobs/economicstatistics/plastics-statistics/year-in-review.pdf (accessed May 29, 2014).

17. IHS Chemical, Directory of Chemical Producers, March 1, 2014. https://www.ihs.com/products/chemical-companies-producers.html (accessed January 2015).

18. Platts McGraw Hill Financial, *Platts Global Benzene Price Index*, http://www.platts.com/news-feature/2012/pgpi/benzene (accessed December 1, 2014).

19. IHS Chemical, Process Economics Program Yearbook, 2012, http://chemical.ihs.com/PEP/yearbook.htm (accessed January 2015).

20. Potter, D.; Choo, C.; Johnson, N. Butadiene: Defying the Odds to Hit New Heights, 2012. *Platts Special Report: Petrochemicals*. http://www.platts.com/IM.Platts.Content/InsightAnalysis/IndustrySolutionPapers/PetchemsButadieneWP.pdf (accessed December 1, 2014).

21. Platts McGraw Hill Financial, *Platts Global Polypropylene Price Index,* http://www.platts.com/news-feature/2012/pgpi/polypropylene (accessed December 1, 2014).

22. BASF evaluates natural gas-based investment in the United States. BASF. http://basf.com/group/pressrelease/P-14-223 (accessed March 10, 2014).

Appendix B: Attributional vs. Consequential Life Cycle Assessment – Case Study in Chemical Manufacturing

B.1 INTRODUCTION

Two major categories of life cycle assessment (LCA) have been developed: attributional LCA (ALCA) and consequential LCA (CLCA). The distinction between the two techniques is whether secondary impacts of a process are included in the system boundary. ALCA accounts for average impacts on immediate material flows in the process being studied, while CLCA also includes consequences of those changes on the operation of the market. CLCA quantifies the indirect impact of changes in physical flows of related processes to determine which secondary supply chains will increase or decrease production with changes in the process being studied.[1,2]

When conducting an LCA of the chemical industry, ALCA is an analysis of one particular process or technology. Changes in raw materials or byproducts that cross the system boundary are usually accounted for using their heating values to quantify the change on a standard basis. However, changes in the materials that cross the system boundary may cause other supply chains to adapt which may have other environmental impacts. To understand those secondary changes, a consequential approach is required to track material flow effects throughout all related supply chains in the industry. In the chemical manufacturing industry, material flows are interconnected – products of one process can be used as inputs in many different processes. So a change in one process can affect raw material availability and the operation of supply chains throughout many different chemical sectors. CLCA requires quantifying those secondary material flows to understand the impacts of one process on the rest of the manufacturing system.

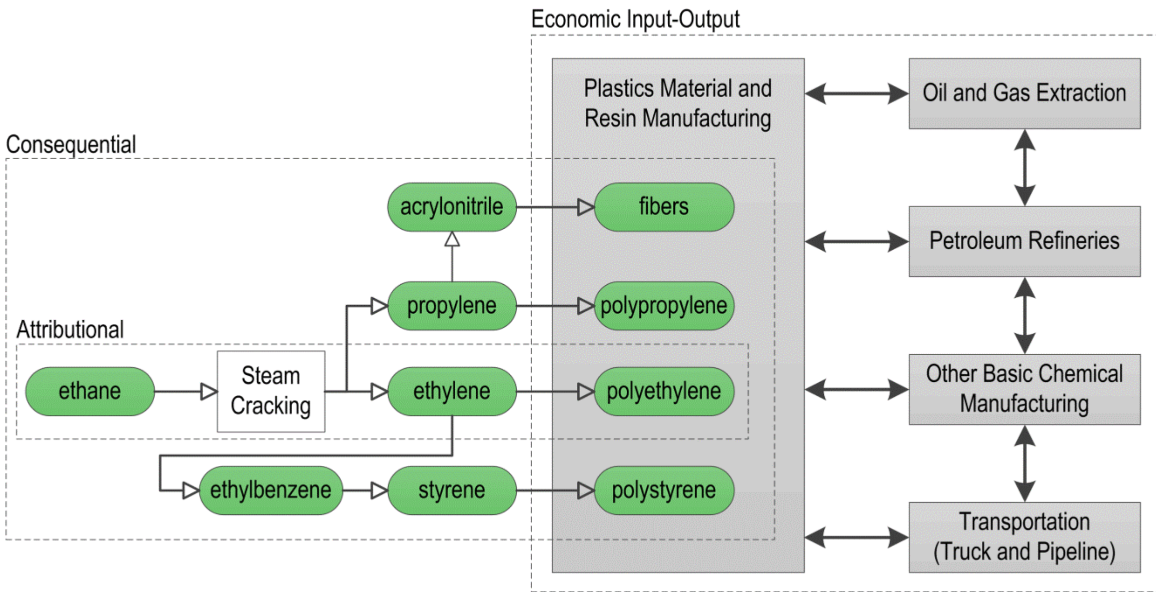
In chemical manufacturing, the large number of interconnected processes makes it difficult to determine which processes are important to include within the system boundary. A boundary just around the system being studied (ALCA) decreases the amount of inventory data required, which improves usability and speed of analysis. These boundaries, however, do not incorporate indirect effects of the process being studied. Broader boundaries, while enabling study of many related supply chains, introduce additional complexity and can make it difficult to compile an accurate inventory.

CLCA expands the system's boundaries to account for upstream and downstream effects of material flows from the studied process. Those effects can be within the sector of interest or outside the sector in the economy as a whole. In chemical manufacturing, accounting for upstream and downstream changes around one process would expand the system boundaries to include byproduct uses in secondary supply chains. Alternatively, the system boundaries can be expanded to include other sectors of the economy that may be impacted by that specific process. A comprehensive study of the indirect effects on the entire economy can be modeled using a variety of techniques. Partial equilibrium modeling has been used to investigate multiple commodities across many global regions and input-output models relate inputs of goods in an economy to outputs in other sectors.[3,4] Both techniques expand the CLCA system boundary to model the whole economy at the expense of details about the specific supply chains being studied.

Using the input-output approach switches the system resolution from individual processes to aggregated sectors of the economy and then each sector influences behavior of other sectors through linear interdependencies. One method to examine intersectoral transactions is an input-output model such as the economic input-output –LCA (EIO-LCA) developed at Carnegie Mellon University.[5] For existing EIO-LCAs, the developed resolution is very coarse. Processes in the chemical manufacturing sector in the EIO-LCA are aggregated into broad categories based on North American Industry Classification System (NAICS) codes. This approach provides good understanding of effects on the rest of the economy, but detail is lost about operations within the one sector being studied. By aggregating manufacturing into these categories, ease of simulation is increased, but granularity of specific processes is lost and instead the contribution of all processes (based on historical average data) is measured as one sector. The organic chemical manufacturing sector in EIO-LCA is based on aggregated data for the entire industry. However, environmental impacts of individual processes can vary substantially so average data is not always accurate. For example, IHS Chemical estimates that the electricity requirement for high density polyethylene (HDPE) production can vary up to 60% per pound HDPE based on the type of technology used and process configuration.[6]

Figure B-1 shows simplified system boundaries for a hypothetical study of polyethylene production from ethylene produced by steam cracking ethane. Three delineations of system boundaries are illustrated: an ALCA, a CLCA within the chemical sector, and a CLCA among different economic sectors using EIO-LCA. The entire polyethylene supply chain is within the ALCA boundary. In this example, two material flows cross the system boundary: propylene as a byproduct from steam cracking and a competing use of ethylene for ethylbenzene production. A CLCA approach which includes changes in those material flows must include all supply chains for which those materials are used (a fiber supply chain based on propylene to acrylonitrile and a polystyrene supply chain including ethylbenzene and styrene). An alternative CLCA approach using EIO relies on historical relationships between plastic manufacturing broadly and other economic sectors. No direct relationship between polyethylene and other sectors is studied, but aggregate data about all plastics manufacturing in general would be used.

Figure B-1: Simplified comparison of chemical manufacturing supply chains that are included in an attributional life cycle assessment, a consequential life cycle assessment within the chemical sector and an economic input-output consequential life cycle assessment with interactions between broad economic sectors.



The relationships between sectors in EIO-LCA are based on incremental economic activity. It is then difficult to use EIO-LCA models to study changes in one process that do not have a large impact on total sector economic output. A change in feedstocks for process, as discussed in the case study below, will impact how materials flow between processes but may not substantially change the economic output of the organic chemicals sector as a whole. It is shown here that the change in material flows within the petrochemical sector can lead to significant changes in energy and water use without necessarily impacting the overall product output of the sector.

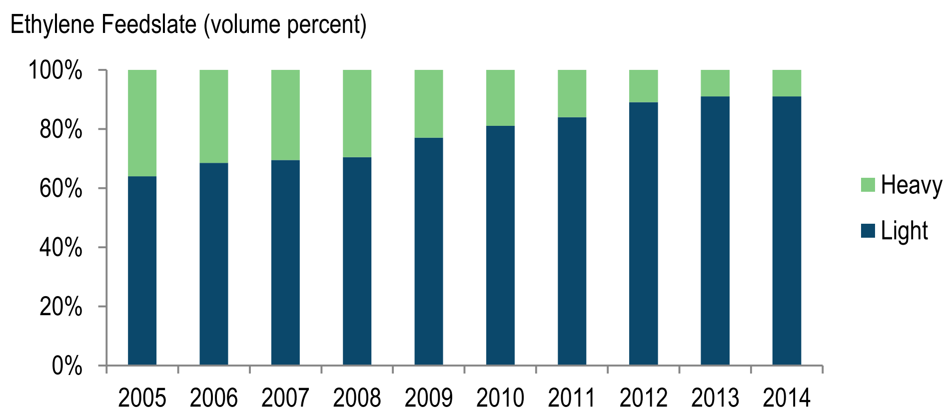
A case study of a CLCA methodology is presented to understand the change in energy and water use in the chemical manufacturing industry that results from steam cracker feedstock substitution. Since 2005, lighter natural gas liquid (NGL) feedstocks (ethane, propane, and n-butane) have continued to replace heavier naphtha-range feedstocks for ethylene production in the U.S. Cracking NGL to ethylene uses different amounts of energy and water than cracking naphtha to ethylene, a trade-off which is quantified using an ALCA approach. However, the switch in cracking feedstocks has also changed steam cracker product distribution, impacting other supply chains in the chemical industry. For example, naphtha cracking produces higher yields of propylene than NGL cracking, so propylene and related supply chains may be affected as feedstocks switch. Quantifying the energy and water changes in those secondary supply chains is the goal of CLCA. In this work, a network model of the U.S. chemical manufacturing industry is used to fully track changes in all related supply chains and process technologies as the ethylene feedslate shifts from heavy to light components. Using data for all indirectly affected supply chains allows for a robust CLCA without losing individual process details that would occur when using an EIO-LCA or other economy-wide model.

B.2 Ethylene Cracking

Ethylene is primarily produced from steam cracking alkane hydrocarbons. In the U.S., the most common raw materials are NGL and naphtha, but gas oil and heavier waxes can also be used. During the cracking process, many co-products are formed in addition to ethylene. The product distribution depends on the type of raw material and the operating conditions, but generally includes fuel gas, propylene, butylenes, butadiene, gasoline-range alkanes, benzene, toluene, xylenes, and fuel oil. Cracking lighter raw materials (NGLs) typically produces a higher quantity of lighter products than cracking heavier raw materials (naphtha).[7]

Due to the recent abundance of NGLs in the U.S., light feedstocks for ethylene production have increased, while naphtha's share of the feedslate has decreased (Figure B-2). In 2006, NGL feedstocks were nearly 70% of the ethylene feedslate with naphtha at 24%. Beginning in 2009 a trend towards lighter feedstocks accelerated and by the beginning of 2014, the feedslate was more than 90% NGL and only 7% naphtha.[8,9] This change in feedslate has led to variations in the production quantities of all coproducts, most prominently propylene and butadiene.[10,11]

Figure B-2: Annual ethylene feedslate distribution, 2005 – 2014.[8,12,13]



B.3 Chemical Industry Model

Because material flows in the chemical manufacturing system are highly interconnected between processes, a model that details all related supply chains can be used for a CLCA of changing ethylene feedstocks. A network model of the industry has been constructed that represents material conversions from a small number of feedstocks (natural gas, NGL, and crude oil) through a variety of manufacturing steps to supply final end product demand (plastics, fibers, fertilizers, etc.). A system of linear equations represents the chemical transformations that consume and produce different chemicals for each technology in the U.S. Using a network model of the industry and a mathematical representation of the material flows allows for a systematic analysis of potential changes in connected supply chains.

The network model represents the 2012 U.S. chemical manufacturing industry and includes 873 chemical processes (index *j*) that produce 283 different materials (index *i*). Stoichiometric and process cost data is from the IHS 2012 Process Economics Program Yearbook. The model is formulated as a linear program (LP), represented as:

$$\begin{aligned}
\min \quad & Total\ Cost = \sum_j C_j X_j \\
\text{s.t.} \quad & -\sum_j a_{ij} X_j < S_i \ \text{ for } i \in \{\text{Primary Raw Materials}\} \\
& \sum_j a_{ij} X_j > 0 \text{ for } i \in \{\text{Intermediate Materials}\} \\
& \sum_j a_{ij} X_j > D_i \text{ for } i \in \{\text{Final End Products}\}
\end{aligned}$$

where C_j is the cost of process j in cents/pound, X_j is the production level of process j in pounds/year, S_i is the annual supply of chemical i (in pounds), D_i is the annual demand for chemical i (in pounds), and a_{ij} is the input-output coefficient of chemical i in process j. The input-output coefficient is the mass of chemical i consumed (negative coefficient) or produced (positive coefficient) in process j per unit mass of primary product. Fifty-three chemicals are included in the set of final end products, accounting for 42% of U.S. chemical industry shipments in 2012.[14] The model and data sources are fully described in previous work.[15] Utility use for each process is included in the model to calculate industry-wide consumption of electricity, natural gas for process fuel, cooling water, and process water for a given optimal configuration. Utility data is also from the IHS 2012

Process Economics Program Yearbook. Total use of electricity, for example, is calculated as $\sum_j E_j X_j$, where E_j is the electricity consumption of process j in kWh/pound main product.

B.4 Consequential Life Cycle Assessment

The model is used to determine the change in optimal industry structure and the resulting change in total utility consumption as ethylene from light feedstocks (NGL) replaces ethylene from heavy feedstocks (naphtha). The amount of NGL feedstock for ethylene production is exogenously varied from 40 to 99% of the ethylene feedslate and the optimal industry structure is calculated for each scenario. The resulting change in total industry energy use is shown in Figure B-3 and the change in total industry water use is shown in Figure B-4 and Figure B-5.

Figure B-3: Modeled change in energy use in the U.S. chemical manufacturing industry as the ethylene feedslate changes.

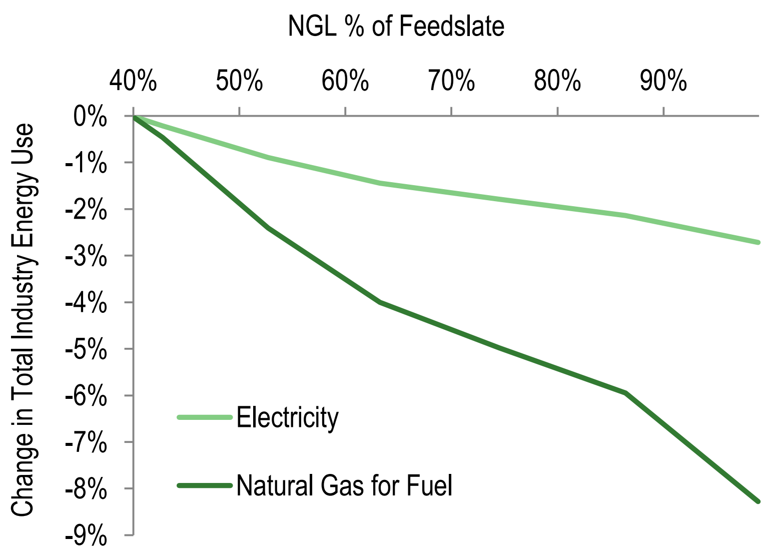


Figure B-4: Modeled change in process water use in the U.S. chemical manufacturing industry as the ethylene feedslate changes.

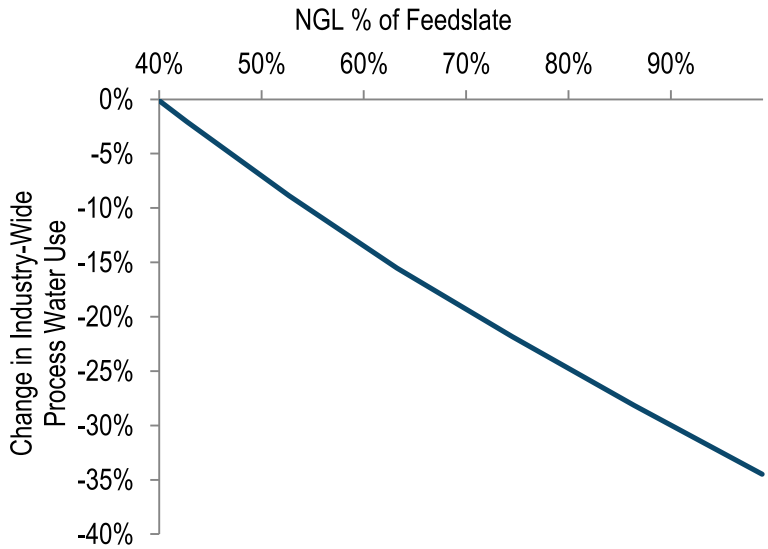
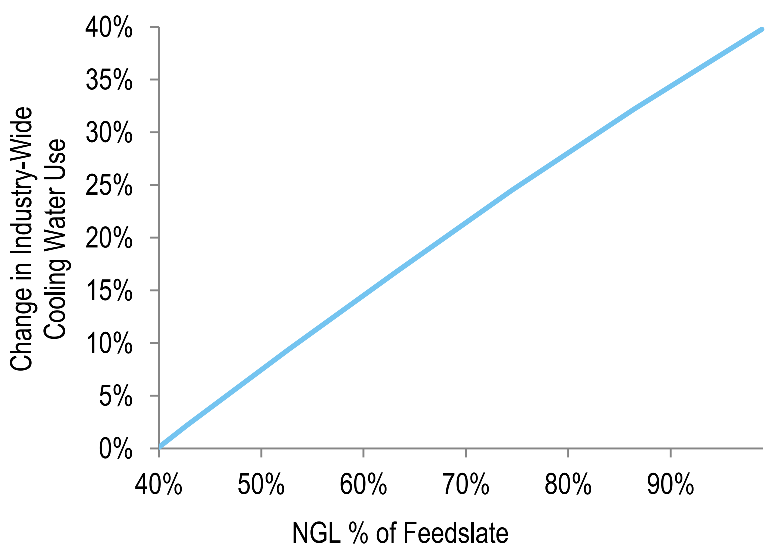


Figure B-5: Modeled changed in cooling water use in the U.S. chemical manufacturing industry as the ethylene feedslate changes.



As NGL cracking increases, the shift in optimal industry structure results in an overall decrease in total electricity, natural gas, and process water use while cooling water use increases. The change in total utility consumption can be attributed not only to the change in ethylene cracking technology (cracking NGLs have different utility consumption than cracking naphthas), but also to a shift in technology utilization in secondary processes. As ethylene raw materials and coproducts change, adaptations in the rest of the industry contribute to the utility changes seen in the figures above.

