INL/RPT-23-72181

Light Water Reactor Sustainability Program

Analysis of Industrial Heat Sources for Hydrogen Production via HTSE

April 2023

U.S. Department of Energy

Office of Nuclear Energy

INL/RPT-23-72181

Analysis of Industrial Heat Sources for Hydrogen Production via HTSE

L. Todd Knighton, Amey Shigrekar, Frederick Joseck, Levi Larsen, Richard Boardman, Idaho National Laboratory

April 2023

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Page intentionally left blank

EXECUTIVE SUMMARY

Interest in the production of hydrogen for use in energy storage and as an energy carrier has increased as the world seeks to decarbonize by using energy that does not release carbon-dioxide or other pollutants into the atmosphere. The DOE Light Water Reactor Sustainability (LWRS) Program has been investigating the integration of hydrogen production with existing light water reactors (LWRs). Because of the size and number of existing reactors, hydrogen could be produced at scale and hydrogen production could also diversify the utility of existing LWRs. LWRs have the potential to produce hydrogen on an industrial scale from a low-carbon-emitting process, while using off-peak energy during changing diurnal cycles caused by the expansion of variable renewable energy (VRE) generation such as solar and wind. Other studies [1, 2] have and continue to evaluate the costs and benefits of extracting heat from existing LWR nuclear reactors to use in combination with electricity for the generation of hydrogen via high-temperature steam electrolysis (HTSE) using a solid oxide electrolysis cell (SOEC) system. Hydrogen production via HTSE can be more efficient than low-temperature electrolysis (LTE) because thermal energy can replace some electricity as part of the energy demand.

The purpose of this current study is to evaluate the merits of using heat from industrial processes to provide the heat required for HTSE hydrogen production while the LWR nuclear power plant (NPP) provides the electricity for the HTSE plant. The advantage of using industrial heat as an alternative would be to alleviate the need to extract heat from an NPP and to allow the NPP to provide the electricity to the HTSE while the HTSE provides the hydrogen needed for the industrial processes. This would accelerate the development of nuclear-integrated hydrogen production by integrating hydrogen production with nuclear without having to extract thermal energy from NPPs. The extraction of thermal energy from NPPs and the associated regulation reviews could then run their course, and thermal energy extraction could be incorporated when ready. In this study the industrial processes of ammonia and synthetic-fuels production were explored in detail. Other industrial processes are mentioned as to the quantity and quality of heat available for hydrogen production but are not analyzed in detail. Some of these industrial processes could provide the heat needed for HTSE but would not demand hydrogen and in such cases the hydrogen produced via HTSE would have to be transported to serve other market demands.

This report provides a broad survey of exothermic industrial processes which produce heat that could be used for hydrogen production via HTSE. It details the quality and quantity of heat available from each source normalized to the mass of product produced, the mass of hydrogen demanded by that product (if applicable), the area of installation (depending on the process), and the levelized cost-of-heat to the extent this could be determined from the literature. A simple levelized cost-of-heat adder was determined to deliver heat from any of these industrial processes which was standardized to a 1 km delivery line and two heat exchangers. This levelized cost-of-heat calculation was roughly the same for each process but individual differences for each process were incorporated as applicable. Heat sources were evaluated and described as to their advantages for use with HTSE, based on the quantity and quality of available heat, opportunity costs of using the heat, and location.

Also presented in this report are detailed examples for NPP-HTSE and ammonia and NPP-HTSE and synthetic-fuels compared to NPP-HTSE alone showing the material and energy balances of an NPP-HTSE plant with hypothetical installations of either an ammonia plant (using either H_2 combustion or a cryogenic air separation unit (ASU) for the N_2 supply) or a synfuels plant within 1 km of the HTSE installation. These example cases show the matchup of NPP electrical capacity, HTSE electricity in MWe and thermal energy in MWth demanded, and the production of hydrogen by the HTSE as well as hydrogen demanded by the ammonia and the synfuels plants. Also determined is the heat generated and used internally by ammonia and synfuels plants and the heat available to be integrated with the HTSE (including any heat in any installation that is used for electricity generation), and the production volume of ammonia and synfuels (naphtha, jet, diesel) paired up with hydrogen production. This analysis is valuable to demonstrate the possibilities of matching ammonia and synthetic-fuels plants with NPP-HTSE

hydrogen production showing the balance of the heat available, the hydrogen and electricity demands, and the excess heat or hydrogen that would be needed in the case of mismatches between the scaling of the various plants.

