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Impact of Natural Gas and Natural Gas Liquids Supplies on the United States Chemical Manufacturing Industry: Production Cost Effects and Identification of Bottleneck Intermediates

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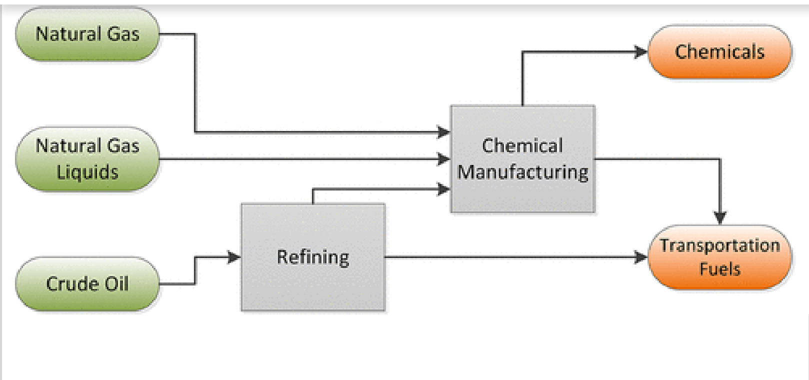
Abstract



A model of the United States petrochemical industry was constructed to explore the chemical manufacturing supply chains that will be impacted by changes in the price and availability of natural gas and natural gas liquids. Production costs of intermediate and end products (polymers, fertilizers, etc.) are impacted, for example, as shale gas production provides expanded primary feedstocks to the chemical industry at a lower cost than petroleum processing. The predicted impact of changes in natural gas and natural gas liquids prices on the production cost and energy intensity of intermediate and final end products is reported. In moving from a 2012 base level group of processes to a variety of long-term projected configurations of chemical manufacturing, acetaldehyde is identified as a potential bottleneck intermediate. Predicted production cost changes in intermediates, such as butadiene, and end products, such as polystyrene, are explored.

Subjects

Aromatic Compounds | Hydrocarbons | Industrial Manufacturing | Materials | Natural Resources

Keywords

Petrochemicals | Shale Gas | Production Cost | Linear Programming | Network Model

Synopsis

The United States chemical manufacturing industry is modeled to determine the impacts of natural gas and natural gas liquid supply and price fluctuations on downstream chemical production costs.

Introduction

Primary feedstocks to the United States 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 United States.

The United States 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

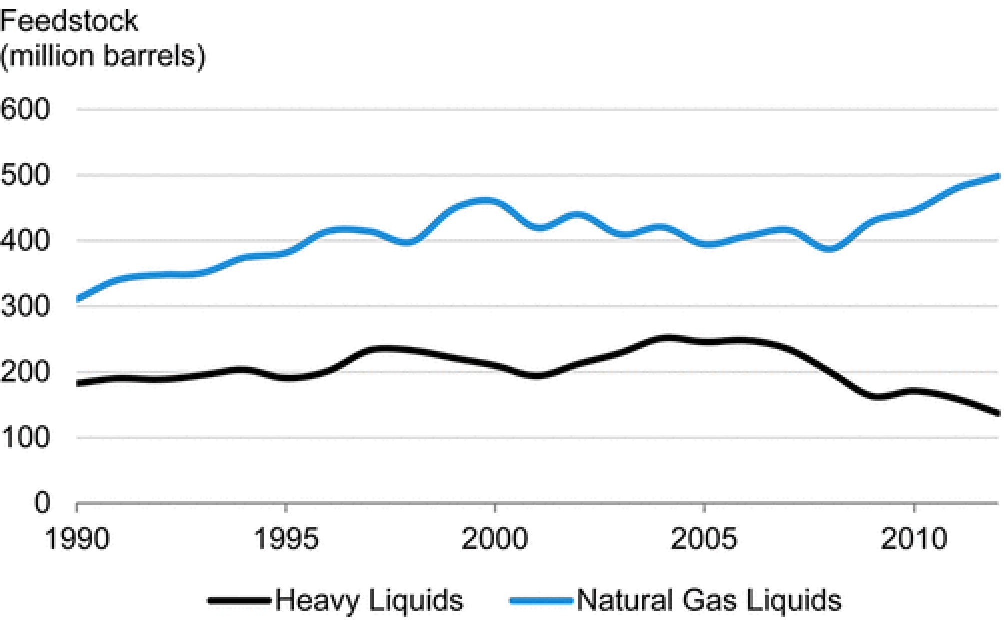


Figure 1. Feedstock sources in the United States chemical manufacturing industry. (1)

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 the natural gas used in the United States 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 United States 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 United States 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.).