Thirty eight secondary processes change utilization as NGL cracking increases, affecting 30 main products as shown in Table B-1. In addition to the change in cracking technology, the change in supply chains for each of these chemicals impacts the magnitude of industry-wide energy and water use. The wide range of chemicals that are affected by a switch in cracking feedstock shows the extent of the impact that cracking products have on the structure of the industry.

Table B-1: Chemicals with utilization and technology changes as ethylene feedslate changes.

Utilization Change		**Technology Change**
acetone	linear alpha olefins	butadiene
benzene	methanol	butene-1
biodiesel	n-methyl-2-pyrrolidone	EPDM rubber
1,4-butanediol	mixed xylenes	hydrogen
butanes	nitrogen	methyl *t*-butyl ether
butene-1	oxygen	sec-butanol
carbon tetrachloride	polystyrene (general purpose)	styrene
chlorine	propylene	
ethanol	propylene oxide	
ethyl *t*-butyl ether	*p*-xylene	
ethylbenzene	sulfuric acid	
isopropanol	tetrahydrofuran	

The chemicals shown in Table B-1 experience changes in utilization to ensure total industry cost is minimized as cracker operation changes. These changes usually occur across multiple supply chains leading to impacts on distantly related chemicals. For example, propylene oxide production changes because of propylene availability as NGL feedstocks increase. The increase in one propylene oxide technology produces more acetone as a byproduct. Therefore, less on-purpose acetone from isopropanol is required, eventually also decreasing demand for nitrogen that is used in the on-purpose acetone process.

In addition to utilization changes, some chemicals undergo technology substitutions. As less butadiene is recovered from steam cracking, on-purpose butadiene from n-butenes is introduced, which changes the economics of styrene production, causing a change in styrene production technology to minimize cost. As butadiene supply becomes limited with more NGL cracking, it is overall more efficient to increase propylene oxide from a Shell process which produces a styrene byproduct than to continue making styrene from butadiene via 4-vinylcyclohexene by the Dow process.

As marginal ethylene production becomes cheaper, EPDM rubber production switches to a technology that uses more ethylene at a cheaper overall process cost. The switch in methyl *t*-butyl ether (MTBE) production technology occurs because of the change in steam-cracked C4 composition. As more NGLs are cracked, the increased availability of ethylene at low cost enables 1-butene production to proceed by ethylene dimerization instead of from MTBE plant raffinate. The change in MTBE and 1-butene availability enables a change in sec-butanol production technology.

It is important to note that the changes discussed here are based on an optimal solution to the modeled industry as total cost is minimized and demand is constant. The model does not reflect consumer or volume trends in the affected markets that may accompany feedslate shifts.

B.4.1 Utility Use

As the optimal structure of the industry adapts to changing ethylene feedslates, some processes increase utilization, some decrease utilization, while others change technologies. The net effect of all of these changes is the total industry change shown in the figures above. The chemicals that are the largest contributors to utility use changes are shown in Table B-2. Energy use in the modeled industry decreases in the feedslate scenarios in this work primarily due to decrease in energy use for polystyrene, xylenes, hydrogen, p-xylene, and isobutylene, despite increases in energy use for isopropanol, propylene, linear alpha olefins, and chlorine. Water use in the modeled industry decreases with changes in polystyrene, hydrogen, butene-1, xylenes, benzene, and butadiene utilization and increases with changes in isopropanol, propylene, linear alpha olefins utilization.

For all four utilities studied, a small number of processes have a large impact on total utility change. The large increase in cooling water use can be almost entirely attributed to increasing production of isopropanol from propylene. Of the processes that contribute to increasing cooling water, isopropanol makes up 83% of cooling water use. Ignoring that one process would actually give an overall net decrease in cooling water use. Process water is affected by hydrogen production. The decrease in hydrogen required by the industry makes up 82% of the process water decrease.

Polystyrene production relies on availability and price of styrene, benzene, ethylene, and ethylbenzene to determine magnitude of production and optimal technology (integrated styrene production and polymerization or polymerization of purchased styrene). All four potential raw materials change availability (directly and indirectly) as NGL cracking increases so polystyrene production sees large utilization changes. Because of the high utility use by styrene production and polymerization, the polystyrene supply chain is the largest contributor to decreases in electricity and natural gas use. Seventy two percent of the decrease in electricity and 81% of the decrease in natural gas use is due to a change in polystyrene utilization.

Table B-2: Chemicals that are major contributors to decreasing and increasing utility use as NGL feedslate changes (listed in decreasing order of importance).

	Energy	**Water**
Decreasing	polystyrene	hydrogen
	xylenes, mixed	polystyrene
	hydrogen	butene-1
	p-xylene	xylenes, mixed
	isobutylene	benzene
	ethanol	butadiene
	butadiene	*p*-xylene
	ethylbenzene	isobutylene
	benzene	ethanol
		ethylbenzene
		ethyl *t*-butyl ether
Increasing	isopropanol	isopropanol
	propylene	propylene
	linear alpha olefins	linear alpha olefins
	chlorine	butanes
	butanes	chlorine
		sulfuric acid

B.5 COMPARISON TO ATTRIBUTIONAL LIFE CYCLE ASSESSMENT

An attributional approach involves comparing energy and water use in the NGL cracking and naphtha cracking technologies without considering secondary supply chain effects. The change in utility use just for the cracking process between the 40% NGL and 99% NGL feedslate is compared to the CLCA approach and shown in Table B-3. The change in utility consumption for just the cracking processes when moving from 40% NGL to 99% NGL feed is a 22% decrease in electricity, 24% decrease in natural gas for fuel, 24% decrease in cooling water, and 19% decrease in process water. The energy use calculation ignores byproduct changes in this ALCA. The results of this attributional analysis only consider utility consumption at the steam cracker so are different than the results of the consequential analysis which accounts for changes in utility consumption in all indirectly affected processes throughout the industry.

Table B-3: Utility use using ALCA and CLCA as NGL feedslate changes from 40% NGL to 99% NGL.

	Electricity	**Cooling Water**	**Natural Gas for Fuel**	**Process Water**
Attributional *(change in cracking process)*	-22%	-24%	-24%	-19%
Consequential *(change in whole industry)*	-2.7%	40%	-8.3%	-35%

B.6 DISCUSSION

Many secondary supply chains are impacted by the switch in cracker feedstock. These supply chains are not limited to the direct products of the cracking processes being studied. For example, changes in propylene from steam crackers cause impacts to propagate through propylene oxide, isopropanol, acetone, and then nitrogen supply chains. However, other chemicals that use propylene did not experience a change in utilization in the modeled scenarios. Acrylic acid, for instance, was not affected by the change in propylene availability. Acrylic acid was most likely not affected because switching acrylic acid technologies from acetylene instead of propylene would increase overall cost. Just mapping connected supply chains is not sufficient to determine what secondary processes will see utilization changes. Instead, material connections, alternative technologies, and relative costs must be taken into account. These complex trade-offs can be quantified with an optimization model.

The supply chains that are affected by the process being studied do not contribute equally to changes in utility consumption. Isopropanol, for example, dictates the majority of the change in total utility use. The effects of these processes vary due to both the magnitude of the process and the utility use per mass of main product. The change in utility use by some secondary processes has the potential to outweigh the process being studied. Isopropanol, propylene, and linear alpha olefins each have a greater magnitude increase in electricity consumption than the 22% decrease in electricity use for the cracking processes.

The change in total industry utility consumption is mostly impacted by a small number of processes that are large utility users and have a large utilization change as a result of a shift in optimal industry structure. The accuracy of the change in utility use for those processes is important because of their large impact. The chemical sector has a large number of highly integrated supply chains, so it is difficult to determine which secondary supply chains are impacted by a process and the magnitude of their change. Identifying which supply chains are those high utility users is accomplished with a model of the entire sector to quantify how the supply chains will adapt. A network model like the one presented here is efficient at screening important supply chains that are large contributors to utility use. The system boundary is then designed from modeled behavior instead of normatively.

The network model loses the granularity of a detailed market/supply chain model that accounts for elasticities and other trends. For those highly influential supply chains, a more detailed ALCA may provide greater accuracy. Instead of building one large model that accurately reflects market behavior for all supply chains throughout the industry, it may be most efficient to use a simplified network model to identify relevant supply chains and then construct detailed integrated models for the most important supply chains interactions.

B.7 CONCLUSIONS

Both ALCA and CLCA were used to understand the impact of shifting ethylene feedslates on utility consumption in the U.S. chemical manufacturing industry. To systematically analyze all potential secondary process changes impacted by ethylene production, a network model of the U.S. chemical industry was used to calculate how the optimal industry structure adapts to minimize overall cost as ethylene feedstocks change. Supply chains for 30 chemicals were impacted by the shifting ethylene feedslate. Each of these secondary supply chains contribute to changes in total industry utility consumption in ways that are not measured when evaluating just the cracking process in a traditional ALCA approach.

A small number of supply chains have a large contribution to overall utility use, suggesting that a detailed understanding of those supply chains will increase the accuracy of the assessment. The diversity of supply chains impacted by ethylene cracking products and their wide variation in utility consumption makes selecting supply chains for further analysis difficult. A network model of the chemical industry is efficient at determining which supply chains are most important for a given scenario. A more detailed ALCA focused on each of those secondary supply chains will then improve the resolution and reliability of the final assessment. This approach provides more detailed resolution than modeling economic sectors, while limiting the size and complexity necessary for a full model of all supply chains in the chemical manufacturing industry.

B.8 References

1. Horne, R. E.; Grant, T.; Verghese, K. *Life Cycle Assessment: Principles, Practice, and Prospects.* CSIRO Publishing, 2009.
2. Earles, J. M.; Halog, A. Consequential life cycle assessment: a review. *Int. J. Life Cycle Assess.*, 2011, 16, 445-453.
3. Earles, J. M.; Halog, A.; Ince, P.; Skog, K. Integrated Economic Equilibrium and Life Cycle Assessment Modeling for Policy-based Consequential LCA. *J. Ind. Ecol.* 2013, 17, 375–384.
4. Matthews, H. S.; Small, M. J. Extending the boundaries of life-cycle assessment through environmental economic input-output models. *J. Ind. Ecol.* 2001, 4 (*3*).
5. Carnegie Mellon University Green Design Institute. Economic Input-Output Life Cycle Assessment (EIO-LCA) US 2002 (428 sectors) Producer model, 2016, http://www.eiolca.net/ (accessed 21 Feb, 2016).
6. IHS Chemical, Process Economics Program Yearbook, 2012.
7. Sundaram, K. M.; Shreehan, M. M.; Olszewski, E. F. Ethylene. *Kirk-Othmer Encyclopedia of Chemical Technology,* 2010.
8. Jacobs Consultancy, Hodson Report, January 2014.
9. RBN Energy, What's Crackin with Steam Crackers? Drill Down Report, 2014.
10. Plotkin, J. S. The propylene gap: how can it be filled? *American Chemical Society*, September 14, 2015. http://www.acs.org/content/acs/en/pressroom/cutting-edge-chemistry/the-propylene-gap-how-can-it-be-filled.html (accessed February 16, 2016).
11. Morris, G. Global prices rise as butadiene supply tightens worldwide. *Chemical Week*, 2008, 170 (*17*), 29.
12. Lippe, D. 2013 ethylene output rises; growth to continue in early 2014, *Oil & Gas Journal*, March 3, 2014.
13. Lippe, D. Maintenance slows first-half 2014 US ethylene production, *Oil & Gas Journal*, September 1, 2014.
14. American Chemistry Council, Business of Chemistry Annual Data, 2013.
15. DeRosa, S. E.; Allen, D. T. Impact of Natural Gas and Natural Gas Liquids Supplies on the United States Chemical Manufacturing Industry: Production Cost Effects and Identification of Bottleneck Intermediates. *ACS Sustainable Chem. Eng.* 2015, 3 (*3*), 451-459.

Appendix C: Chemical Manufacturing in the San Juan Basin

Supporting Information for Chapter 5

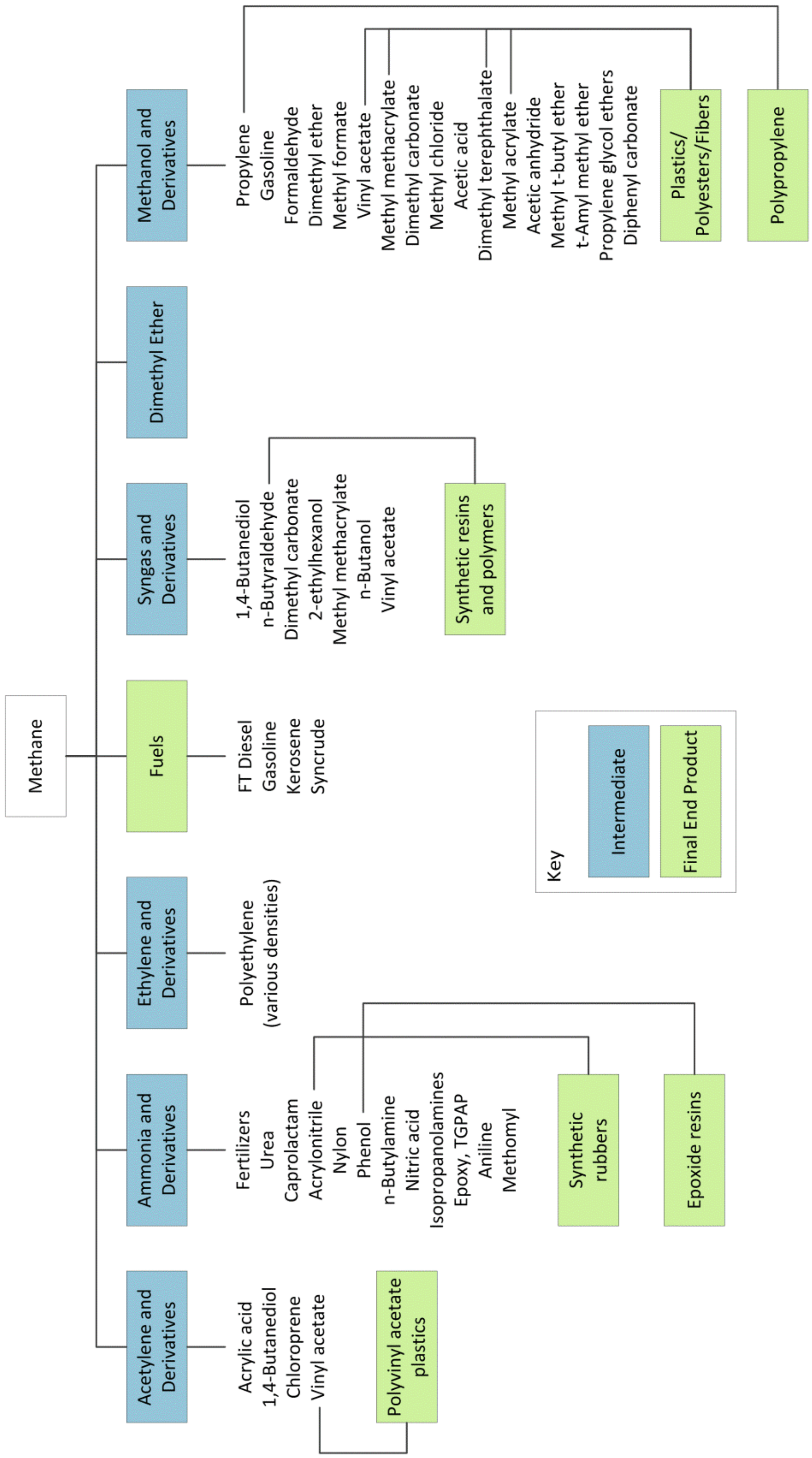
C.1 Methane-to-Chemicals

Methane produced in the Four Corners is typically used in-state or sent to interstate pipelines from the Blanco Hub, which connects Rocky Mountain natural gas to West Coast and Midwest markets.[1]

In addition to its use as a fuel, methane can be used as a raw material for chemical manufacturing. Syngas (mixtures of carbon monoxide and hydrogen) is the most commonly produced intermediate from methane as a feedstock,[2] but many other chemicals can be manufactured beginning with methane, as shown in Figure C-1.

From an economic development perspective, as natural gas prices have decreased, there is wide-spread regional interest in enabling another use of gas in the region to drive production. Relatively cheap and abundant locally available methane enables unique market opportunities for potential chemical production in the Four Corners. Through application of optimization and agent-based modeling, three potential chemical manufacturing uses for existing methane sources in the Four Corners region are identified and evaluated.

Figure C-1: Chemical derivatives of methane.



C.1.1 Feasible Sectors for Greenfield Manufacturing

The chemicals shown in Figure C-1 are grouped into nine different sectors: fertilizers, fibers, monomers, olefins, plastics, epoxies, rubbers, ethers, and gas-to-liquid (GTL) fuels. Each of these sectors is evaluated as a potential area for new methane-based manufacturing in the Four Corners. Feasible chemical sectors are defined as those for which

1. Methane is a feedstock material
2. Production is feasible at small and large scale operations
3. Economic growth potential exists and market volatility is low
4. Transportation requirements are manageable.

For sectors that are found to be feasible, specific chemicals within each sector are then further evaluated to determine optimal chemicals to manufacture in the Four Corners. This method of screening each sector for feasibility is used to eliminate unnecessary economic modeling for chemicals that would face significant barriers to entry.

To determine initial feasibility, nine factors are considered: required capital, market competition, domestic market growth, technological maturity, potential for a feedstock advantage relative to other manufacturers, a need for co-raw materials besides methane, if additional integrated plants are required for those raw materials, potential for permitting challenges, and ease of product transport. Each factor is assessed on a three point scale. The results are summarized in Table C-1 and Table C-2, followed by a detailed description of each sector in the subsequent sections.

Table C-1: Business factor analysis of potential chemical sectors in the Four Corners.

	Business Factors		
	Required Capital	Competition	Domestic Market
Fertilizers	Low	High	Growing
Fibers	High	Med	Stable
Monomers	Med	High	Low Growth
Olefins	High	Med	Growing
Plastics	Med	Med	Growing
Epoxies	Low	High	Shrinking
Rubbers	Med	High	Growing
Ethers	High	High	Shrinking
Fuels	High	High	Stable

Table C-2: Technology factor analysis of potential chemical sectors in the Four Corners.

	Technology Factors					
	Technology Maturity	Feedstock Advantage	Co-Raw Materials	Integrated Plants	Permit Challenge	Product Transport
Fertilizers	High	No	No	No	Low	Easy
Fibers	High	No	Yes	No	Average	Easy
Monomers	Low	Yes	Yes	Yes	High	Hard
Olefins	Low	Yes	No	No	Average	Med
Plastics	Low	Yes	Maybe	No	Average	Easy
Epoxies	High	Yes	Yes	Yes	High	Easy
Rubbers	High	Potential	Yes	Yes	Average	Easy
Ethers	High	Yes	Yes	Yes	Average	Med
Fuels	Med	Yes	No	No	Average	Med

C.1.1.1 Fertilizers

Fertilizers are currently the largest chemical end consumption of methane. Fertilizer plants typically have low fixed capital investments (<$500 million for average capacity) and require only natural gas as a feedstock. Fertilizer demand is projected to increase from 2015-2019.[3] In the long term, global fertilizer demand will continue to grow as available arable land per capita decreases due to land use changes and a projected global population increase.[4] Production through a syngas intermediate is a well-developed technology, with existing plants operating at a wide range of capacities. Also, product diversification can be achieved by incorporating multiple fertilizer production trains in one facility.