For an ammonia plant with a capacity of 3360 ton/day of ammonia production, 451.6 MWth of heat is theoretically available from the ammonia reactors. A portion of this heat is necessarily used in feed preheat. Tables ES1, ES2 and Table ES3 show the quantity and quality of heat available from typical ammonia reactors and Fischer-Tropsch (FT) synfuels processes. Some of this heat is used for feed preheating and other internal uses while the remainder can be exported for use in HTSE.

Table ES1. Heat quality generated from typical ammonia reactors with integration of a water splitting electrolyzer with a NPP.

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Nitrogen generator Ammonia Rx	1,815,000 lb/hr.	1,515 psi, 598°F (saturated)
Medium Pressure Steam	Ammonia Rx Let down turbines System heat integration	605,000 lb/hr.	165 psi, 366°F (saturated)
Low Pressure Steam	System heat integration	524,000 lb/hr.	30 psi, 250°F (saturated)

Table ES2. Heat quality generated from typical ammonia reactors with integration of a water splitting electrolyzer with a NPP.

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Natural gas steam methane reformer Ammonia Rx	734,000 lb/hr.	1,515 psi, 598°F (saturated)
Medium Pressure Steam	Ammonia Rx Let down turbines System heat integration	755,000 lb/hr.	165 psi, 366°F (saturated)
Low Pressure Steam	System heat integration	549,000 lb/hr.	30 psi, 250°F (saturated)

Table ES3. Quality and quantity of steam available from an FT synthetic-fuels process.

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Waste-gas boiler	35,000 lb/hr.	1,515 psi, 940°F (superheated)
Low Pressure Steam	FT reactor	35,000 lb/hr.	75 psi, 300°F (saturated)

Based on a modified Aspen HYSYS model, a block flow diagram (BFD) of an ammonia plant integrated with HTSE and an NPP is presented in Figure 23. It is evident that all of the 158 MWth heat required by the 932 MWe/655 MT/d-H_2 HTSE can be met by diverting thermal energy from the ammonia plant balance-of-plant (BOP). This, however, results in a 46 MWe (~29%) reduction in the electricity produced by the ammonia plant's BOP from 159 MWe to 113 MWe, which will have to be taken from the grid.

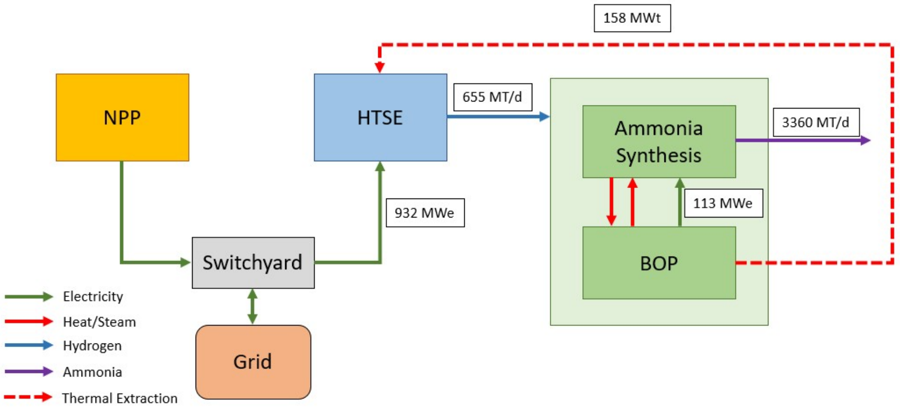


Figure ES1. Simplified baseline BFD for hydrogen-to-ammonia process (without ASU).

Similarly, a BFD for the modified synfuels production plant is presented in Figure ES2. It is evident that all of the 54 MWth heat required by the 317 MWe/223 MT/day-H_2 HTSE plant can be met by diverting thermal energy from the BOP coupled with the FT process. This, however, results in a 9 MWe (56%) drop in electricity produced by the BOP (from 16 MWe to 7 MWe) which can be made up for by using electricity from the grid.