Model Development

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 2

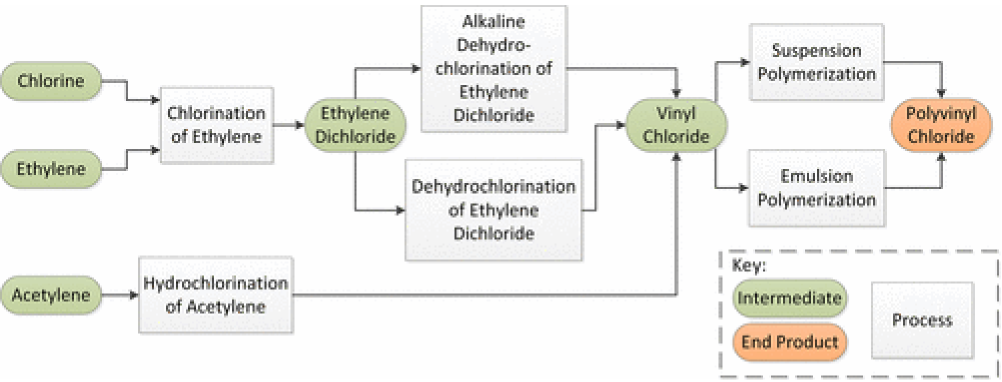


Figure 2. Process pathways to produce polyvinyl chloride (adapted from Chang (3)).

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.

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

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

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 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

$$0 \leq F_i \leq S_i \quad (2)$$

$$Q_i \geq D_i \quad (3)$$

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)

Problem Statement

The problem can be stated as

$$\text{min Total cost} = \sum_j C_j \cdot X_j \quad (4)$$

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 coproduct. 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 the Supporting Information.

The problem is subject to the following material constraints:

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

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

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

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 S3 of the Supporting Information. Supply and demand of all components was constrained using 2012 data, shown in Tables S2 and S3 of the Supporting Information. The

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, will affect downstream process costs. Changes in raw material costs and byproduct credits from the data provided were calculated as

$$\Delta \mathrm{Cost}_{\text{raw materials}} = \sum_{i \cap j} -a_{i,j} \cdot \Delta B_i \quad (8)$$

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 may 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 the Supporting Information. 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.

Model Limitations

The model is designed to be illustrative of industry structure but not to represent individual plants throughout the United States. 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 for which data is available are included.

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 that 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 eq 3. Demand values used are provided in Table S3 of the Supporting Information. The 53 final end products represent 42% of the United States chemical industry shipments in 2012. (1)

Results

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 (nonexclusive) materials show production cost responses when NGL costs change (31 intermediates and 34 final end products), as shown in Tables 1 and 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.

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 United States Energy Information Administration 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 S5, Supporting Information). 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 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 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 m
intermediates		
acetylene	0.22	15
acrylamide	0.00	1.9
acrylic acid (glacial)	0.00	11

adipic acid	0.00	0.73
ammonia	1.2	2.9
1,4-butanediol	0.00	5.2
carbon dioxide	0.00	0.99
carbon monoxide	0.00	9.3
methyl methacrylate	0.00	1.9
nitric acid (60%)	0.00	1.2
synthesis gas (2:1)	0.15	5.5
synthesis gas (3:1)	0.00	7.6
tetrahydrofuran	0.00	−0.14
final end products		
ABS resin	0.15	0.36
ammonium nitrate fertilizer	0.00	1.7
copolyester ether elastomer	1.2	0.10
diammonium phosphate	0.065	0.83
kerosene jet fuel	0.87	3.6
methylene diphenylene isocyanate	0.00	4.1
monoamonium phosphate	0.00	0.52
nitrile barrier resin	0.00	1.7
nylon-6,6 chips	0.00	0.48
polyacrylamide	0.00	1.8
polyacrylate latex	0.00	0.67
polyacrylate pellets	0.00	1.7
polycarbonate	0.28	0.79

polypropylene	0.00	18
polyurethane elastomer	0.00	1.6
SAN resin	0.14	0.49
urea (agricultural grade)	0.00	3.1

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.

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, the 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.

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 United States 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 in polyvinyl acetate plants.

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 United States 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 United States. (14)

Vinyl Acetate

All major vinyl acetate monomer production in the United States 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 United States 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.