However, market competition is high due to many different plants all utilizing the same feedstock. There are also significant new projects that may come online within the next few years. As of August 2015, 33 fertilizer plant expansions or new-builds have been announced to come online in the U.S. and Canada between 2016 and 2019.[5] IHS Chemical projects that if at least half of announced world-wide projects become operational, the global ammonia supply/demand balance will move towards a surplus.[4] Fertilizers are produced as a solid, which makes transport relatively easy for the Four Corners region, as a product pipeline is not necessary.

C.1.1.2 Fibers

The most common synthetic fibers include nylon, polyester, and olefin/acrylic fibers. Fibers from methane would include nylon through ammonia as an intermediate. Generally, capital costs for a nylon/ammonia facility are higher than other sectors – greater than \$1.2 billion for a mid-size plant (2012 dollars). Nylon production from ammonia requires a number of co-raw materials, including cyclohexane, caustic soda, hydrogen, and phosphoric acid. Acquiring these materials in the Four Corners would pose a logistical challenge, as manufacturing that many materials locally would have substantial additional costs.

Global fiber production is dominated by Asia, with more than 73% of 2012 global production from China and India.[6] While Chinese demand for nylon is growing, U.S. demand is relatively stable, especially since the surge in carpet recycling has dampened demand growth for nylon and high-performance fibers have been applied in more areas.[7] As a solid, fiber product transport out of the Four Corners region could utilize rail or truck and a pipeline would not be necessary.

C.1.1.3 Monomers

Production of monomers such as vinyl acetate and methyl acrylate typically have average capital costs ($500 million - $1 billion). Vinyl acetate monomer is most commonly produced from ethylene and acetic acid. Alternatively, production can proceed with acetylene (from methane) and acetic acid. This technology is conceptual and not based on patents or pilot projects. Using methane instead of ethylene as a feedstock would differentiate Four Corners production from other market participants, but ethylene supplies are currently abundant in the U.S. so diversification may not provide significant competitive advantage. Local acetic acid production would be required, which would increase capital costs and raw material requirements. While vinyl acetate consumption is projected to increase by 3% per year from 2013 to 2018 in the U.S., supplier competition will increase as there are only a small number of vinyl acetate producers in the U.S. and significant capacity additions in China.[8]

Other types of monomers besides vinyl acetate may require a local chlorine plant, which would be prohibitively expensive in a remote location and difficult to permit in the region. Monomer transportation is difficult because of their flammability and tendency to form polyperoxides in the presence of oxygen which can lead to polymerization.[9]

C.1.1.4 Olefins

Olefins such as ethylene and propylene are typically produced from steam cracking natural gas liquids or from refinery FCC units. Methane to olefins technologies are not common in the U.S., although a new plant has recently been announced. Utilizing a different feedstock than almost all olefin production in the U.S. could offer a competitive advantage. Estimated capital costs for methane to olefins technologies are high compared to other sectors (>$1 billion). Olefin demand is increasing in the U.S., driven by increasing demand for linear low-density polyethylene (LLDPE) and polypropylene plastics. IHS projects about 5% annual growth for ethylene demand in the U.S. between 2014 and 2019[10] and 4.6% annual growth for propylene from 2015-2020.[11] Propylene capacity in the U.S. has increased at a slower rate, indicating favorable market trends for some olefins. Olefins are typically produced close to polymerization or other chemical demand facilities because transport by means other than pipeline can be difficult.

C.1.1.5 Plastics

The plastics sector encompasses a wide variety of materials, including olefin polymers such as polyethylene and more complicated poly(vinyl acetate) and subsequent copolymers. In general, polymerization technologies have average capital costs ($500 million - $1 billion). Plants designed to integrate polymerization reactions with monomer production can achieve substantial cost savings although large volume facilities are usually required to remain economically competitive.[12] Through recent consolidation of plastics manufacturers, competition has increased, although utilizing methane as the primary raw material is different than almost all existing plastics manufacturers in the U.S. More complicated copolymers would require additional co-products besides methane, but PE, LLDPE, LDPE, HDPE, and polypropylene resins can all be manufactured directly from methane.

Plastics demand is distributed around the U.S. (as opposed to specific industrial consumers) and IHS projects annual consumption growth of 5% per year from 2014 – 2019 for polypropylene (globally),[13] 5.5% per year for LLDPE (globally),[14] 3% per year from 2013-2018 for polyvinyl acetate (U.S.),[15] and 2.7% per year from 2012-2018 for acrylic resins and plastics (U.S.).[16] Because plastics are solid, transportation out of the Four Corners region is feasible by truck or rail.

C.1.1.6 Epoxies

Epoxy resins are versatile polymers derived from monomers containing an epoxy group. Some types of epoxies can be synthesized from methane through an ammonia intermediate, although many other chemicals are required as co-raw materials, making these polymers difficult to manufacture in the Four Corners. Typical capacities for epoxy plants are very small, so capital costs are low (<$500 million). However, in the Four Corners region, many other plants would be necessary to synthesize chlorine-based raw materials which may not be feasible to transport. Product transport, however, is much easier. The North American phenol market is currently weak, with demand growth led by China.[17]

C.1.1.7 Rubbers

The most common rubbers include styrene-butadiene elastomers and acrylonitrile-butadiene-styrene (ABS) polymers. Methane can be used to synthesize acrylonitrile from ammonia, which is different than most ABS production throughout the world. Significant other raw materials would be required to produce a rubber final end product, including polybutadiene and styrene, which would be expensive to manufacture independently and difficult to transport to the Four Corners. Even though ABS resin demand is project to grow at 3.7% per year from 2015 – 2019, the market is currently oversupplied with excess global capacity, so competition is high.[18]

C.1.1.8 Ethers

Ethers are typically synthesized from butylenes and methanol. Common ethers include methyl t-butyl ether (MTBE) and propylene glycol ether. Mixed C4 streams typically come from steam crackers or refinery streams, so using methanol as a raw material could require a very high capital cost, depending on the scale of methanol required and the amount of infrastructure required to bring a C4 stream into the region.

The market is competitive and demand is small. There are very few MTBE producers in the U.S. and all production is exported, because domestic MTBE consumption has fallen to zero since passage of the Energy Policy Act of 2005 and the Energy Independence and Security Act of 2007. Ethylene glycol ether and propylene glycol ether are used as solvents. Between 2009 and 2013, China overtook the U.S. to become the largest consumer of glycol ethers. Growth in demand is expected to continue in China through 2018.[19] Manufacture of propylene glycol ether would require a propylene oxide source and other minor chemicals, increasing the cost requirements for glycol ether production from methane to methanol.

C.1.2 Feasible Sector Results

Based on the numerical assessment of each factor shown in Table C-1 and Table C-2, the sectors are ranked from most to least feasible and shown in Table C-3.

Table C-3: Feasibility of nine sectors analyzed for the Four Corners.

Rank	Sector	Example Chemicals
1	Fertilizers	ammonia, urea
2	Plastics	polyethylene, polyvinyl acetate
3	Olefins	ethylene, propylene
4	Fuels	gasoline, kerosene, diesel
5	Fibers	nylon
6	Rubbers	acrylonitrile-butadiene-styrene
7	Epoxies	phenol
8	Ethers	methyl t-butyl ether
9	Monomers	vinyl acetate, methyl acrylate

Based on this classification of the sectors, fertilizers, olefins, and plastics are the three most feasible to manufacture in the Four Corners. To determine the optimal chemicals within these three sectors, an investment model was developed for representative chemicals in each sector.

C.2 Economic Modeling Methodology

Process economics were estimated for 27 processes to manufacture representative chemicals from the three sectors selected. IHS Process Economics Program (PEP) Yearbook (2012) data was used for stoichiometry, capital costs, and operating costs. Reaction stoichiometry is consistent for installed technologies (within operational controls), so 2012 stoichiometry data is accurate for future years, assuming no major new technology is introduced for the technologies analyzed. Capital and operating costs use

2012 dollars. While estimates for costs in 2012 will not accurately reflect costs in 2015 and later, this analysis does not attempt to project actual profitability in a future year, but optimizes technology selection. Therefore, all potential chemicals and processes use 2012 cost data as a baseline. If future work requires plant cost estimates for a future year besides the baseline, a number of cost indexes are available to scale 2012 data (CE Plant Cost Index,[20] Nelson-Farrar,[21] etc.).

Total fixed capital estimates included battery limits and off-sites (including utilities). Capital costs were scaled using

$$\frac{Cost\ 2}{Cost\ 1} = \left[\frac{Plant\ Size\ 2}{Plant\ Size\ 1}\right]^{m}$$

where *m* was provided by the PEP Yearbook. Production cost components are shown in Table C-4.

Utility calculations include electricity, natural gas for process fuel, process water, cooling water, inert gas, steam, and fuel. An important distinction for water use in the Four Corners is water withdrawal versus consumption, which is not differentiated in the IHS utility consumption metrics. In consultation with Russell Heinen, IHS, process consumption and production of water was estimated using PEP flowsheets and applied to the processes used in this analysis.

Table C-4: Production cost components included in the model.

Production Costs				
G&A, Sales, Res				
Plant Gate Cost				
	Depreciation			
	Plant Cash Costs			
		Plant Overhead		
		Taxes and Insurance		
		Total Direct Costs		
			Maintenance Materials	
			Operating Supplies	
			Operating Labor	
			Maintenance Labor	
			Control Laboratory	
			Variable Costs	
				Raw Materials
				By-Product Credits
				Utilities

Profitability was estimated using 2012 IHS PEP chemical prices, with processes operating at three different representative capacities. Major assumptions include:

- License fees will be similar for all options
- 15% ROI
- 10 year plant life
- Linear depreciation
- U.S. Gulf Coast construction costs
- Byproducts cannot be sold, except for gasoline-range alkanes

Primary intermediate plants (i.e. ammonia, methanol, acetylene) were designed first at three different representative capacities that reflect typical plant sizes. Downstream processes were then scaled to utilize all intermediate chemical output for each capacity. Annual operating cost for each configuration was then calculated, using the assumptions listed above. Total profit was then estimated, assuming sales of only the final end product at a 2012 price.

C.3 RESULTS

The optimal chemicals to produce based on the economic analysis can be defined as either maximizing profit or adding the most value per unit of methane consumed. The optimal products based on these two objective functions are shown in Table C-5. If equal weight is assigned to each objective function, the top four products for further analysis are polypropylene, polyvinyl acetate, urea, and propylene. Because of the large number of raw materials required and byproducts produced when manufacturing polyvinyl acetate, this material is not ideal for distributed manufacturing so no further analysis is conducted for polyvinyl acetate.

Table C-5: Optimal chemicals to manufacture from methane in this analysis.

	Objective Function	
Rank	**Value-Added per Unit Methane**	**Maximum Profit**
1	polyvinyl acetate	polypropylene
2	urea	propylene
3	polypropylene	polyethylene/polypropylene
4	ammonia	polyethylene
5	propylene	urea
6	polyethylene/polypropylene	polyvinyl acetate
7	polyethylene	ammonia
8	ethylene	ethylene

The three products selected for further analysis are chosen based on the economics modeled previously. Each of the three potential chemicals will serve as a case study of different types of manufacturing in the region, with further analysis determining market opportunities and potential competitiveness for each case.

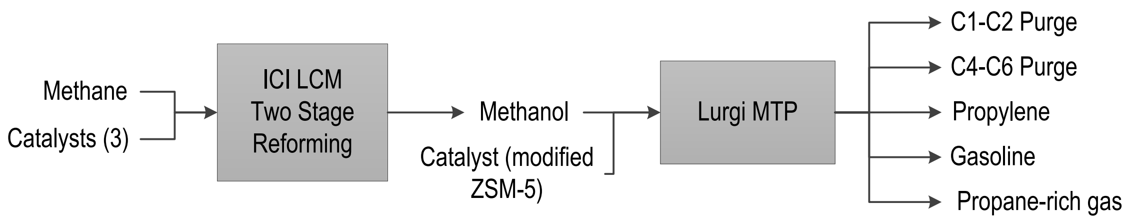
Propylene is a petrochemical intermediate, so potential customers will be other industrial users, not end use consumers. Transporting propylene poses unique challenges because of its volatility and flammability.[22] In comparison, polypropylene is the simplest end product of propylene because of its ease of transport (as a solid) and wide-spread demand. Comparing the difference between the feasibility of propylene and polypropylene will show the potential for manufacturing intermediates versus simple end products in the Four Corners, primarily determining if the ease of transporting and larger market for final end products outweighs the additional capital investment.

Urea is unique to analyze because of both its local and global markets. Local demand for fertilizer use and selective catalytic reduction units at the Four Corners and San Juan coal-fired power plants can supplement sales to fertilizer markets throughout the West Coast. However, after 2022, continued operation of the San Juan power plant is uncertain,[23] eliminating a portion of local demand. The potential for a major change in local market underscores the importance of verifying additional regional and global customer potential.

C.3.1 Propylene

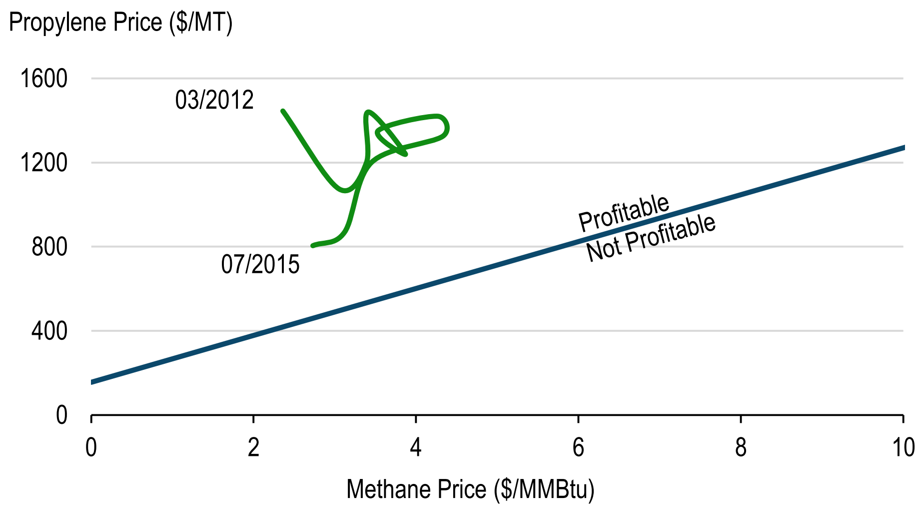
Propylene is produced by two integrated processes: an ICI reforming step to produce methanol followed by Lurgi's methanol to propylene (MTP) technology (Figure C-2). A 1 billion metric ton per year (MTA) facility would require 278 MMcfd methane, 4.79 MW electricity, 24 million pounds steam/day, and 3.55 million gallons/day of process water (0.53 million gallons/day of that process water is consumed).

Figure C-2: Methane to propylene process flow diagram.



The profitability curve for the process compared to market prices of the feedstock and final end product is shown in Figure C-3. Historical prices for methane and propylene have consistently been in the profitable range since before March 2012. Propylene prices have decreased from January to July 2015, but the concurrent drop in methane prices improves the feedstock economics of propylene production.

Figure C-3: Profitability range for methane to propylene manufacturing in this analysis.[24,25]



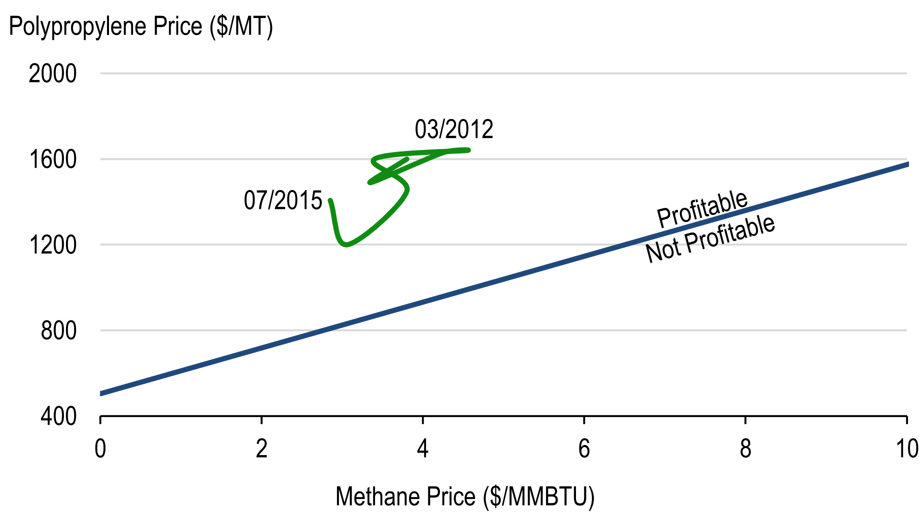
Propylene production in the U.S. is from steam cracking, refinery catalytic-cracking, and propane directly. The use of methane as a feedstock that is different than most producers in the U.S. would enable a unique market position. During the high oil price period in 2014, the margin for producing propylene from methane was higher than the margin for producing propylene from propane.[26] As oil prices have decreased throughout 2015, both margins have fallen, but in the long term natural gas prices have been less volatile and are expected to remain low,[27] while propane prices experience significant variability based on seasonal demand shortages (i.e. the Polar Vortex during the winter of 2013-2014). BASF has announced the potential construction of a methane-to- propylene facility in Freeport, TX with a target start-up in 2019.[28]

C.3.2 Polypropylene

Methane to polypropylene utilizes the same propylene production technologies as the methane to propylene option, but with an added polymerization unit

(LyondellBasell's Spherizone polymerization). A 1 billion metric ton per year (MTA) facility would require 278 MMcfd methane, 34.2 MW electricity, 24 million pounds steam/day, and 3.65 million gallons of process water/day (0.53 million gallons/day of that process water is consumed). The profitability curve for the process compared to market prices of feedstock and final end product is shown in Figure C-4. Polypropylene prices held relatively stable from March 2012 to November 2014 before dropping slightly, but the drop has not been as significant as the overall propylene price drop since March 2012. The more stable polypropylene prices may increase a project's feasibility, despite the added capital cost of a polymerization unit.

Figure C-4: Profitability range for methane to polypropylene manufacturing in this analysis.[25,29]



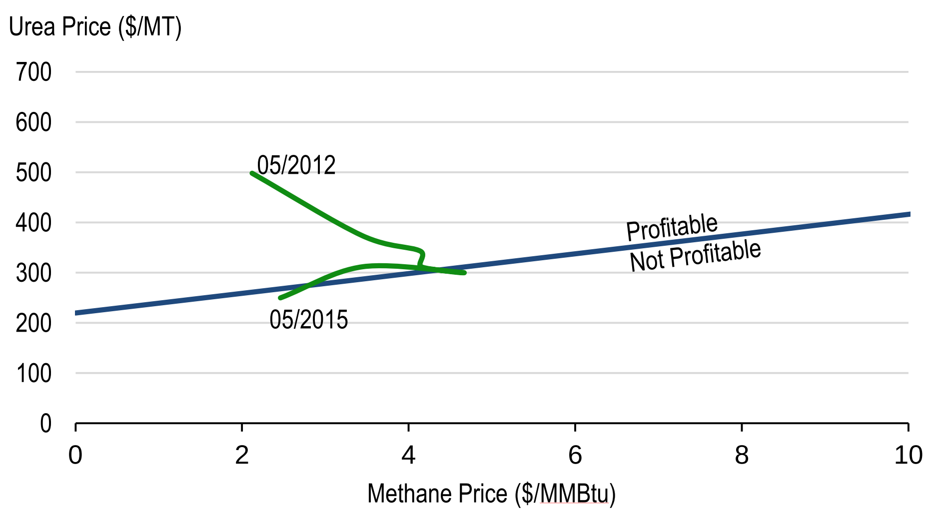
Polypropylene producers in the U.S. use propylene entirely from steam crackers, refinery catalytic-crackers, and directly from propane. Using methane as the primary feedstock would differentiate Four Corners production from others in the U.S.