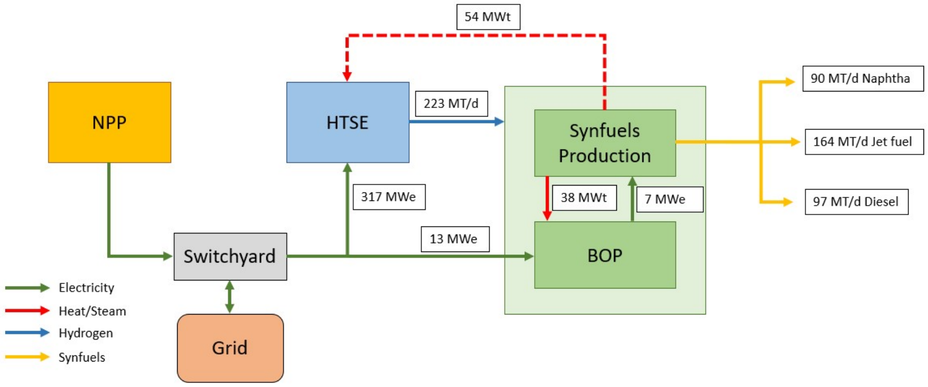


Figure ES2. Simplified baseline BFD for synfuels integrated HTSE hydrogen production.

Page intentionally left blank

CONTENTS

FIGURES

TABLES

Page intentionally left blank

ACRONYMS

ANL	Argonne National Laboratory
ASU	air separation unit
BFD	block flow diagram
BOP	balance-of-plant
CAPEX	capital expenses
DOE	Department of Energy
EIA	Energy Information Administration
FT	Fischer-Tropsch
GTL	gas to liquids
HTGR	high-temperature gas-cooled reactor
HTSE	high-temperature steam electrolysis
IEA	International Energy Agency
INL	Idaho National Laboratory
LCOH	levelized cost of hydrogen
LTE	low-temperature electrolysis
LWR	light water reactors
LWRS	Light Water Reactor Sustainability
NG	natural gas
NGNP	Next Generation Nuclear Plant
NOAK	*n*th of-a kind
NO_x	nitrogen oxides
NPP	nuclear power plant
OPEX	operating expenses
PFD	process flow diagram
RWGS	reverse water-gas shift
SMR	steam methane reforming
SOEC	solid oxide electrolysis cell
TDL	thermal delivery loop
UAN	urea ammonium-nitrate
US	United States
VRE	variable renewable energy

Page intentionally left blank

Analysis of Industrial Heat Sources for Hydrogen Production via HTSE

1. INTRODUCTION

High-temperature steam electrolysis (HTSE) can produce hydrogen at higher efficiency and without precious metal catalysts needed for low-temperature electrolysis (LTE). The higher temperatures allow the reaction kinetics of splitting water to be accelerated. Increased efficiency is also because a large amount of direct thermal energy can be used to preheat feedwater to the electrolysis stack temperatures needed, thus displacing the electrical energy needed for the reaction. This study surveys and compares various industrial processes that could be the source of exothermic reaction or process heat that could be used in HTSE as feed preheat. Other previous reports [1,2] have shown conceptual designs of nuclear power plant (NPP) coupled HTSE hydrogen production where the thermal energy for the HTSE is provided by the NPP. This work builds on that knowledge but instead of using the thermal delivery loop to extract the thermal energy from the NPP for use in the HTSE, the thermal energy is taken from an industrial process. The processes modeled include ammonia and synfuels which themselves need hydrogen, creating a synergistic integration.

First, a survey of industrial processes as potential sources of heat for HTSE is conducted and reported. The focus was on established industries where large amounts of thermal energy are available from either exothermic reactions or process heat. In this survey, the markets and sizes of the various industries are described, as well as the amount of heat available for each process per product generated to give an idea of the scale of thermal energy that might be available. The heat is quantified based on the quantity and quality of the heat available. The heat is accounted for at the point in the process at which it is produced and its current use within the plant and including any exportable heat. It is recognized that most industrial plants try to use excess heat to the largest extent possible for direct heat integration such as feed preheats, reboilers for separation, etc. Any heat not used directly that is sufficient quality can be used in a steam turbine for electricity generation. For this report, any heat that is used in electricity generation was assumed to be exportable heat available for use by an HTSE unit because the direct use of heat is a more efficient use of the energy when there is a use case for it.