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 2. The downstream production cost change of each material affected for these two scenarios is shown in Table 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 2. Natural Gas Liquid Prices Used in Increasing and Decreasing Price Scenarios (in 2012 dollars)

	2012 benchmark price (13)		50% increase in NGL price		50% decrease in NGL price	
material	¢/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. Production Cost Changes from 2012 Levels for Materials Affected by an Increase or 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
ethyl *t*-butyl ether	−1.1	−0.22
ethyl acrylate	7.6	−7.6
ethylbenzene	−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-butyl acrylate	5.7	−5.7
n-butylene	8.6	−9.4
nitrile barrier resin	19	−17
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
poly(methyl 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.

Figure 3

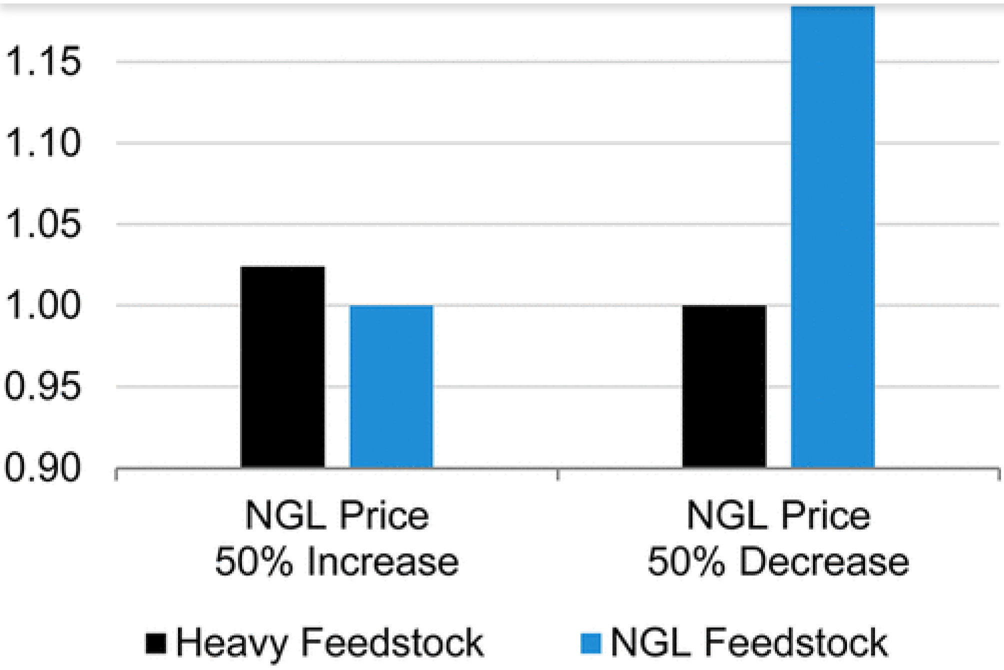


Figure 3. Feedstock utilization in the two NGL price scenarios relative to consumption of each feedstock in the baseline. Heavy feedstocks are all materials derived from crude oil and NGLs are light feedstocks.

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), ethylbenzene, 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 the Supporting Information. Explanations of observed cost changes for adipic acid, benzene, butadiene, *p*-xylene, and propylene are presented below.

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.

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 remaining 10% 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). 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)

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 to 2012; as ethane prices dropped more than 50% from 2008 to 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) is a large portion of the United States 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 United States 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 counterintuitive that byproduct prices would rise. However, the C4 separation from ethane feedstocks generates less value because 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 copolymer, 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.

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 United States, 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.

Propylene

polypropylene cost when methane prices increase (Table 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 toward 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 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 United States. 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.

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.

NGL 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.

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 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 United States, that is changing, is the availability of lighter crude oils (from oils coproduced 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 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.

Conclusion

This systems study of the United States 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 United States. [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 United States 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 United States chemical manufacturing industry.

Supporting Information

List of chemicals included in the model, supply data for raw materials, demand data for end products, description of the solution procedure, and further discussion of the results. This material is available free of charge via the Internet at http://pubs.acs.org.

Effects and Identification of Bottleneck Intermediates

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Abbreviations

ABS	acrylonitrile butadiene styrene
EPDM	ethylene propylene diene monomer
ETBE	ethyl t-butyl ether
EVOH	ethylene vinyl alcohol
HD	high density
lb	pound
LD	low density
LLDPE	linear low density polyethylene
MMBtu	million British thermal units
MTBE	methyl t-butyl ether
NG	natural gas
NGL	natural gas liquid
SAN	styrene-acrylonitrile
VDC-EA-MA	vinylidene chloride-ethyl acetate-methacrylate
VDC-VCM	vinylidene chloride-vinyl chloride monomer

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