C.3.3 Urea

Because of the abundant methane supplies in the Four Corners, a 1.27 billion MTA facility is feasible, which would consume 62 MMcfd methane, 10.5 MW electricity, 7.1 million pounds steam/day, and 0.658 million gallons process water/day (0.114 million gallons of that process water is consumed per day). Because ammonia is produced as an intermediate, it is possible to switch production between ammonia and urea fertilizer as market conditions change. Integration of monoammonium phosphate trains is also possible and would increase product diversity.

Since the entire global urea industry utilizes methane as a feedstock, as methane prices have dropped since 2012, urea prices have followed. The profitability curve (Figure C-5) shows that the current price environment is very close to the profitability threshold of this process. The scalability of the technology could enable distributed manufacturing, which may be necessary given water availability or other constraints in the Four Corners.

Figure C-5: Profitability range for methane to urea manufacturing in this analysis.[25,30]



C.4 Technology Comparison

Electricity and process water withdrawal varies drastically between the three potential processes, as shown in Table C-6. During May 2015, total net electricity summer capacity in New Mexico was 8,090 MW.[1] The two largest coal-fired power plants in New Mexico have capacities of 2,100 MW (Four Corners) and 1,643-MW (San Juan). The largest of the proposed chemical manufacturing facilities (polypropylene) would consume approximately 34.2 MW. If all three potential technologies were constructed, electricity consumption would be about 50 MW.

Propylene and polypropylene withdraw the most amount of water of the three technologies. All economic calculations do not include additional costs or utilities associated with treating process water. The process water quantity does not include cooling water or steam requirement. Most process water is demineralized/deionized water.

Table C-6: Comparison of three feasible manufacturing technologies.

	Propylene	**Polypropylene**	**Urea**
Maximum Capacity (MTA)	1,000,000	1,000,000	1,270,000
Methane Consumed (MMcfd)	278	278	62
Electricity Consumed (MW)	4.79	34.2	10.5
Water Consumed (MM gal/d)	0.53	0.53	0.114
Process Water (MM gal/d)	3.02	3.12	0.544
Steam (MM lb/d)	24	24	7.1

The process capacities presented in Table C-6 represent the maximum plant size based on typical world scale production. Propylene and polypropylene use the largest amount of methane. Regional natural gas production in 2015 is shown in Table C-7. The introduction of new methane demand for manufacturing would utilize at most 15% of current processing plant output (for the propylene or polypropylene technologies).

Table C-7: Natural gas processing plant operating data for the six plants in the Four Corners region.[31]

Date	Production (MMcfd)	Processing Plant Operating Rate
January 2015	2,167	89%
February 2015	1,993	82%
March 2015	2,194	91%
April 2015	2,100	87%

C.5 References

1. U.S. Energy Information Administration (EIA), *State Energy Profile: New Mexico*, August 21, 2014, http://www.eia.gov/state/print.cfm?sid=NM (accessed August 18, 2015).

2. Woodcock, K. E.; Gottlieb, M. Natural Gas, In: *Kirk-Othmer Encyclopedia of Chemical Technology*, 2004.

3. International Fertilizer Industry Association, *Fertilizer Outlook 2015-2019*, May 2015, http://www.fertilizer.org/imis20/images/Library_Downloads/2015_ifa_istanbul_summary.pdf?WebsiteKey=411e9724-4bda-422f-abfc-8152ed74f306&=404%3bhttp%3a%2f%2fwww.fertilizer.org%3a80%2fen%2fimages%2fLibrary_Downloads%2f2015_ifa_istanbul_summary.pdf (accessed August 31, 2015).

4. IHS Chemical, *Chemical Economics Handbook: Ammonia, Abstract*, February 2014, https://www.ihs.com/products/ammonia-chemical-economics-handbook.html (accessed August 31, 2015).

5. AmmoniaIndustry.com, http://ammoniaindustry.com/category/ammonia-plants/ (accessed August 31, 2015).

6. IHS Chemical, *Chemical Economics Handbook: Fibers Overview, Abstract*, November 2012, https://www.ihs.com/products/fibers-chemical-economics-handbook.html (accessed August 31, 2015).

7. IHS Chemical, *Chemical Economics Handbook: Nylon Fibers, Abstract*, April 2014, https://www.ihs.com/products/nylon-fibers-chemical-economics-handbook.html (accessed August 31, 2015).

8. IHS Chemical, *Chemical Economics Handbook: Vinyl Acetate, Abstract*, March 2014, https://www.ihs.com/products/vinyl-acetate-chemical-economics-handbook.html (accessed August 31, 2015).

9. Cordeiro, C. F.; Petrocelli, F. P. Vinyl Acetate Polymers, In: *Kirk-Othmer Encyclopedia of Chemical Technology*, 2005.

10. IHS Chemical, *Chemical Economics Handbook: Ethylene, Abstract*, October 2014, https://www.ihs.com/products/ethylene-chemical-economics-handbook.html (accessed August 31, 2015).

11. IHS Chemical, *Chemical Economics Handbook: Propylene, Abstract*, February 2015, https://www.ihs.com/products/propylene-chemical-economics-handbook.html (accessed August 31, 2015).

12. Kissel et al. Polypropylene: Structure, Properties, Manufacturing Processes, and Applications. In H.G. Karian (Ed.) *Handbook of Polypropylene and Polypropylene Composites*, 2003 (page 22).

13. IHS Chemical, *Chemical Economics Handbook: Polypropylene Resins, Abstract*, January 2015, https://www.ihs.com/products/polypropylene-resins-chemical-economics-handbook.html (accessed August 31, 2015).

14. IHS Chemical, *Chemical Economics Handbook: Linear Low-Density Polyethylene (LLDPE) Resins, Abstract,* December 2014, https://www.ihs.com/products/linear-low-density-polyethylene-chemical-economics-handbook.html (accessed August 31, 2015).

15. IHS Chemical, *Chemical Economics Handbook: Polyvinyl Acetate, Abstract*, November 2014, https://www.ihs.com/products/polyvinyl-acetate-chemical-economics-handbook.html (accessed August 31, 2015).

16. IHS Chemical, *Chemical Economics Handbook: Acrylic Resins and Plastics, Abstract*, August 2013, https://www.ihs.com/products/acrylic-resins-chemical-economics-handbook.html (accessed August 31, 2015).

17. IHS Chemical, *Chemical Economics Handbook: Phenol, Abstract*, December 2014, https://www.ihs.com/products/phenol-chemical-economics-handbook.html (accessed August 31, 2015).

18. IHS Chemical, *Chemical Economics Handbook: Acrylonitrile-Butadiene-Styrene Resins (ABS), Abstract,* November 2014, https://www.ihs.com/products/acrylonitrile-butadiene-styrene-chemical-economics-handbook.html (accessed August 31, 2015).

19. IHS Chemical, *Chemical Economics Handbook: Glycol Ethers*, *Abstract*, March 2014, https://www.ihs.com/products/glycol-ethers-chemical-economics-handbook.html (accessed September 1, 2015).

20. *Chemical Engineering*, http://www.chemengonline.com/pci-home (accessed September 2, 2015).

21. *Oil & Gas Journal*, http://www.ogj.com/articles/print/volume-113/issue-1/processing/nelson-farrar-cost-indexes.html (accessed September 2, 2015).

22. American Chemistry Council, *Propylene Product Stewardship Guidance Manual*, January 2007, http://www.lyondellbasell.com/techlit/techlit/3303.pdf (accessed August 21, 2015).

23. Trabish, H. PNM strikes deal to keep coal plant operating through 2022, *UtilityDIVE*, May 5, 2015, http://www.utilitydive.com/news/pnm-strikes-deal-to-keep-coal-plant-operating-through-2022/394042/ (accessed August 31, 2015).

24. Platts McGraw Hill Financial, *Platts Global Propylene Index*, 2012, 2013, 2014, 2015, http://www.platts.com/news-feature/2015/petrochemicals/pgpi/propylene (accessed February 25, 2016).

25. GO-TECH New Mexico Price Sheet http://octane.nmt.edu/gotech/Marketplace/year_prices.aspx?year=2015 (accessed January 12, 2016).

26. RBN Energy, *Got My MTP Working? Making Propylene from Natural Gas?* Sandy Fielden, July 30, 2015.

27. U.S. Energy Information Administration (EIA), *Short-Term Energy Outlook*, August 11, 2015.

28. Chang, J. BASF US methane-topropylene plant targets '19 start-up, *ICIS* News, http://www.icis.com/resources/news/2014/05/02/9777829/basf-us-methane-to-propylene-plant-targets-19-start-up/ (accessed July 27, 2015).

29. Platts McGraw Hill Financial, *Platts Global Polypropylene Index*, 2012, 2013, 2014, 2015, http://www.platts.com/news-feature/2014/petrochemicals/pgpi/polypropylene (accessed February 25, 2016).

30. Urea Know How, http://www.ureaknowhow.com/ukh2/index.php (accessed February 25, 2016).

31. Polston, R. Enterprise Products, communication through Ray Hagerman, Four Corners Economic Development, July 2, 2015.

Appendix D: Four Corners Model Methodology

Supporting Information for Chapter 5

D.1 Agent Methodology

The structure of the agent-based model and firm behavior is illustrated using urea as an example. A urea manufacturing firm is created for each U.S. urea plant. Each seller agent is given a unit production cost based on nameplate capacity. The production cost assumes 2013 raw material prices, and raw material supply is unconstrained, so the production sub-agent (Figure 5-2) can produce a quantity in each time step up to the maximum capacity with no constraints. The production level for each time step is dictated by the strategist sub-agent based on the available space in product storage and the magnitude of orders received. If an order comes in but not enough material is in storage to fulfill the order, the order is denied and the production sub-agent is instructed to increase urea production if possible. A buyer agent for urea fertilizer consumption is created for each county with estimated wholesale fertilizer distribution. The rate of consumption is estimated based on the methodology in the section below. For example, the Maricopa County, AZ urea buying agent seeks to purchase 15,000 MT of urea per year. The buyer sub-agent for Maricopa County demand goes to the urea Market to buy urea. When the material is delivered it is placed in storage, so the buyer sub-agent works to keep the warehouse stocked at a given level. The actual urea consumption occurs when urea is removed from storage and "consumed." Consumption is simulated by a production sub-agent that is similar to the seller's production sub-agent, although with no material produced.

The shipper is a separate agent which ships discrete quantities of urea from one seller to a buyer in the Market. The manufacturer's seller sub-agent ships a product by requesting the shipper to pick up and deliver the material to its destination. The shipper agent uses the transportation network to deliver urea so the cost of delivery is determined based on the transportation mode and distance. Maricopa County, for example, can receive shipments by truck or rail, but not by water. So Maricopa County can only buy urea from a seller that has access to the truck or rail urea Markets. Intermodal transport is included so a shipment can originate on a waterway network and transfer to the truck or rail network for eventual delivery to Maricopa County. The Maricopa County buyer sub-agent attempts to place an order at a supplier that enables the lowest transportation cost (since urea sales at the point of production are uniform at the 2013 average urea price in the baseline scenario so all sellers sell urea the same price). The lowest transportation cost between buyer and seller is based on distance and transport mode. If the order placed by Maricopa County is denied because the seller does not have enough material in storage, the Maricopa County buyer sub-agent continues to contact other sellers on the Market until a desirable sale can be made. Purchases of urea on the Market are subject to constraints such as minimum quantities (wholesale or retail quantities).

The buyer agent can inquire about sales prices and availability on the urea Market before placing an order so is continually able to search for the lowest price available. This behavior is important for simulations where sales price is set entirely by the seller agents and not the 2013 market price. As sellers change prices, exploring profit margin flexibility, each buyer evaluates the price it is willing to pay based on transportation mode, distance, and delivery timing. These individual agent actions of buying and selling discrete quantities of urea that occur for each time step are aggregated to provide the overall results presented in Chapter 5 that represent one year of market operation.

D.2 UREA

The 2013 urea market is simulated by estimating domestic supply, import supply, domestic demand, export demand, and retail and wholesale prices.

D.2.1 Domestic Supply

Urea plant locations and capacities are reported by AmmoniaIndustry.com.[1] Urea production for any plants with missing urea capacity data is estimated by allocating total U.S. 2013 production[2] weighted by the anhydrous ammonia capacity of the plant reported by AmmoniaIndustry.com or USGS 2013 Minerals Yearbook: Ammonia.[3]

The urea unit production cost for each plant was estimated based on the approximate cost of ammonia and then urea production. The ammonia unit cost was calculated using the plant's anhydrous ammonia capacity and the 2012 IHS Chemical Process Economics Program (PEP) Yearbook data for *Ammonia from Natural Gas by Steam Reforming – M.W. Kellogs Improved Process* with an operating rate of 100%. The unit production cost calculated from the 2012 PEP Yearbook is assumed to represent a 2013 production cost. The feedstock natural gas price used is a representative 2013 industrial natural gas price from the U.S. Energy Information Administration (EIA).[4] The unit cost of producing ammonia for each plant was then used as the input ammonia cost for the urea production process. The urea unit production cost was calculated from the 2012 PEP Yearbook data for *Urea, Agricultural Grade, by the Stamicarbon Process* and is assumed to represent a 2013 production cost. For the urea process it was assumed that all existing plants have completely paid off all fixed assets, so the unit operating cost does not contain a fixed cost component. The calculated process costs for five plants (Agrium Borger, CF Industries Woodward, CF Industries Yazoo City, LSB Industries Cherokee, and LSB Industries Pryor) were higher than the approximated wholesale price of urea in 2013. The calculated process costs for these five plants were corrected to reflect the average profit margin of the other plants.

D.2.2 Import Supply

Quantities of urea imports from all countries to the United States were retrieved from the United Nations Comtrade database for commodity 310210 (urea including aqueous solution in packs >10 kg).[5] The trade value in U.S. dollars was divided by the trade quantity to provide an approximate unit price, which is used as the production cost for each import supply node (country). Country locations were approximated as the location of the largest ocean port, river port, or port city in the country. Countries with import quantities that were less than 100 metric tons (MT) during 2013 were removed from the model. The calculated unit cost for imports from Mexico and India are an order of magnitude higher than all other countries. A mass-weighted average unit cost for their global region was used to replace the reported unit cost for the two countries.

To improve resolution of the urea industry in North America, total reported imports from Canada were split up to each province using Canadian Business Patterns data instead of representing Canada as one import node. Approximate magnitude of urea imported from each province was calculated by weighting total Canadian urea imports by the number of chemical fertilizer manufacturing employees in each province (identified by 2012 NAICS 325313).[6]

D.2.3 Domestic Demand

The spatial distribution of urea fertilizer use in the U.S. was calculated using the number of wholesale farm supplies employees in each county to approximate the magnitude of demand. Employee data by county are from the 2013 U.S. Census County Business Pattern data for 2012 NAICS 424910 (farm supplies merchant wholesalers).

The reported number of employees in each county was used to calculate the fraction of total U.S. urea fertilizer demand (5,471,024 MTA in 2013)[2,7] assigned to each county. The county locations used the interpolated coordinate of the county's centroid from the USGS 2013 Gazetteer.[8] Domestic consumption of urea for non-fertilizer use is not included.

D.2.4 Export Demand

Quantities of urea exports by trade partner country were retrieved from the United Nations Comtrade database for commodity 310210 (urea including aqueous solution in packs >10 kg).[5] Country locations were approximated as the location of the largest ocean port, river port, or port city in the country.

To improve resolution of the urea industry in North America, total reported Canadian exports were split up to each province using Canadian Business Patterns data instead of representing Canada as one export node. Approximate magnitude of urea exports to each province was calculated by weighting total urea exports to Canada by the total number of agricultural chemical and other farm supplies merchant wholesalers employees (2012 NAICS Canada 418390) in each province.[9]

D.2.5 Prices

Retail urea prices in the U.S. and Canada vary based on sales region because of differences in fertilizer taxes. The GABLES software places a lower bound on the price difference between demand node regions based on input data. The 2013 average urea price for each region in the U.S. and Canada was calculated using prices reported by Green Markets.[10] Shipment volumes below 10 MT are considered retail, while shipments above 10 MT are considered wholesale. Each region is given historical retail and wholesale prices.

D.3 Propylene

The 2013 propylene market is simulated by estimating domestic supply, import supply, domestic demand, and export demand.

D.3.1 Domestic Supply

Propylene in the U.S. is supplied from fractionation (concentrators/splitters), steam cracking, and propane dehydrogenation (PDH) plants. Refinery production is not included in this model. 2012 propylene plants and their propylene production capacity were reported by ICIS Chemical Business and are assumed to be representative of 2013 suppliers.[11] ICIS does not report the type of propylene production facility, so steam crackers were identified using the Oil & Gas Journal 2013 International Survey of Ethylene from Steam Crackers.[12] Fractionation and PDH units were identified from company websites.

The unit production cost for the PetroLogistics Houston PDH plant (acquired by Flint Hills Resources in 2014) was estimated using the 2012 PEP Yearbook data for *Propylene from Propane by OLEFLEX Dehydrogenation Process* with a production capacity of 544,000 MT/yr. The unit production cost calculated from the 2012 PEP Yearbook is assumed to represent a 2013 production cost.

The unit production costs for the fractionation locations were estimated using the 2012 PEP Yearbook data for *Propylene, Polymer Grade from Refinery Grade Propylene (66 wt % C3H6)* and is assumed to represent a 2013 production cost. There are six fractionation units at Mont Belvieu, with a total capacity of 95 thousand barrels per day (MBPD).[13] It is assumed that all six units are the same capacity, so the economics were calculated for a 660,000 MT/yr unit. Baton Rouge Propylene Concentrator LLC's assets are assumed to be one 23 MBPD unit.[13] The assumed refinery grade propylene purchase cost is $1,257/MT (average of 2013 Q2, Q3, and Q4 prices).[14]

The unit production cost for each steam cracker requires stoichiometric data for the amount of propylene produced per unit of ethylene. The propylene production capacity published by ICIS was divided by the Oil & Gas Journal reported ethylene capacity[12] (which utilizes a typical 2013 feedslate to calculate ethylene capacity) to determine the mass ratio of propylene to ethylene for typical operations during 2013. The unit cost of ethylene production was calculated using the 2012 PEP Yearbook data for *Ethylene from Ethane-Propane by Conventional Cracking/Front-End Deethanization*. The unit production cost calculated from the 2012 PEP Yearbook is assumed to represent a 2013 production cost. Using the stoichiometric ratio calculated for propylene production, the unit cost was converted to a mass propylene basis and corrected for sale of ethylene coproduct using an ethylene price of $1,168/MT.