Last, example cases are shown for ammonia and synthetic-fuels plants integrated with HTSE hydrogen production. The location of heat extraction from the plants is noted and the heat is identified in quantity and quality available for the HTSE plant. Heat and material balances are shown for the integrated plant to demonstrate the matchup of the product (ammonia or synthetic fuel), hydrogen demand by the process and production by the HTSE, as well as heat and electricity demands of the HTSE. Some preliminary costing is done to compare the options based on the quality and quantity of heat available.

2. SURVEY OF INDUSTRIAL HEAT SOURCES FOR NPP-HTSE

A survey of industrial heat sources of thermal energy for HTSE hydrogen production has been performed. This study focused on identifying industrial exothermic processes, and the quantity and quality of heat they generated. Table 1 provides a summary of the industrial processes, the heat available and the H_2 demand if applicable.

It is noted that many industrial processes are highly heat integrated, and much of the exothermic heat produced in processes is usually used internally e.g. reboiler heat, feed recuperators, etc. This fact is noted and will be commented on as to the percentage of internal heat integration that is typically employed in the various industries surveyed. The heat is usually transferred to steam and then steam is used as the heat "currency" across the plant. Any heat used for electricity production is considered exportable to the HTSE plant for this report. Using the data presented in this section, the analysis in Section 3 shows specific scaling and integrations of the NPP, HTSE, ammonia, and synfuels plants on a heat- and material-balance balance basis to suggest the scales of the plants that would be most advantageous and the surplus or deficit of hydrogen and heat given such an integration.

Table 1. Industrial Heat Sources for HTSE.

Industrial Plant	Annual U.S. Production	Range and Average Plant Capacity	Total Heat Produced	Current Use of heat in the plant (not including electricity generation)	Available Heat for HTSE	H_2 Demand	Notes
Ammonia(Conventional process with natural gas feedstock	14,000,000 MT/yr.	(min-max)[3], average 500,000-3,930,000MT/yr (~1,000,000) MT/yr.	13,300 Btu/kg of product	13,300 Btu/kg of product Preheat Reboiling Reaction	7,500 Btu/kg of product	0.21 kg of H_2/kg of product	Conventional ammonia process that includes urea production
Ammonia (Process with NPP integration with ammonia production)			27,300 Btu/kg of product	27,300 Btu/kg of product Preheat Reboiling Reaction	22,500 Btu/kg of ammonia	0.21 kg of H_2 /kg of product	NPP integration with ammonia production that includes urea production
Synfuels	0	130,000 gal/d	0.02 GJ/kg of total product	Preheat	307.6 GJ/hr.	0.62 kg of H_2/kg of product	FT process only with externally produced H_2
Naphtha	Not reported	90,000 kg/d					
Jet	Not reported	164,000 kg/d					
Diesel	Not reported	97,000 kg/d					
Refineries	17,900,000 bbl/d	(min-max), average	0.6 MM Btu/bbl of crude feedstock	Preheat Reboiling Reaction		500-700 scf/bbl of crude	This information is for a generic complex coking refinery
Methanol	5,730,000 MT/yr.	(min-max), average 1,000,000-1,800,000 MT/yr. (1,400,000 MT/yr)	11,600 Btu/kg of methanol	11,600 Btu/kg of product Preheat Reboiling	11,600 Btu/kg of methanol	0.15-0.2 kg of H_2/kg of methanol product	Conventional methanol includes a natural gas reformer

2.1 Ammonia

2.1.1 Ammonia Market: Production, Pricing, Demand

The fertilizer industry is the largest user of ammonia, accounting for approximately 70% of global ammonia production. This can be in the form of anhydrous ammonia or other forms such as ammonium-nitrate or urea ammonium-nitrate (UAN). Ammonia is a crucial component in the production of nitrogen-based fertilizers, which are used to enhance crop growth and increase agricultural yields. Additionally, it is used as a refrigerant in the food industry and as a chemical feedstock in the production of various chemicals, including plastics, fibers, and nitric acid used in explosives.

Urea, an ammonia derivative that accounts for 55% of ammonia demand, is produced through additional processing where carbon-dioxide is reacted with ammonia. As with ammonia, the fertilizer industry is the largest user of urea, accounting for approximately 90% of global urea demand. Urea is a versatile fertilizer that can be used for a wide range of crops and is also used in animal feed. Additionally, urea is used as a component in the production of various chemicals, including adhesives, resins, and plastics.