Three fractionators and two crackers (ExxonMobil Beaumont and Formosa Plastics Point Comfort) had production costs that are greater than the polymer grade propylene market price in 2013 ($1471.14/MT), so their production cost was reduced to reflect the average profit margin from other similar plants. Unlike the urea suppliers, capital costs were included in the propylene unit production cost because many steam crackers in the United States have received investments in recent years to maximize runs of light feedstocks,[15] Enterprise Products Partners' fractionators have been expanded within the last decade,[16] and the Houston PDH plant began operation in October 2010.[17]

D.3.2 Import Supply

Propylene was only imported from Canada in 2013. Propylene import data was retrieved from the United Nations Comtrade database for commodity 290122 (propene/propylene). The trade value in U.S. dollars was divided by the trade quantity to provide an approximate unit price, which was used as the production cost for Canadian imports. The location for Canadian imports was assumed to be Edmonton, Alberta.

D.3.3 Domestic Demand

Propylene is used primarily for the manufacture of polypropylene (PP), propylene oxide, acrylonitrile, cumene, acrylic acid, n-butanol, 2-ethyl hexanol (2-EH), and isopropanol. These eight products represented about 97% of domestic propylene demand in 2014.[18] Propylene demand is estimated at plants where these eight products are produced domestically. To determine the location and capacity of each of these chemical plants that require propylene, the latest available ICIS U.S. Chemical Profile was used. The operating rate of each plant was assumed to be 90% unless more accurate 2013 operating rate data was found. The stoichiometric ratio of propylene required per mass product was from the 2012 IHS Chemical PEP Yearbook. This methodology provided an approximation of the magnitude of propylene demand required by each chemical plant based on product capacity, operating rate, and stoichiometry. The specific sources and assumptions for each propylene demand chemical plant are shown in Table D-1.

Table D-1: Data sources and assumptions for propylene demand at chemical plants.

Chemical	Plant Location Source	Operating Rate (%)	Source
Polypropylene	US Chemical Profile: Polypropylene, ICIS Chemical Business, July 2-15, 2012	79.23	(a)
Propylene oxide	U.S. Chemical Profile: Propylene oxide, ICIS Chemical Business, March 28, 2011	90	Assumed
Acrylonitrile	U.S. Chemical Profile: Acrylonitrile, ICIS Chemical Business, June 30 - July 6, 2014	75.47	(b)
Cumene	U.S. Chemical Profile: Cumene, ICIS Chemical Business, August 15, 2011	85.61	(c)
Acrylic acid	U.S. Chemical Profile: Acrylic acid, ICIS Chemical Business, February 18-24, 2013	90	Assumed
n-Butanol	U.S. Chemical Profile: N-butanol, ICIS Chemical Business, September 23-29, 2013	90	Assumed
2-Ethyl hexanol	U.S. Chemical Profile: 2-EH, ICIS Chemical Business, January 7-13, 2013	90	ICIS
Isopropanol	U.S. Chemical Profile: Isopropanol, ICIS Chemical Business, April 14-20, 2014	90	Assumed

a: Total North America PP production in 2013 was 16,427 million pounds.[19] U.S. PP sales were 84% of the North America total in 2014.[20] The same percentage is assumed to apply to U.S. production and be valid for 2013. Therefore, 84% of 16,427 million pounds gives the approximate U.S. PP production in 2013, which compared to the nameplate capacity gives the apparent operating rate.

b: Total U.S. production of acrylonitrile from ICIS News[21] was compared to the ICIS Chemical Business total reported nameplate capacity.

c: Total U.S. production of cumene in 2012 from ICIS News[22] was scaled to a 2013 production level using the American Chemistry Council U.S. Chemical Production Regional Index, which indicated a 1.2% growth for 2013 as a whole.[23] This total level of production was compared to the ICIS Chemical Business total reported nameplate capacity to calculate an approximate operating rate.

D.3.4 Export Demand

2013 propylene exports were retrieved from the United Nations Comtrade database for commodity 290122 (propene/propylene). Country locations were approximated as the location of the largest ocean port, river port, or port city in the country.

D.4 POLYPROPYLENE

The 2013 polypropylene (PP) market is simulated by estimating domestic supply, import supply, domestic demand, and export demand.

D.4.1 Domestic Supply

Polypropylene plant names and capacities were retrieved from ICIS Chemical Business[24]with specific plants locations retrieved from individual company websites. The unit production cost at each plant was calculated using the 2012 IHS Chemical PEP Yearbook data for *Polypropylene via Bassel's Multizone Circulating Reactor Process* based on the ICIS reported nameplate capacity and a propylene raw material price of $1,471/MT (average polymer grade propylene price for 2013 Q2, Q3, and Q4).[14] The unit production cost calculated from the 2012 PEP Yearbook is assumed to represent a 2013 production cost. It was assumed that all plants have completely paid off all fixed assets, so the unit operating cost does not contain a fixed cost component. The calculated production costs were then scaled to give at most a 10% profit margin from the 2013 PP price.

D.4.2 Import Supply

Polypropylene import data was retrieved from the United Nations Comtrade database for commodity 390210 (polypropylene in primary forms). The trade value in U.S. dollars was divided by the trade quantity to provide an approximate unit price, which was used as the production cost for each import node. The country category "Other Asia" was added to the imports from China. Country locations were approximated as the location of the largest ocean port, river port, or port city in the country. The location for Canadian imports was assumed to be Edmonton, AB.

The calculated unit costs for Nicaragua, New Zealand, Ireland, and Guatemala were an order of magnitude higher than all other countries. To correct the unit costs for these countries, a mass-weighted average unit cost for their global region was calculated and used to replace the reported number.

D.4.3 Domestic Demand

Total polypropylene sales and captive use in the U.S., Mexico, and Canada was 16,396 million pounds in 2013 (7,437,100 MT).[19] U.S. PP sales were 84% of the North America total in 2014.[20] This distribution of U.S. sales in the North America region is assumed to also be valid in 2013. Therefore, total PP sales in the U.S. in 2013 total 6,247,000 MT.

The spatial distribution of PP use was calculated using the number of plastics product manufacturing employees in each county to approximate the magnitude of demand. Employee data by county are from the 2013 U.S. Census County Business Pattern data for 2012 NAICS 3261 (plastics product manufacturing). The NAICS industries included in plastics processing are shown in Table D-2. The reported number of employees in each county was used to calculate the fraction of total U.S. PP demand assigned to each county. The county locations used the interpolated coordinate of the county's centroid from the USGS 2013 Gazetteer.[8]

Table D-2: NAICS industries included in plastics processing demand calculation.

Industry Description	**2012 NAICS Code**
Plastic bag and pouch manufacturing	326111
Plastic film and sheet manufacturing	326114
Unlaminated plastic profile shape manufacturing	326121
Plastic pipe and pipe fitting manufacturing	326122
Laminated plastic plate, sheet (except packaging), and shape manufacturing	326130
Plastic plumbing fixture manufacturing	326191
Motor vehicle plastic parts manufacturing	326193
Plastic window and door manufacturing	326196
All other plastic product manufacturing	326198

D.4.4 Export Demand

U.S. 2013 polypropylene exports were retrieved from the United Nations Comtrade database for commodity 390210 (polypropylene in primary forms). Country locations were approximated as the location of the largest ocean port, river port, or port city in the country.

To improve resolution of the PP industry in North America, total reported Canadian exports were split up to each province using Canadian Business Patterns data instead of representing Canada as one import node. As with domestic PP demand, approximate magnitude of PP exported to each province was calculated by weighting total Canadian PP exports by the number of plastics processing industry employees (2012 NAICS 3261) in each province.[25]

D.5 References

1. AmmoniaIndustry.com, Ammonia Plants in North America, March 2015.
2. U.S. Geological Survey (USGS), *2013 Minerals Yearbook: Nitrogen*, August 2015, http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/myb1-2013-nitro.pdf (accessed September 16, 2015) Table 3.
3. U.S. Geological Survey (USGS), *2013 Minerals Yearbook: Nitrogen*, August 2015, http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/myb1-2013-nitro.pdf (accessed September 16, 2015) Table 4.
4. U.S. Energy Information Administration (EIA), *Natural Gas Prices*, Industrial Price, http://www.eia.gov/dnav/ng/ng_pri_sum_dcu_nus_a.htm (accessed September 16, 2015).
5. United Nations Comtrade Database, http://comtrade.un.org/data/ (accessed February 25, 2016).
6. Statistics Canada, *Table 551-0005 - Canadian business patterns, location counts, employment size and North American Industry Classification System (NAICS), national industries, by Canada and provinces, December 2013, semi-annual,* CANSIM. NAICS 325313 – Chemical fertilizer (except potash) manufacturing, http://www5.statcan.gc.ca/cansim/pick-choisir?lang=eng&p2=33&id=5510005 (accessed September 14, 2015).
7. International Fertilizer Industry Association (IFA), Data, http://ifadata.fertilizer.org/ucSearch.aspx, accessed September 14, 2015.
8. United States Census Bureau, *2013 U.S. Gazetteer Files*, https://www.census.gov/geo/maps-data/data/gazetteer2013.html (accessed February 25, 2016).
9. Statistics Canada, *Table 551-0005 - Canadian business patterns, location counts, employment size and North American Industry Classification System (NAICS), national industries, by Canada and provinces, December 2013, semi-annual,* CANSIM. NAICS 418390 – Agricultural chemical and other farm supplies merchant wholesalers, http://www5.statcan.gc.ca/cansim/pick-choisir?lang=eng&p2=33&id=5510005 (accessed September 14, 2015).
10. Green Markets, http://www.fertilizerpricing.com/, accessed September 14, 2015.
11. ICIS Chemical Business, *Propylene: U.S. Chemical Profile*, 19-25 November 2012, page 35.
12. Koottungal, L. International Survey of Ethylene from Steam Crackers – 2013, *Oil & Gas Journal*, 2013, 111 (*7*), http://www.ogj.com/content/dam/ogj/print-articles/Volume%20111/july-1/International-Survey-of-Ethylene-From-Stream-Crackers.pdf (accessed September 15, 2015).

13. Enterprise Products, *Propylene Fractionation & Services*, http://www.enterprise products.com/operations/propyleneFract.shtm (accessed September 15, 2015).

14. Lippe, D. 2013 ethylene output rises; growth to continue in early 2014, *Oil & Gas Journal*, 2014, 112 (*3*), http://www.ogj.com/articles/print/volume-112/issue-3/ processing/2013-ethylene-output-rises-growth-to-continue-in-early-2014.html (accessed September 16, 2015).

15. RBN Energy, *What's Crackin' with Steam Crackers*, Drill Down Report, September 2014.

16. Enterprise Announces Construction of New Propylene Splitter and Expansion of Propylene Gathering Pipelines, *Houston Chronicle*, March 23, 2006, http:// www.chron.com/news/article/BW-Enterprise-Announces-Construction-of-New-1906915.php (accessed February 25, 2016).

17. Flint Hills Resources, http://www.petrologistics.com/operations.html (accessed February 25, 2016).

18. Plotkin, J. The propylene gap: how can it be filled? *American Chemical Society Cutting-Edge Chemistry*, September 15, 2015, http://www.acs.org/content/acs/en/ pressroom/cutting-edge-chemistry/the-propylene-gap-how-can-it-be-filled.html (accessed December 16, 2015).

19. American Chemistry Council, *U.S. Resin Production & Sales 2014 vs. 2013*, March 2015, http://www.americanchemistry.com/Jobs/EconomicStatistics/Plastics-Statistics/Production-and-Sales-Data-by-Resin.pdf (accessed September 11, 2015).

20. American Chemistry Council, *Year in Review for Resins - 2014, "North American Resins Industry Expands in 2014 Despite Weakness in Key Export Markets"*, https://www.americanchemistry.com/2009-year-in-review (accessed September 11, 2015).

21. Dang, T. US Q4 2013 ACN output up 1.3% year on year - AFPM, *ICIS News*, February 6, 2014, http://www.icis.com/resources/news/2014/02/06/9751006/us-q4-2013-acn-output-up-1-3-year-on-year-afpm/ (accessed September 11, 2015).

22. Dietrich, J. US 2012 cumene production increase 0.2% year on year, *ICIS News*, January 31, 2013, http://www.icis.com/resources/news/2013/01/31/9636780/us-2012-cumene-production-increases-0-2-year-on-year/ (accessed September 11, 2015).

23. American Chemistry Council, *U.S. Chemical Production Expanded in December; 2013 Ends on a High Note*, January 24, 2014, http:// www.americanchemistry.com/Media/PressReleasesTranscripts/ACC-news-

releases/US-Chemical-Production-Expanded-in-December-2013-Ends-on-a-High-Note.html (accessed September 21, 2015).

24. ICIS Chemical Business, *US Chemical Profile: Polypropylene*, July 2-15, 2012.

25. Statistics Canada, *Table 551-0005 - Canadian business patterns, location counts, employment size and North American Industry Classification System (NAICS), national industries, by Canada and provinces, December 2013, semi-annual,* CANSIM. NAICS 326111, 326114, 326121, 326122, 326130, 326191, 326193, 326196, 326198.

Appendix E: Accuracy of Chemical Manufacturing Network Models

The network model in this work is used to identify general trends in pricing and utilization of chemicals and technologies. The results are not forecasts of market behavior or specific technology utilization levels. This Appendix analyzes previously developed network models to assess the accuracy of this semi-quantitative approach.

E.1 1970 Industry Model

Stadtherr and Rudd developed a network model of the 1970 U.S. chemical industry.[1] The first accuracy analysis to consider is if the optimal industry structure as determined by the model represents the actual industry structure. The model's optimal representation of the static 1970 industry was compared to the actual 1970 industry. Of the 124 chemicals in the model, 20 chemicals have a difference in actual and optimal technology. Of these 20 chemicals not accurately represented by the model, 14 chemicals had optimal processes that were the subject of ongoing research at the time. Only six of the 124 chemicals in the model (acetone, ethylene oxide, phenol, ethyl acetate, acetic anhydride, and vinyl acetate) have inaccurate representations of process technologies.[1]

Another accuracy analysis to consider is the choice of objective function. Because of the difficulty in implementing a profit maximization criterion, Stadtherr and Rudd used minimum feedstock consumption as the objective function, as feedstock costs typically dominate production costs and are therefore similar alternatives. Minimizing feedstock costs is not as accurate as minimizing feedstock consumption, because market prices are not necessarily accurate indicators of material value due to integration with petroleum refining.[2]

The optimal industry as determined by the model was then compared to actual industry structure in 1940, 1950, 1960, and 1970 to determine if the optimization criterion of minimizing feedstock consumption accurately reflected industry development. By studying the evolution of the industry, Stadtherr and Rudd showed that "processes not dominant in the actual industry are more likely candidates for eventual importance if they appear in the optimal industry."[2] Minimizing feedstock consumption in these scenarios was the most accurate criteria to track process investments.

The 1970 network model was also used to accurately predict incorporation of new technologies. Four new technologies were introduced to the model industry and two of those processes were determined to be the closest to incorporation based on necessary developments in process yields. The two processes selected by the model were actually in commercialization stages.[3]

E.2 Minimizing Intermediate Chemicals

Chang and Allen utilized a network model to assess the environmental impact of the chemical manufacturing system as a whole.[4] By exploring the trade-off between total industry cost and total use of chlorine, Chang and Allen quantified the impact of lessening chlorinated intermediates on the industry's total production cost. A multi-objective optimization framework was used to screen new technologies that could reduce chlorine use, identifying the magnitude of their impact when considered as part of the integrated industry.

Chang and Allen used a network representation of the 1996 U.S. chemical industry to evaluate six potential technologies to be included with the goal of reducing chlorinated intermediate volumes. Five of the six technologies were integrated into the optimal solution at different utilization levels depending on the objective function. The five technologies are:

- Chlorine via electrolysis of hydrogen chloride (Ker-Chlor process)
- Chlorine via oxidation of hydrogen chloride (HNO_3 catalyst)
- Methylene diphenylene diisocyanate via carbonylation of nitrobenzene
- Toluene diisocyanate via carbonylation of dinitrotoluene
- Polycarbonate via solid-state polymerization.

The motivation for this work was to address technological alternatives for chlorine use in the industry. The results (which potential technologies achieve a reduction in chlorinated intermediates while maintaining capacity to produce all required products) can be compared to actual industry utilization. Chlorine via electrolysis of hydrogen chloride is used throughout the world and was used in the U.S. at a Bayer plant in Baytown, TX[5] and DuPont Corpus Christi.[6] Polycarbonate via solid state polymerization has continued to receive research and commercialization attention.[7,8]

E.3 Price Impacts

The analyses completed in Chapter 3 show that general cost trends are captured by the 2012 network model. For example, the NGL price scenarios showed that as NGL prices decrease, butadiene costs increase. This correctly models the movement of the butadiene market from 2008-2012: as ethane prices dropped more than 50% from 2008-2012, butadiene prices increased 9.29% over the same time period.[9] The \$0.21/lb change in butadiene production cost in the NGL decrease scenario (Table 3-3) is a large portion of the U.S. spot price, which was around \$1.35/lb at the beginning of 2012.[10] The network model does not capture market dynamics so is not used to predict prices.

However, the results can be used to semi-quantitatively assess which chemical supply chains may be impacted by upstream changes in price or supply.

Network models of the chemical industry have been used for a number of different applications as documented in this Appendix and in Chapter 2. These models accurately track general trends in structural evolution, new technology acceptance, and production cost impacts.

E.4 References

1. Stadtherr, M. A.; Rudd, D. F. Systems study of the petrochemical industry. *Chem. Eng. Sci.* 1976, 31, 1019-1028.

2. Stadtherr, M. A.; Rudd, D. F. Resource use by the petrochemical industry. *Chem. Eng. Sci.* 1978, 33, 923-933.

3. Stadtherr, M.A. A Systems Study of the Petrochemical Industry. Ph.D. Thesis. The University of Wisconsin – Madison, Madison, WI, 1976.

4. Chang, D.; Allen, D. T. Minimizing chlorine use: Assessing the trade-offs between cost and chlorine reduction in chemical manufacturing. *J. Ind. Ecol.* 1997, 1, 111−134.

5. Bommaraju, T. V.; Luke, B.; O'Brien, T. F.; Blackburn, M. C. Chlorine. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2002.

6. Chauvel, A.; Lefebvre, G. Petrochemical Processes Technical and Economic Characteristics: 2. Major oxygenated, chlorinated, and nitrated derivatives. Editions Technip: Paris, 1989.

7. Brunelle, D. J.; Smigelski, P. M.; Boden, E. P. Advances in Polycarbonates, *ACS Symposium Series, Vol. 898*, 2009.

8. Brunelle, D. J.; Staff, U. b. Polycarbonates. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2014.

9. IHS Chemical, Process Economics Program Yearbook, 2012.

10. Potter, D.; Choo, C.; Johnson, N. *Butadiene: Defying the Odds to Hit New Heights,* Platts Special Report: Petrochemicals, 2012. http://www.platts.com/IM.Platts.Content/InsightAnalysis/IndustrySolutionPapers/PetchemsButadieneWP.pdf (accessed December 1, 2014).

References

Chapter 1

1. U.S. Energy Information Administration (EIA), *Natural Gas Gross Withdrawals and Production,* http://www.eia.gov/dnav/ng/ng_prod_sum_a_EPG0_FGW_mmcf_m.htm (accessed August 24, 2015).

2. U.S. Energy Information Administration (EIA), *Crude Oil Production*, http://www.eia.gov/dnav/pet/pet_crd_crpdn_adc_mbbl_m.htm (accessed August 24, 2015).

3. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production,* http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_m.htm (accessed August 24, 2015).

4. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production,* http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_m.htm (accessed August 24, 2015).

5. U.S. Energy Information Administration (EIA), *Today in Energy: What are natural gas liquids and how are they used*, April 20, 2012, https://www.eia.gov/todayinenergy/detail.cfm?id=5930 (accessed August 24, 2015).

6. U.S. Energy Information Administration (EIA), *U.S. Natural Gas Plant Field Production*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbblpd_m.htm (accessed August 24, 2015).

7. U.S. Energy Information Administration (EIA), *Hydrocarbon Gas Liquids (HGL): Recent Market Trends and Issues*, November 2014, http://www.eia.gov/analysis/hgl/pdf/hgl.pdf (accessed August 25, 2015).

8. U.S. Energy Information Administration (EIA), *Refinery Net Production (Annual-Thousand Barrels* and *Monthly-Thousand Barrels)*, http://www.eia.gov/dnav/pet/pet_pnp_refp2_dc_nus_mbbl_a.htm (accessed August 25, 2015).

9. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Annual-Thousand Barrels* and *Monthly-Thousand Barrels)*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_a.htm (accessed August 25, 2015).

10. U.S. Energy Information Administration (EIA), *Natural Gas Plant Processing*, http://www.eia.gov/dnav/ng/ng_prod_pp_a_EPG0_ygp_mmcf_a.htm (accessed August 25, 2015).

11. National Petroleum Council, *NPC NGL Study: NGL Supply and Demand through 2035*, Paper #1-13 of the NPC North American Resource Development Study, September 15, 2011.

12. Troner, A. *Natural Gas Liquids in the Shale Revolution*, James A. Baker III Institute for Public Policy, Rice University, April 29, 2013.

13. RBN Energy, *Spotcheck: Gas Processing Frac Spread*, October 2013.

14. U.S. Energy Information Administration (EIA), *Natural Gas Plant Processing (Natural Gas Processed* and *Total Liquids Extracted)*, http://www.eia.gov/dnav/ng/ng_prod_pp_a_EPG0_ygp_MMcf_a.htm (accessed August 25, 2015).

15. Troner, A. *Natural Gas Liquids in the Shale Revolution*, James A. Baker III Institute for Public Policy, Rice University, April 29, 2013.

16. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Monthly-Thousand Barrels per Day*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_r10_mbblpd_m.htm (accessed September 30, 2015).

17. Oil & Gas Journal, *Ethane, polyurethane processing to grow in West Virginia*, November 15, 2013, http://www.ogj.com/articles/2013/11/ethane-polyurethane-processing-to-grow-in-west-virginia.html (accessed September 30, 2015).

18. Shell Appalachian petrochemical project, http://www.shell.us/about-us/projects-and-locations/appalachian-petrochemical-project.html (accessed September 30, 2015).

19. ICIS Chemical Business, *AFPM: Ethane exports begin to build*, March 20, 2015, http://www.icis.com/resources/news/2015/03/20/9869769/afpm-ethane-exports-begin-to-build/ (accessed September 30, 2015).

20. Enterprise Products Partners, L.P., *NGL Pipelines*, http://www.enterpriseproducts.com/operations/nglPipelines.shtm (accessed September 30, 2015).

21. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Monthly-Thousand Barrels per Day*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_r10_mbblpd_m.htm (accessed September 30, 2015).

22. U.S. Energy Information Administration (EIA), *Today in Energy: High value of liquids drives U.S. producers to target wet natural gas resources.* May 8, 2014, http://www.eia.gov/todayinenergy/detail.cfm?id=16191 (accessed August 25, 2015).

23. RBN Energy, *Spotcheck: Ethane to HH Gas Ratio*, July 2015.

24. U.S. Energy Information Administration (EIA), *Today in Energy: High value of liquids drives U.S. producers to target wet natural gas resources.* May 8, 2014, http://www.eia.gov/todayinenergy/detail.cfm?id=16191 (accessed August 25, 2015).

25. U.S. Energy Information Administration (EIA), *Natural Gas Spot and Futures Prices (NYMEX),* http://www.eia.gov/dnav/ng/ng_pri_fut_s1_m.htm (accessed August 25, 2015).

26. U.S. Energy Information Administration (EIA), *Spot Prices – Monthly,* http://www.eia.gov/dnav/pet/pet_pri_spt_s1_m.htm (accessed August 25, 2015).

27. U.S. Energy Information Administration (EIA), *Today in Energy: Midwest propane markets tighten further on cold weather*, January 23, 2014, http://www.eia.gov/todayinenergy/detail.cfm?id=14711 (accessed August 25, 2015).

28. U.S. Energy Information Administration (EIA), *Spot Prices for Crude Oil and Petroleum Products*, http://www.eia.gov/dnav/pet/pet_pri_spt_s1_m.htm (accessed September 22, 2015).

29. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Monthly-Thousand Barrels)*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_m.htm (accessed September 22, 2015).

30. U.S. Energy Information Administration (EIA), *Natural Gas Spot and Futures Prices (NYMEX),* http://www.eia.gov/dnav/ng/ng_pri_fut_s1_m.htm (accessed September 22, 2015).

31. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Annual-Thousand Barrels* and *Monthly-Thousand Barrels)*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_a.htm (accessed August 25, 2015).

32. Enterprise Products Partners, *NGL Pipelines,* http://www.enterpriseproducts.com/operations/nglPipelines.shtm (accessed August 25, 2015).

33. U.S. Energy Information Administration (EIA), *Today in Energy: Without the Cochin pipeline, western Canadian propane seeks new outlets,* March 27, 2015, http://www.eia.gov/todayinenergy/detail.cfm?id=20552 (accessed August 25, 2015).

34. U.S. Energy Information Administration (EIA), *Hydrocarbon Gas Liquids (HGL): Recent Market Trends and Issues*, November 2014, http://www.eia.gov/analysis/hgl/pdf/hgl.pdf (accessed August 25, 2015).

35. U.S. Energy Information Administration (EIA), *Exports (Monthly-Thousand Barrels per Day)*, http://www.eia.gov/dnav/pet/pet_move_exp_dc_NUS-Z00_mbblpd_m.htm (accessed August 25, 2015).

36. National Petroleum Council, *NPC NGL Study: NGL Supply and Demand through 2035*, Paper #1-13 of the NPC North American Resource Development Study, September 15, 2011.

37. American Chemistry Council, *Business of Chemistry Annual Data*, 2015.

38. American Chemistry Council, *U.S. Chemical Investment Linked to Shale Gas: $145 Billion and Counting*, June 2015, http://www.americanchemistry.com/Policy/Energy/Shale-Gas/Fact-Sheet-US-Chemical-Investment-Linked-to-Shale-Gas-145B-and-Counting.pdf (accessed August 28, 2015).

39. Carr, C. *BASF Chemical Evaluates Investment in World-Scale Methane-to-Propylene Complex on U.S. Gulf Coast*, IHS Chemical Research Note, May 5, 2014, https://www.ihs.com/pdf/Research-Note-BASF-Propylene_186332110913049832.pdf (accessed August 28, 2015).

40. RBN Energy, *It's Not Supposed to Be That Way – Part 1*, Drill Down Report, June 2015.

Chapter 2

1. Rudd, D. F.; Fathi-Afshar, S.; Trevino, A. A.; Stadtherr, M. A. *Petrochemical Technology Assessment*; Wiley Series in Chemical Engineering; Wiley: New York, 1981.

2. Chang, D. Minimization of Production Cost and Chlorine Use in the Petrochemical Industry. Master's Thesis, University of California Los Angeles, Los Angeles, CA, 1996.

3. Stadtherr, M.; Rudd, D. F. Systems study of the petrochemical industry. *Chem. Eng. Sci.* 1976, 31, 1019−1028.

4. Stadtherr, M.A. A Systems Study of the Petrochemical Industry. Ph.D. Thesis. The University of Wisconsin – Madison, Madison, WI, 1976.

5. Chang, D.; Allen, D. T. Minimizing chlorine use: Assessing the trade-offs between cost and chlorine reduction in chemical manufacturing. *J. Ind. Ecol.* 1997, 1, 111−134.

6. Al-Sharrah, G. K.; Alatiqi, I.; Elkamel, A.; Alper, E. Planning an integrated petrochemical industry with an environmental objective. *Ind. Eng. Chem. Res.* 2001, 40, 2103−2111.

7. Jimenez, A.; Rudd, D. F.; Meyer, R. R. A study of the development of a Mexican petrochemical industry using mixed-integer programming. *Comput. Chem. Eng.* 1982, 6, 219−229.

8. Fathi-Afshar, S.; Rudd, D. F. The economic impact of new chemical technology. *Chem. Eng. Sci.* 1981, 36, 1421−1425.

9. Sahinidis, N. V.; Grossman, I. E.; Fornari, R. E.; Chathrathi, M. Optimization model for long range planning in the chemical industry. *Comp. Chem. Eng.* 1989, 13, 1049-1063.

10. Sahinidis, N. V.; Grossman, I.E. Multiperiod investment model for processing networks with dedicated and flexible plants. *Ind. Eng. Chem. Res.* 1991, 30, 1165-1171.

11. Norton, L. C.; Grossman, I. E. Strategic planning model for complete process flexibility. *Ind. Eng. Chem. Res.* 1994, 33, 68-76.

12. Bok, J-K; Grossman, I. E.; Park, S. Supply chain optimization in continuous flexible process networks. *Ind. Eng. Chem. Res.* 2000, 39, 1279-1290.

13. North, M. J.; Macal, C. M. *Managing Business Complexity: Discovering Strategic Solutions with Agent-Based Modeling and Simulation*; Oxford University Press: New York, 2007.

14. Garcia-Flores, R.; Wang, X. Z. A multi-agent system for chemical supply chain simulation and management support, *OR Spectrum*, 2002, 24, 343-370.

15. Ito, T.; Mousavi Jahan Abadi, S. M. Agent-based material handling and inventory planning in warehouse, *Journal of Intelligent Manufacturing*, 2002, 13, 201-210.

16. Srinivasan, R.; Bansal, M.; Karimi, I. A. A multi-agent approach to supply chain management in the chemical industry. In B. Chaib-draa and J. Muller (Eds.), *Multiagent Based Supply Chain Management* (p 419-450). Berlin: Springer, 2006.

17. Julka, N.; Karimi, I.; Srinivasan, R. Agent-based supply chain management: Framework and a refinery application. *Comp. Chem. Eng.* 2002, 26, 1755-1769.

18. Ehlen, M. *Economics Definitions, Methods, Models, and Analysis Procedures for Homeland Security Applications*, Sandia National Laboratories SAND2010-4315, Prepared for The Science and Technology Directorate, U.S. Department of Homeland Security Chemical Sector and Resilience Project, January 29, 2010.

19. Ehlen, M. A.; Sun, A. C.; Pepple, M. A.; Eidson, E. D.; Jones, B. S. Chemical supply chain modeling for analysis of homeland security events, *Comp. Chem. Eng.* 2014, 60, 102-111.

20. Vugrin, E. D.; Warren, D. E.; Ehlen, M. A. A resilience assessment framework for infrastructure and economic systems: quantitative and qualitative resilience analysis of petrochemical supply chains to a hurricane, *Process Safety Progress*, 2011, 30.

21. Boudreaux, M. T.; Hoff, A. L. FERC/Not FERC? Determining Jurisdictional Status of NGL Pipeline Service, *Natural Gas & Electricity*. November 2013, 30, 15-20.

22. Declaratory Order re Williams Olefins Feedstock Pipelines, L.L.C., FERC Docket No. OR13-29.

23. Boudreaux, M. T.; Hoff, A. L. FERC/Not FERC? Determining Jurisdictional Status of NGL Pipeline Service, *Natural Gas & Electricity*. November 2013, 30, 15-20.

24. Petition for Declaratory Order of Williams Olefins Feedstock Pipelines, L.L.C., FERC Docket No. OR13-29.

25. 42 USS §6202(3)

26. Supplement No. 1 to 15 CFR Part 754 – Crude Petroleum and Petroleum Products, http://www.ecfr.gov/cgi-bin/text-idx?SID=da7d61ba2719e58b59fd62abf2bde661&mc=true&node=ap15.2.754_17.1&rgn=div9 (accessed September 25, 2015).

27. Kemp, J. Column-History of controls on U.S. oil exports. *Reuters*, October 23, 2014, http://www.reuters.com/article/2014/10/23/usa-oil-export-controls-kemp-idUSL6N0SI37X20141023 (accessed September 25, 2015).

28. Vann, A. Applicability of Federal Export Requirements to Natural Gas Liquids and Condensate [Memorandum]. Senate Committee on Energy and Natural Resources Committee, January 6, 2014, http://www.energy.senate.gov/public/index.cfm/files/serve?File_id=3e18847c-cf43-48f6-ad3a-f8f896a5cc5c (accessed September 25, 2015).

29. U.S. Energy Information Administration (EIA), *Hydrocarbon Gas Liquids (HGL): Recent Market Trends and Issues*, November 2014, http://www.eia.gov/analysis/hgl/pdf/hgl.pdf (accessed September 28, 2015).

30. S. 2086, Sec. 3, http://www.gpo.gov/fdsys/pkg/BILLS-113s2086rfh/pdf/BILLS-113s2086rfh.pdf (accessed September 28, 2015).

31. 49 CFR Chapter III, Parts 390-399.

32. National Propane Gas Association (NPGA), *New law helps propane consumers during winter emergencies; mandates early warning system*, July 1, 2014, https://www.npga.org/i4a/pages/index.cfm?pageid=1867 (accessed September 28, 2015).

33. U.S. Department of Energy, *Heating Oil Reserve*, http://energy.gov/fe/services/petroleum-reserves/heating-oil-reserve (accessed September 28, 2015).

34. Eastman, A. D.; Mears, D. Hydrocarbons, C1-C6. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2000.

35. U.S. Energy Information Administration (EIA), *Blender Net Input*, http://www.eia.gov/dnav/pet/pet_pnp_inpt3_dc_nus_mbblpd_m.htm (accessed January 8, 2015).

36. U.S. Energy Information Administration (EIA), *Integrating Module of the National Energy Modeling System: Model Documentation 2013*, June 2013.

37. U.S. Energy Information Administration (EIA), *Model Documentation Report: Industrial Demand Module of the National Energy Modeling System*, August 2014, http://www.eia.gov/forecasts/aeo/nems/documentation/industrial/pdf/m064(2014).pdf (accessed September 28, 2015).

38. U.S. Energy Information Administration (EIA), *Today in Energy: Bulk chemical feedstock use a key part of increasing industrial energy demand*, May 29, 2015, http://www.eia.gov/todayinenergy/detail.cfm?id=21432 (accessed September 29, 2015).

39. U.S. Energy Information Administration (EIA), *Annual Energy Outlook 2015*, Table: Bulk Chemical Industry Energy Consumption, Case: Reference Case, http://www.eia.gov/beta/aeo/#/?id=38-AEO2015&cases=ref2015 (accessed September 29, 2015).

40. U.S. Energy Information Administration (EIA), *Today in Energy: Bulk chemical feedstock use a key part of increasing industrial energy demand*, May 29, 2015, http://www.eia.gov/todayinenergy/detail.cfm?id=21432 (accessed September 29, 2015).

41. Bentek Energy, *The Future of U.S. Natural Gas: Supply, Demand & Infrastructure Developments*, July 9, 2014. Prepared for the U.S. Department of Energy Quadrennial Energy Review, http://energy.gov/sites/prod/files/2015/04/f22/QER%20Analysis%20-%20The%20Future%20of%20U.S.%20Natural%20Gas%20Supply%2C%20Demand%20%26%20Infrastructure%20Developments.pdf (accessed September 28, 2015).

42. IHS Global, *Oil & Natural Gas Transportation & Storage Infrastructure: Status, Trends, & Economic Benefits*, Prepared for American Petroleum Institute, December 2013, http://www.api.org/~/media/Files/Policy/SOAE-2014/API-Infrastructure-Investment-Study.pdf (accessed September 28, 2015).

43. Interstate Natural Gas Association of America (INGAA) Foundation, *North American Midstream Infrastructure through 2035: Capitalizing on Our Energy Abundance*, Prepared by ICF International, March 18, 2014, http://www.ingaa.org/File.aspx?id=21498 (accessed September 28, 2015).

44. The White House, Office of the Press Secretary, *Presidential Memorandum – Establishing a Quadrennial Energy Review*, https://www.whitehouse.gov/the-press-office/2014/01/09/presidential-memorandum-establishing-quadrennial-energy-review (accessed September 28, 2015).

45. U.S. Department of Energy, QER Report: Energy Transmission, Storage, and Distribution Infrastructure, April 2015, Chapter 4 Page 13, http://energy.gov/sites/prod/files/2015/07/f24/QER%20Full%20Report_TS%26D%20April%202015_0.pdf (accessed September 28, 2015).

46. U.S. Government Accountability Office, Propane and Heating Oil: Federal Oversight of the Propane Education and Research Council and National Oilheat Research Alliance Should Be Strengthened, GAO-10-583, June 2010, http://www.gao.gov/assets/310/306329.pdf (accessed September 28, 2015).

47. RBN Energy, Can't Get Next to You (But Now I Can!) – Propane Supply Growth Close to Largest Centers of Demand, Rusty Braziel, September 1, 2015, https://rbnenergy.com/can-t-get-next-to-you-but-now-i-can-propane-supply-growth-close-to-largest-centers-of-demand (accessed September 28, 2015).

48. RBN Energy, Can't Get Next to You Part 7 – Weather the Next Worst-Case Propane Market Scenario, Sandy Fielden, September 27, 2015, https://rbnenergy.com/can-t-get-next-to-you-part-7-weathering-the-next-worst-case-propane-market-scenario (accessed September 28, 2015).

Chapter 3

1. American Chemistry Council, Business of Chemistry Annual Data, 2013.

2. U.S. Energy Information Administration (EIA), Annual Energy Review 2011.

3. Chang, D. Minimization of Production Cost and Chlorine Use in the Petrochemical Industry. Master's Thesis, University of California Los Angeles, Los Angeles, CA, 1996.

4. Stadtherr, M.; Rudd, D. F. Systems study of the petrochemical industry, *Chem. Eng. Sci.* 1976, 31, 1019– 1028.

5. Rudd, D. F.; Fathi-Afshar, S.; Trevino, A. A.; Stadtherr, M. A. *Petrochemical Technology Assessment*; Wiley Series in Chemical Engineering; Wiley: New York, 1981.

6. Fathi-Afshar, S.; Rudd, D. F. The economic impact of new chemical technology, *Chem. Eng. Sci.* 1981, 36, 1421– 1425.

7. Chang, D.; Allen, D. T. Minimizing chlorine use: Assessing the trade-offs between cost and chlorine reduction in chemical manufacturing, *J. Ind. Ecol.* 1997, 1, 111–134.

8. Fathi-Afshar, S.; Yang, J.-C. Designing the optimal structure of the petrochemical industry for minimum cost and least gross toxicity of chemical production, *Chem. Eng. Sci.* 1985, 40, 781– 797.

9. Al-Sharrah, G. K.; Alatiqi, I.; Elkamel, A.; Alper, E. Planning an integrated petrochemical industry with an environmental objective, *Ind. Eng. Chem. Res.* 2001, 40, 2103– 2111.

10. Jimenez, A.; Rudd, D. F.; Meyer, R. R. A study of the development of a Mexican petrochemical industry using mixed-integer programming, *Comput. Chem. Eng.* 1982, 6, 219– 229.

11. Elia, J.; Baliban, R. C.; Floudas, C. Nationwide, regional, and statewide energy supply chain optimization for natural gas to liquid transportation fuel (GTL) systems, *Ind. Eng. Chem. Res.* 2014, 53, 5366– 5397.

12. U.S. Energy Information Administration (EIA), Annual Energy Outlook 2014.

13. IHS Chemical, Process Economics Program Yearbook, 2012.

14. IHS Chemical, Directory of Chemical Producers, March 1, 2014.

15. Cordeiro, C. F.; Petrocelli, F. P. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons: New York, 2005, 44.

16. U.S. Energy Information Administration (EIA), *Today in Energy: High Value of Liquids Drives U.S. Producers to Target Wet Natural Gas Resources*, May 8,

2014. http://www.eia.gov/todayinenergy/detail.cfm?id=16191 (accessed November 23, 2014).

17. Platts McGraw Hill Financial, Platts Global Benzene Price Index. http://www.platts.com/news-feature/2012/pgpi/benzene (accessed December 1, 2014).

18. Potter, D.; Choo, C.; Johnson, N. *Butadiene: Defying the Odds to Hit New Heights,* Platts Special Report: Petrochemicals, 2012. http://www.platts.com/IM.Platts.Content/InsightAnalysis/IndustrySolutionPapers/PetchemsButadieneWP.pdf (accessed December 1, 2014).

19. Platts McGraw Hill Financial, Platts Global Polypropylene Price Index. http://www.platts.com/news-feature/2012/pgpi/polypropylene (accessed December 1, 2014).

20. BASF, *BASF Evaluates Natural Gas-Based Investment in the United States*. https://www.basf.com/en/company/news-and-media/news-releases/2014/05/p-14-223.html (accessed March 10, 2014).

21. Oil & Gas Journal, *Tesoro plans to boost xylene recovery at US West Coast*. http://www.ogj.com/articles/2014/07/tesoro-plans-to-boost-xylene-recovery-at-us-west-coast.html (accessed March 10, 2014).

22. U.S. Energy Information Administration (EIA), Annual Energy Outlook 2013.

Chapter 4

1. U.S. Energy Information Administration (EIA), *Monthly Energy Review,* September 2015.

2. U.S. Energy Information Administration (EIA), *Today in Energy: Growing U.S. HGL production spurs petrochemical industry investment.* January 29, 2015, http://www.eia.gov/todayinenergy/detail.cfm?id=19771 (accessed Oct 9, 2015).

3. American Chemistry Council, *U.S. Chemical Investment Linked to Shale Gas: $145 Billion and Counting*, June 2015. http://www.americanchemistry.com/Policy/Energy/Shale-Gas/Fact-Sheet-US-Chemical-Investment-Linked-to-Shale-Gas-145B-and-Counting.pdf (accessed Oct 9, 2015).

4. DeRosa, S. E.; Allen, D. T. Impact of natural gas and natural gas liquids supplies on the United States chemical manufacturing industry: production cost effects and identification of bottleneck intermediates. *ACS Sustainable Chem. Eng.* 2015, *3* (3), 451-459.

5. Stadtherr, M. A. A Systems Study of the Petrochemical Industry. Ph.D. Dissertation, The University of Wisconsin-Madison, Madison, WI, 1976.

6. Rudd, D. F.; Fathi-Afshar, S.; Trevino, A. A.; Stadtherr, M. A. *Petrochemical Technology Assessment;* Wiley-Interscience: New York, 1981.

7. Stadtherr, M. A.; Rudd, D. F. Resource use by the petrochemical industry. *Chem. Eng. Sci.* 1978, *33* (7), 923-933.

8. Sokic, M.; Stevancevic, D. The optimal structure of the system of the petrochemical industry. *Chem. Eng. Sci.* 1983, *38* (2), 265-273.

9. Al-Sharrah, G. K.; Alatiqi, A.; Elkamel, A.; Alper E. Planning an integrated petrochemical industry with an environmental objective. *Ind. Eng. Chem. Res.* 2001**,** *40*, 2103-2111.

10. Rudd, D. F.; Fathi-Afshar, S.; Trevino, A. A.; Stadtherr, M. A. *Petrochemical Technology Assessment;* Wiley-Interscience: New York, 1981.

11. Fathi-Afshar, S.; Rudd, D. F. The economic impact of new chemical technology. *Chem. Eng. Sci.* 1981, *36,* 1421-1425.

12. Jimenez, A.; Rudd, D. F.; Meyer, R. R. A study of the development of a Mexican petrochemical industry using mixed-integer programming. *Comp. Chem. Eng.* 1982, *6* (3), 219-229.

13. Jimenez, A.; Rudd, D. F. Use of a recursive mixed-integer programming model to detect an optimal integration sequence for the Mexican petrochemical industry. *Comp. Chem. Eng.* 1987, *11* (3), 291-301.

14. Chang, D.; Allen, D. T. Minimizing chlorine use: assessing the trade-offs between cost and chlorine reduction in chemical manufacturing. *J. Ind. Ecol.* 1997, *1* (2), 11-34.

15. American Chemistry Council, *Business of Chemistry Annual Data*, 2013.

16. Bazaraa, M. S., Jarvis, J. J.; Sherali, H. D. *Linear programming and network flows*; Wiley: Hoboken, NJ, 2011.

17. Farris, M. C.; Mangasarian, O. L; Wright, S. J. *Linear Programming with MATLAB*; MOS-SIAM Series on Optimization; Society for Industrial and Applied Mathematics and Mathematical Programming Society: Philadelphia, PA, 2007.

18. Vanderbei, R. *Linear Programming: Foundations and Extensions*; Springer: New York, 2014.

19. Atkinson, S. E.; Primont, D. Stochastic estimation of firm technology, inefficiency, and productivity growth using shadow cost and distance functions. *J. Econometrics* 2002, *108* (2), 203-225.

20. Lee, S-c; Oh, D-h; Lee, J-d. A new approach to measuring shadow price: Reconciling engineering and economic perspectives. *Energ. Econ.* 2014, *46*, 66-77.

21. Atkinson S. E.; Halvorsen, R. Parametric efficiency tests, economies of scale, and input demand in U.S. electric power generation. *Int. Econ. Rev*. 1984, *25* (3), 647-662.

22. Holmen, A. Direct conversion of methane to fuels and chemicals. *Catal. Today* 2009, *142*, 2-8.

23. Xu, Y.; Bao, X.; Lin, L. Direct conversion of methane under nonoxidative conditions. *J. Catal.* 2003, *216*, 386-395.

24. Ohnishi, R.; Liu, S.; Dong, Q.; Wang, L.; Ichikawa, M. Catalytic dehydrocondensation of methane with CO and CO_2 toward benzene and naphthalene on Mo/HZSM-5 and Fe/Co-modified MO/HZSM-5. *J. Catal.* 1999, *182*, 92-103.

25. Cui, Y.; Xu, Y.; Lu J.; Suzuki, Y.; Zhang, Z-G. The effect of zeolite particle size on the activity of Mo/HZSM-5 in non-oxidative methane dehydroaromatization. *Appl. Catal., A* 2011, *393*, 348-358.

26. Xu, Y.; Lin, L. Recent advances in methane dehydro-aromatization over transition metal ion-modified zeolite catalysts under non-oxidative conditions. *Appl. Catal., A* 1999, *188*, 53-67.

27. Wang, L.; Ohnishi, R.; Ichikawa, M. Selective dehydroaromatization of methane toward benzene on Re/HZSM-5 catalysts and effects of CO/CO_2 addition. *J. Catal.* 2000, *190*, 276-283.

28. Fallas, B. *$5/gal benzene: Here to stay, or recurring but shortlived fad?* Platts, February 6, 2014. http://blogs.platts.com/2014/02/06/high-benzene/ (accessed Oct 2, 2015).

29. Notte, P. The AlphOx process or the one-step hydroxylation of benzene into phenol by nitrous oxide. Understanding and tuning the ZSM-5 catalyst activities. *Top. Catal.* 2000, *13* (4), 387-394.

30. IHS Chemical, Process Economics Program Yearbook, 2012.

Chapter 5

1. U.S. Energy Information Administration (EIA), Annual Energy Outlook 2015.

2. Siirola, J. The impact of shale gas in the chemical industry, *AIChE J.* 2014, 60 (*3*).

3. Swift, T. K.; Moore, M. G. Shale gas brightens outlook for U.S. chemicals, *Chemical Engineering Progress*, January 2013.

4. American Chemistry Council, *Year-End 2015 Chemical Industry Situation and Outlook*, December 2015, http://www.americanchemistry.com/Jobs/Economic Statistics/Year-End-2015-Situation-and-Outlook.pdf (accessed January 8, 2016).

5. State of New Mexico Oil Conservation Division, *Statewide Natural Gas and Oil Production Summary Including Produced Water and Injection by Month*, January 7, 2016, https://wwwapps.emnrd.state.nm.us/ocd/ocdpermitting//Reporting/

Production/ExpandedProductionInjectionSummaryReport.aspx (accessed January 7, 2016).

6. GO-TECH New Mexico Price Sheet http://octane.nmt.edu/gotech/Marketplace/year_prices.aspx?year=2015 (accessed January 12, 2016).

7. U.S. Geological Survey (USGS), *U.S. Coalbed Methane Field Boundaries (2007) in CO & NM*, http://my.usgs.gov/eerma/data/index/4f501131e4b022a71b94a911?q=&facetType=Shapefile (accessed January 12, 2016).

8. U.S. Energy Information Administration (EIA), *Layer Information for Interactive States Maps* https://www.eia.gov/maps/layer_info-m.cfm (accessed January 12, 2016).

9. U.S. Geological Survey (USGS), *National Oil and Gas Assessment - San Juan Basin*, http://energy.usgs.gov/OilGas/AssessmentsData/NationalOilGasAssessment/USBasinSummaries.aspx?provcode=5022 (accessed January 12, 2016).

10. Wooldridge, M.; Jennings, N. R. Intelligent agents: theory and practice, *The Knowledge Engineering Review*, 1995, 10, 115-152.

11. Vugrin, E. D.; Camphouse, R. C.; Downes, P. S.; Ehlen, M. A.; Warren, D. E. Measurement of System Resilience: Application to Chemical Supply Chains, *Proceedings of the 2009 SIAM Conference on 'Mathematics for Industry'*, 2010.

12. North, M. J.; Macal, C. M. *Managing Business Complexity: Discovering Strategic Solutions with Agent-Based Modeling and Simulation*; Oxford University Press: New York, 2007.

13. Ehlen, M. A.; Sun, A. C.; Pepple, M. A.; Eidson, E. D.; Jones, B. S. Chemical supply chain modeling for analysis of homeland security events, *Comp. Chem. Eng*. 2014, 60, 102-111.

14. Julka, N.; Srinivasan, R.; Karimi, I. Agent-based supply chain management – 1: framework, *Comp. Chem. Eng.* 2002, 26, 1755-1769.

15. Garcia-Flores, R.; Wang, X. Z. A multi-agent system for chemical supply chain simulation and management support, *OR Spectrum*, 2002, 24, 343-370.

16. Ito, T.; Mousavi Jahan Abadi, S. M. Agent-based material handling and inventory planning in warehouse, *Journal of Intelligent Manufacturing*, 2002, 13, 201-210.

17. Srinivasan, R.; Bansal, M.; Karimi, I. A. A multi-agent approach to supply chain management in the chemical industry. In B. Chaib-draa and J. Muller (Eds.), *Multiagent Based Supply Chain Management* (p 419-450). Springer: Berlin, 2006.

18. Julka, N.; Karimi, I.; Srinivasan, R. Agent-based supply chain management: Framework and a refinery application. *Comp. Chem. Eng.* 2002, 26, 1755-1769.

19. Sha, M.; Srinivasan, R. Fleet sizing in chemical supply chains using agent-based simulation, *Comp. Chem. Eng.* 2016, 84, 180-198.

20. Ehlen, M. *Economics Definitions, Methods, Models, and Analysis Procedures for Homeland Security Applications*, Sandia National Laboratories SAND2010-4315, Prepared for The Science and Technology Directorate, U.S. Department of Homeland Security Chemical Sector and Resilience Project, January 29, 2010.

21. Vugrin, E. D.; Warren, D. E.; Ehlen, M. A. A resilience assessment framework for infrastructure and economic systems: quantitative and qualitative resilience analysis of petrochemical supply chains to a hurricane, *Process Safety Progress*, 2011, 30 (*3*).

22. PRISM Analytics Corporation, http://www.prismanalytics.net/PRISM_Analytics_Corporation/Home.html (accessed January 13, 2016).

23. IHS Chemical, *Chemical Economics Handbook: Urea, Abstract*, January 2014, https://www.ihs.com/products/urea-chemical-economics-handbook.html (accessed January 21, 2016).

24. IHS Chemical, Process Economics Program Yearbook, 2012.

25. Kelley, L. INEOS declares PP force majeure on feedstock issue, *ICIS News*, December 2, 2015 http://www.icis.com/resources/news/2015/12/02/9949705/ineos-declares-pp-force-majeure-on-feedstock-issue/ (accessed January 20, 2016).

Chapter 6

1. U.S. Energy Information Administration (EIA), *U.S. Natural Gas Plant Field Production*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbblpd_m.htm (accessed August 24, 2015).

2. U.S. Energy Information Administration (EIA), *Hydrocarbon Gas Liquids (HGL): Recent Market Trends and Issues*, November 2014, http://www.eia.gov/analysis/hgl/pdf/hgl.pdf (accessed August 25, 2015).

3. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production (Monthly-Thousand Barrels per Day*, http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_r10_mbblpd_m.htm (accessed September 30, 2015).

4. U.S. Energy Information Administration (EIA), *Today in Energy: High value of liquids drives U.S. producers to target wet natural gas resources.* May 8, 2014, http://www.eia.gov/todayinenergy/detail.cfm?id=16191 (accessed August 25, 2015).

5. The White House, Office of the Press Secretary, *Presidential Memorandum – Establishing a Quadrennial Energy Review*, https://www.whitehouse.gov/the-press-office/2014/01/09/presidential-memorandum-establishing-quadrennial-energy-review (accessed February 25, 2016).

6. U.S. Department of Energy, The Quadrennial Energy Review (QER). http://energy.gov/epsa/quadrennial-energy-review-qer (accessed February 22, 2016).

7. U.S. Energy Information Administration (EIA), *Exports (Monthly-Thousand Barrels per Day)*, http://www.eia.gov/dnav/pet/pet_move_exp_dc_NUS-Z00_mbblpd_m.htm (accessed August 25, 2015).

8. RBN Energy, *It's Not Supposed to Be That Way – Part 1.* Drill Down Report, June 2015.

9. Poten & Partners Ltd., *U.S. Ethane Export – Activity, Challenges and Outlook.* Platts 4th NGLs Conference, September 2014.

10. Van Hull, K. *NGLs and Gas – Pricing, Supply and Demand: An Overview of Current Conditions*, RBN Energy, 8th Annual Midstream Summit, February 19, 2014.

11. RBN Energy, Midstream Infrastructure Database Interface, accessed February 22, 2016.

12. INTEK, Inc. *United States Fuel Resiliency Part II: U.S. Fuels Supply Infrastructure Vulnerability to Natural and Physical Threats*, prepared for Office of Energy Policy and Systems Analysis, U.S. Department of Energy, September 2014.

13. INTEK, Inc. *United States Fuel Resiliency Part III: U.S. Fuels Supply Infrastructure Vulnerabilities and Resiliency*, prepared for Office of Energy Policy and Systems Analysis, U.S. Department of Energy, September 2014.

14. ICF International, *Impact of the Cochin Pipeline Reversal on Consumer Propane Markets in the Midwest*, August 2014, presented by Propane Education & Research Council.

15. U.S. Energy Information Administration (EIA), *Weekly Supply Estimates, Stocks – Propane/Propylene*, https://www.eia.gov/dnav/pet/pet_sum_sndw_a_EPLLPZ_sae_mbbl_w.htm (accessed February 23, 2016).

16. U.S. Department of Energy, The Quadrennial Energy Review (QER). Page 2-38, http://energy.gov/epsa/quadrennial-energy-review-qer (accessed February 22, 2016).

17. U.S. Department of Energy, The Quadrennial Energy Review (QER). Page 6-13, http://energy.gov/epsa/quadrennial-energy-review-qer (accessed February 22, 2016).

18. Pemex, *Statistical Yearbook 2014*, http://www.pemex.com/en/investors/publications/Anuario%20Estadstico%20Archivos/2014_full.pdf (accessed February 22, 2016).

19. Pemex, *Proceso de gas y fraccionamiento de liquidos*, http://www.pemex.com/ri/Publicaciones/Indicadores%20Petroleros/eprocesogas_esp.pdf (accessed February 22, 2016).

20. Pemex, *Volumen de las ventas internas de productos petroliferos y gas natural*, http://www.pemex.com/ri/Publicaciones/Indicadores%20Petroleros/evolumenventas_esp.pdf (accessed February 22, 2016).

21. Pemex, *Volumen de las importaciones de productos petroliferos, gas natural y petroquimicos*, http://www.pemex.com/ri/Publicaciones/Indicadores%20Petroleros/eimporpetro_esp.pdf (accessed February 22, 2016).

22. Carr, H. *Enciende Mi Fuego (Light My Fire) – Moving U.S. LPG to Mexican Consumers*, RBN Energy, August 27, 2015.

23. Fielden, S. *Enciende Mi Fuego (Light My Fire) – LPG Pipelines To and Through Mexico*. RBN Energy, September 29, 2015.

24. Vaughan, V. NuStar, Pemex Plan pipeline project to Northern Mexico, *FuelFix*, October 15, 2014 http://fuelfix.com/blog/2014/10/15/nustar-pemex-plan-pipeline-project-to-northern-mexico/ (accessed February 22, 2016).

25. Sibaja, A. M. *A turning point: defining the future of midstream and downstream activities.* PEMEX Investor Day London, October 29, 2014. http://www.pemex.com/ri/herramientas/pemexday/PemexDay/4_PEMEX%20Day%20London_IT_2014.pdf (accessed February 22, 2016).

26. Carr, H. *Enciende Mi Fuego (Light My Fire) – Opening Up Mexico's LPG Market*, RBN Energy, October 27, 2015.

27. RBN Energy, *Next to You: A Transformation in Propane Markets*, Drill Down Report, October 6, 2015.

28. Brooks, R. Modeling the North American Market for Natural Gas Liquids. *United States Association for Energy Economics Dialogue*, 2013, 21 (*3*).

29. IHS Chemical, *Chemical Economics Handbook: Ethane*, May 2015.

30. IHS Chemical, *Chemical Economics Handbook: Ethylene*.

31. IHS Chemical, *Chemical Economics Handbook: Propane*, October 2012.

32. IHS Chemical, *Chemical Economics Handbook: Propylene.*

33. RBN Energy, *Tailgate Blues: NGL Markets and Natural Gas Processing Economics*, Drill Down Report, August 2014.

Appendix A

1. U.S. Energy Information Administration (EIA), *Natural Gas Annual Respondent Query System*. http://www.eia.gov/cfapps/ngqs/ngqs.cfm?f_report=RP1&f_sortby=&f_items=&f_year_start=&f_year_end=&f_show_compid=&f_fullscreen=.

2. National Energy Technology Laboratory, *Life Cycle Greenhouse Gas Inventory of Natural Gas Extraction , Delivery and Electricity Production*, DOE/NETL-2011-1522, 2011.

3. American Petroleum Institute, *Compendium of greenhouse gas emissions methodologies for the oil and natural gas industry*, 2009.

4. U.S. Energy Information Administration (EIA), *Natural Gas Plant Field Production,* http://www.eia.gov/dnav/pet/pet_pnp_gp_dc_nus_mbbl_m.htm.

5. U.S. Energy Information Administration (EIA), *Refinery & Blender Net Input*, http://www.eia.gov/dnav/pet/pet_pnp_inpt_dc_nus_mbbl_a.htm.

6. U.S. Energy Information Administration (EIA), *Crude Oil Input Qualities,* http://www.eia.gov/dnav/pet/pet_pnp_crq_dcu_nus_m.htm.

7. U.S. Energy Information Administration (EIA), *Refinery Yield*, http://www.eia.gov/dnav/pet/pet_pnp_pct_dc_nus_pct_a.htm.

8. American Chemistry Council, Business of Chemistry Annual Data, 2013.

9. Lackluster year for chemical output. *Chem. Eng. News*. 2013, 91 (*40*), http://cen.acs.org/content/dam/cen/91/26/FF_Production_2013.pdf.

10. US ammonia demand will be robust. *ICIS News*, December 26, 2012, http://www.icis.com/resources/news/2012/12/26/9625085/outlook-13-us-ammonia-demand-will-be-robust/ (accessed May 29, 2014).

11. Toxicology Data Network. http://toxnet.nlm.nih.gov/index.html.

12. U.S. Energy Information Administration (EIA), *Monthly Biodiesel Production Report*, http://www.eia.gov/biofuels/biodiesel/production/.

13. U.S. Energy Information Administration (EIA), *Weekly Refiner & Blender Net Production*, http://www.eia.gov/dnav/pet/pet_pnp_wprodrb_a_epm0f_YPT_mbblpd_w.htm.

14. Chang, D. Minimization of Production Cost and Chlorine Use in the Petrochemical Industry. Master's Thesis, University of California Los Angeles, Los Angeles, CA, 1996.

15. American Chemistry Council, *U.S. Resin Production & Sales*, http://www.americanchemistry.com/Jobs/EconomicStatistics/Plastics-Statistics/Production-and-Sales-Data-by-Resin.pdf (accessed May 29, 2014).

16. American Chemistry Council, *U.S. resins industry strengthens in 2013,* http://www.americanchemistry.com/jobs/economicstatistics/plastics-statistics/year-in-review.pdf (accessed May 29, 2014).

17. IHS Chemical, Directory of Chemical Producers, March 1, 2014. https://www.ihs.com/products/chemical-companies-producers.html (accessed January 2015).

18. Platts McGraw Hill Financial, *Platts Global Benzene Price Index*, http://www.platts.com/news-feature/2012/pgpi/benzene (accessed December 1, 2014).

19. IHS Chemical, Process Economics Program Yearbook, 2012, http://chemical.ihs.com/PEP/yearbook.htm (accessed January 2015).

20. Potter, D.; Choo, C.; Johnson, N. Butadiene: Defying the Odds to Hit New Heights, 2012. *Platts Special Report: Petrochemicals*. http://www.platts.com/IM.Platts.Content/InsightAnalysis/IndustrySolutionPapers/PetchemsButadieneWP.pdf (accessed December 1, 2014).

21. Platts McGraw Hill Financial, *Platts Global Polypropylene Price Index,* http://www.platts.com/news-feature/2012/pgpi/polypropylene (accessed December 1, 2014).

22. BASF evaluates natural gas-based investment in the United States. BASF. http://basf.com/group/pressrelease/P-14-223 (accessed March 10, 2014).

Appendix B

1. Horne, R. E.; Grant, T.; Verghese, K. *Life Cycle Assessment: Principles, Practice, and Prospects.* CSIRO Publishing, 2009.

2. Earles, J. M.; Halog, A. Consequential life cycle assessment: a review. *Int. J. Life Cycle Assess.*, 2011, 16, 445-453.

3. Earles, J. M.; Halog, A.; Ince, P.; Skog, K. Integrated Economic Equilibrium and Life Cycle Assessment Modeling for Policy-based Consequential LCA. *J. Ind. Ecol.* 2013, 17, 375–384.

4. Matthews, H. S.; Small, M. J. Extending the boundaries of life-cycle assessment through environmental economic input-output models. *J. Ind. Ecol.* 2001, 4 (*3*).

5. Carnegie Mellon University Green Design Institute. Economic Input-Output Life Cycle Assessment (EIO-LCA) US 2002 (428 sectors) Producer model, 2016, http://www.eiolca.net/ (accessed 21 Feb, 2016).

6. IHS Chemical, Process Economics Program Yearbook, 2012.

7. Sundaram, K. M.; Shreehan, M. M.; Olszewski, E. F. Ethylene. *Kirk-Othmer Encyclopedia of Chemical Technology,* 2010.

8. Jacobs Consultancy, Hodson Report, January 2014.

9. RBN Energy, What's Crackin with Steam Crackers? Drill Down Report, 2014.

10. Plotkin, J. S. The propylene gap: how can it be filled? *American Chemical Society*, September 14, 2015. http://www.acs.org/content/acs/en/pressroom/cutting-edge-chemistry/the-propylene-gap-how-can-it-be-filled.html (accessed February 16, 2016).

11. Morris, G. Global prices rise as butadiene supply tightens worldwide. *Chemical Week*, 2008, 170 (*17*), 29.

12. Lippe, D. 2013 ethylene output rises; growth to continue in early 2014, *Oil & Gas Journal*, March 3, 2014.

13. Lippe, D. Maintenance slows first-half 2014 US ethylene production, *Oil & Gas Journal*, September 1, 2014.

14. American Chemistry Council, Business of Chemistry Annual Data, 2013.

15. DeRosa, S. E.; Allen, D. T. Impact of Natural Gas and Natural Gas Liquids Supplies on the United States Chemical Manufacturing Industry: Production Cost Effects and Identification of Bottleneck Intermediates. *ACS Sustainable Chem. Eng.* 2015, 3 (*3*), 451-459.

Appendix C

1. U.S. Energy Information Administration (EIA), *State Energy Profile: New Mexico*, August 21, 2014, http://www.eia.gov/state/print.cfm?sid=NM (accessed August 18, 2015).

2. Woodcock, K. E.; Gottlieb, M. Natural Gas, In: *Kirk-Othmer Encyclopedia of Chemical Technology*, 2004.

3. International Fertilizer Industry Association, *Fertilizer Outlook 2015-2019*, May 2015, http://www.fertilizer.org/imis20/images/Library_Downloads/2015_ifa_istanbul_summary.pdf?WebsiteKey=411e9724-4bda-422f-abfc-8152ed74f306&=404%3bhttp%3a%2f%2fwww.fertilizer.org%3a80%2fen%2fimages%2fLibrary_Downloads%2f2015_ifa_istanbul_summary.pdf (accessed August 31, 2015).

4. IHS Chemical, *Chemical Economics Handbook: Ammonia, Abstract*, February 2014, https://www.ihs.com/products/ammonia-chemical-economics-handbook.html (accessed August 31, 2015).

5. AmmoniaIndustry.com, http://ammoniaindustry.com/category/ammonia-plants/ (accessed August 31, 2015).

6. IHS Chemical, *Chemical Economics Handbook: Fibers Overview, Abstract*, November 2012, https://www.ihs.com/products/fibers-chemical-economics-handbook.html (accessed August 31, 2015).

7. IHS Chemical, *Chemical Economics Handbook: Nylon Fibers, Abstract*, April 2014, https://www.ihs.com/products/nylon-fibers-chemical-economics-handbook.html (accessed August 31, 2015).

8. IHS Chemical, *Chemical Economics Handbook: Vinyl Acetate, Abstract*, March 2014, https://www.ihs.com/products/vinyl-acetate-chemical-economics-handbook.html (accessed August 31, 2015).

9. Cordeiro, C. F.; Petrocelli, F. P. Vinyl Acetate Polymers, In: *Kirk-Othmer Encyclopedia of Chemical Technology*, 2005.

10. IHS Chemical, *Chemical Economics Handbook: Ethylene, Abstract*, October 2014, https://www.ihs.com/products/ethylene-chemical-economics-handbook.html (accessed August 31, 2015).

11. IHS Chemical, *Chemical Economics Handbook: Propylene, Abstract*, February 2015, https://www.ihs.com/products/propylene-chemical-economics-handbook.html (accessed August 31, 2015).

12. Kissel et al. Polypropylene: Structure, Properties, Manufacturing Processes, and Applications. In H.G. Karian (Ed.) *Handbook of Polypropylene and Polypropylene Composites*, 2003 (page 22).

13. IHS Chemical, *Chemical Economics Handbook: Polypropylene Resins, Abstract*, January 2015, https://www.ihs.com/products/polypropylene-resins-chemical-economics-handbook.html (accessed August 31, 2015).

14. IHS Chemical, *Chemical Economics Handbook: Linear Low-Density Polyethylene (LLDPE) Resins, Abstract,* December 2014, https://www.ihs.com/products/linear-low-density-polyethylene-chemical-economics-handbook.html (accessed August 31, 2015).

15. IHS Chemical, *Chemical Economics Handbook: Polyvinyl Acetate, Abstract*, November 2014, https://www.ihs.com/products/polyvinyl-acetate-chemical-economics-handbook.html (accessed August 31, 2015).

16. IHS Chemical, *Chemical Economics Handbook: Acrylic Resins and Plastics, Abstract*, August 2013, https://www.ihs.com/products/acrylic-resins-chemical-economics-handbook.html (accessed August 31, 2015).

17. IHS Chemical, *Chemical Economics Handbook: Phenol, Abstract*, December 2014, https://www.ihs.com/products/phenol-chemical-economics-handbook.html (accessed August 31, 2015).

18. IHS Chemical, *Chemical Economics Handbook: Acrylonitrile-Butadiene-Styrene Resins (ABS), Abstract,* November 2014, https://www.ihs.com/products/acrylonitrile-butadiene-styrene-chemical-economics-handbook.html (accessed August 31, 2015).

19. IHS Chemical, *Chemical Economics Handbook: Glycol Ethers*, *Abstract*, March 2014, https://www.ihs.com/products/glycol-ethers-chemical-economics-handbook.html (accessed September 1, 2015).

20. *Chemical Engineering*, http://www.chemengonline.com/pci-home (accessed September 2, 2015).

21. *Oil & Gas Journal*, http://www.ogj.com/articles/print/volume-113/issue-1/processing/nelson-farrar-cost-indexes.html (accessed September 2, 2015).

22. American Chemistry Council, *Propylene Product Stewardship Guidance Manual*, January 2007, http://www.lyondellbasell.com/techlit/techlit/3303.pdf (accessed August 21, 2015).

23. Trabish, H. PNM strikes deal to keep coal plant operating through 2022, *UtilityDIVE*, May 5, 2015, http://www.utilitydive.com/news/pnm-strikes-deal-to-keep-coal-plant-operating-through-2022/394042/ (accessed August 31, 2015).

24. Platts McGraw Hill Financial, *Platts Global Propylene Index*, 2012, 2013, 2014, 2015, http://www.platts.com/news-feature/2015/petrochemicals/pgpi/propylene (accessed February 25, 2016).

25. GO-TECH New Mexico Price Sheet http://octane.nmt.edu/gotech/Marketplace/year_prices.aspx?year=2015 (accessed January 12, 2016).

26. RBN Energy, *Got My MTP Working? Making Propylene from Natural Gas?* Sandy Fielden, July 30, 2015.

27. U.S. Energy Information Administration (EIA), *Short-Term Energy Outlook*, August 11, 2015.

28. Chang, J. BASF US methane-topropylene plant targets '19 start-up, *ICIS* News, http://www.icis.com/resources/news/2014/05/02/9777829/basf-us-methane-to-propylene-plant-targets-19-start-up/ (accessed July 27, 2015).

29. Platts McGraw Hill Financial, *Platts Global Polypropylene Index*, 2012, 2013, 2014, 2015, http://www.platts.com/news-feature/2014/petrochemicals/pgpi/polypropylene (accessed February 25, 2016).

30. Urea Know How, http://www.ureaknowhow.com/ukh2/index.php (accessed February 25, 2016).

31. Polston, R. Enterprise Products, communication through Ray Hagerman, Four Corners Economic Development, July 2, 2015.

Appendix D

1. AmmoniaIndustry.com, Ammonia Plants in North America, March 2015.

2. U.S. Geological Survey (USGS), *2013 Minerals Yearbook: Nitrogen*, August 2015, http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/myb1-2013-nitro.pdf (accessed September 16, 2015) Table 3.

3. U.S. Geological Survey (USGS), *2013 Minerals Yearbook: Nitrogen*, August 2015, http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/myb1-2013-nitro.pdf (accessed September 16, 2015) Table 4.

4. U.S. Energy Information Administration (EIA), *Natural Gas Prices*, Industrial Price, http://www.eia.gov/dnav/ng/ng_pri_sum_dcu_nus_a.htm (accessed September 16, 2015).

5. United Nations Comtrade Database, http://comtrade.un.org/data/ (accessed February 25, 2016).

6. Statistics Canada, *Table 551-0005 - Canadian business patterns, location counts, employment size and North American Industry Classification System (NAICS), national industries, by Canada and provinces, December 2013, semi-annual,* CANSIM. NAICS 325313 – Chemical fertilizer (except potash) manufacturing, http://www5.statcan.gc.ca/cansim/pick-choisir?lang=eng&p2=33&id=5510005 (accessed September 14, 2015).

7. International Fertilizer Industry Association (IFA), Data, http://ifadata.fertilizer.org/ucSearch.aspx, accessed September 14, 2015.

8. United States Census Bureau, *2013 U.S. Gazetteer Files*, https://www.census.gov/geo/maps-data/data/gazetteer2013.html (accessed February 25, 2016).

9. Statistics Canada, *Table 551-0005 - Canadian business patterns, location counts, employment size and North American Industry Classification System (NAICS), national industries, by Canada and provinces, December 2013, semi-annual,* CANSIM. NAICS 418390 – Agricultural chemical and other farm supplies merchant wholesalers, http://www5.statcan.gc.ca/cansim/pick-choisir?lang=eng&p2=33&id=5510005 (accessed September 14, 2015).

10. Green Markets, http://www.fertilizerpricing.com/, accessed September 14, 2015.

11. ICIS Chemical Business, *Propylene: U.S. Chemical Profile*, 19-25 November 2012, page 35.

12. Koottungal, L. International Survey of Ethylene from Steam Crackers – 2013, *Oil & Gas Journal*, 2013, 111 (*7*), http://www.ogj.com/content/dam/ogj/print-articles/Volume%20111/july-1/International-Survey-of-Ethylene-From-Stream-Crackers.pdf (accessed September 15, 2015).

13. Enterprise Products, *Propylene Fractionation & Services*, http://www.enterpriseproducts.com/operations/propyleneFract.shtm (accessed September 15, 2015).

14. Lippe, D. 2013 ethylene output rises; growth to continue in early 2014, *Oil & Gas Journal*, 2014, 112 (*3*), http://www.ogj.com/articles/print/volume-112/issue-3/processing/2013-ethylene-output-rises-growth-to-continue-in-early-2014.html (accessed September 16, 2015).

15. RBN Energy, *What's Crackin' with Steam Crackers*, Drill Down Report, September 2014.

16. Enterprise Announces Construction of New Propylene Splitter and Expansion of Propylene Gathering Pipelines, *Houston Chronicle*, March 23, 2006, http://www.chron.com/news/article/BW-Enterprise-Announces-Construction-of-New-1906915.php (accessed February 25, 2016).

17. Flint Hills Resources, http://www.petrologistics.com/operations.html (accessed February 25, 2016).

18. Plotkin, J. The propylene gap: how can it be filled? *American Chemical Society Cutting-Edge Chemistry*, September 15, 2015, http://www.acs.org/content/acs/en/pressroom/cutting-edge-chemistry/the-propylene-gap-how-can-it-be-filled.html (accessed December 16, 2015).

19. American Chemistry Council, *U.S. Resin Production & Sales 2014 vs. 2013*, March 2015, http://www.americanchemistry.com/Jobs/EconomicStatistics/Plastics-Statistics/Production-and-Sales-Data-by-Resin.pdf (accessed September 11, 2015).

20. American Chemistry Council, *Year in Review for Resins - 2014, "North American Resins Industry Expands in 2014 Despite Weakness in Key Export Markets"*, https://www.americanchemistry.com/2009-year-in-review (accessed September 11, 2015).

21. Dang, T. US Q4 2013 ACN output up 1.3% year on year - AFPM, *ICIS News*, February 6, 2014, http://www.icis.com/resources/news/2014/02/06/9751006/us-q4-2013-acn-output-up-1-3-year-on-year-afpm/ (accessed September 11, 2015).

22. Dietrich, J. US 2012 cumene production increase 0.2% year on year, *ICIS News*, January 31, 2013, http://www.icis.com/resources/news/2013/01/31/9636780/us-2012-cumene-production-increases-0-2-year-on-year/ (accessed September 11, 2015).

23. American Chemistry Council, *U.S. Chemical Production Expanded in December; 2013 Ends on a High Note*, January 24, 2014, http://www.americanchemistry.com/Media/PressReleasesTranscripts/ACC-news-releases/US-Chemical-Production-Expanded-in-December-2013-Ends-on-a-High-Note.html (accessed September 21, 2015).

24. ICIS Chemical Business, *US Chemical Profile: Polypropylene*, July 2-15, 2012.

25. Statistics Canada, *Table 551-0005 - Canadian business patterns, location counts, employment size and North American Industry Classification System (NAICS), national industries, by Canada and provinces, December 2013, semi-annual,* CANSIM. NAICS 326111, 326114, 326121, 326122, 326130, 326191, 326193, 326196, 326198.

Appendix E

1. Stadtherr, M. A.; Rudd, D. F. Systems study of the petrochemical industry. Chem. Eng. Sci. 1976, 31, 1019-1028.

2. Stadtherr, M. A.; Rudd, D. F. Resource use by the petrochemical industry. Chem. Eng. Sci. 1978, 33, 923-933.

3. Stadtherr, M.A. A Systems Study of the Petrochemical Industry. Ph.D. Thesis. The University of Wisconsin – Madison, Madison, WI, 1976.

4. Chang, D.; Allen, D. T. Minimizing chlorine use: Assessing the trade-offs between cost and chlorine reduction in chemical manufacturing. J. Ind. Ecol. 1997, 1, 111−134.

5. Bommaraju, T. V.; Luke, B.; O'Brien, T. F.; Blackburn, M. C. Chlorine. Kirk-Othmer Encyclopedia of Chemical Technology, 2002.

6. Chauvel, A.; Lefebvre, G. Petrochemical Processes Technical and Economic Characteristics: 2. Major oxygenated, chlorinated, and nitrated derivatives. Editions Technip: Paris, 1989.

7. Brunelle, D. J.; Smigelski, P. M.; Boden, E. P. Advances in Polycarbonates, ACS Symposium Series, Vol. 898, 2009.

8. Brunelle, D. J.; Staff, U. b. Polycarbonates. Kirk-Othmer Encyclopedia of Chemical Technology, 2014.

9. IHS Chemical, Process Economics Program Yearbook, 2012.

10. Potter, D.; Choo, C.; Johnson, N. Butadiene: Defying the Odds to Hit New Heights, Platts Special Report: Petrochemicals, 2012. http://www.platts.com/IM.Platts.Content/InsightAnalysis/IndustrySolutionPapers/PetchemsButadieneWP.pdf (accessed December 1, 2014).