Demand for nitrogen-based products such as ammonia and urea has increased in recent years. Since 2010, nitrogen global demand has grown roughly 1.7%. Fertilizer nitrogen[a] demand grew at an average rate of 0.9% while non-fertilizer nitrogen demand grew an average of 4% per year. Ultimately, demand for both ammonia and urea is largely determined by the agriculture industry's needs. When looking specifically at the U.S. these growth numbers are relatively similar. Figure 1. highlights the changes in demand for nitrogen fertilizer between 2000 and 2020. It shows that demand since 2010 has grown an average of 0.79% per year or 3% in total.

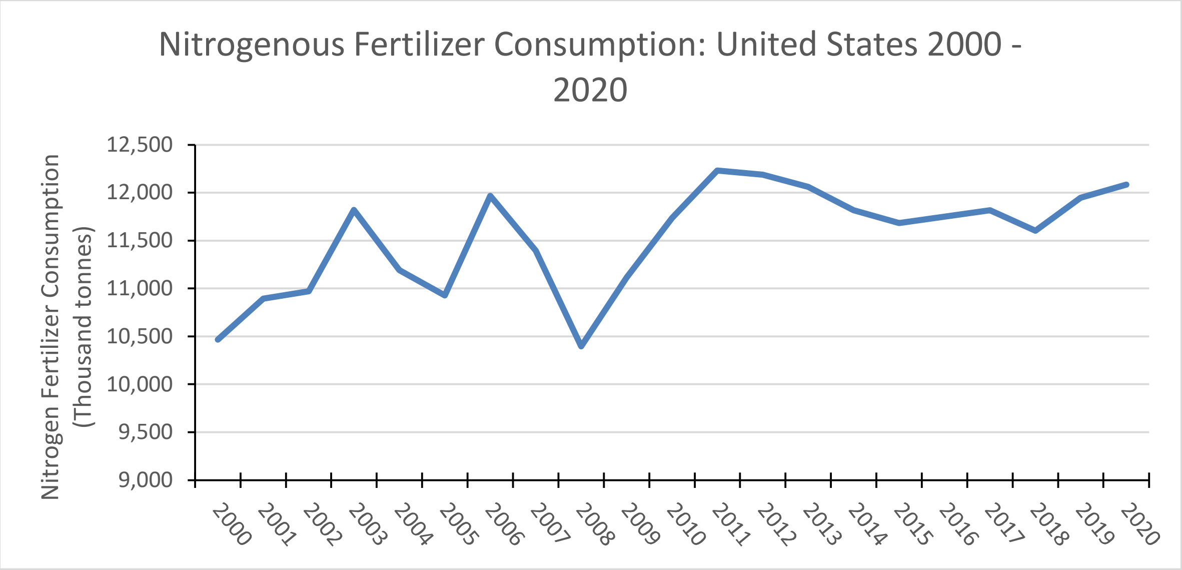


Figure 1. Nitrogenous Fertilizer Consumption, source: International Fertilizer Association.

The Ammonia Technology Roadmap report, produced by the International Energy Agency (IEA), projects that between 2020 and 2050 global nitrogen fertilizer demand will grow at a rate of 1% per year with non-fertilizer nitrogen demand growing at a rate of 1.3% per year. Fertilizer demand is typically

---

[a] Nitrogen fertilizer products encompasses ammonia-based fertilizers and includes ammonia, urea, ammonium nitrate, calcium ammonium nitrate, urea ammonium nitrate, diammonium phosphate, monoammonium phosphate and ammonium sulphate.

driven by a multiplicity of factors including population growth, pricing, rain levels, and crop types, to name a few. As these factors change it is possible for demand to also shift unexpectedly.

The United States fulfills both ammonia and urea demand through a relatively small group of producers. Ammonia in the U.S. is produced by 17 different firms, with CF Industries Inc. being the largest producer providing roughly 40% of the total ~18,124,000 metrics tons of U.S. capacity. Urea is produced by 10 different firms totaling ~12,422,000 metrics tons of annual capacity. CF Industries is also the largest urea producer in the U.S., outputting roughly 50% of total U.S. capacity. Figure 2 illustrates U.S. production capacity of the top five firms for both ammonia and urea. Just under 68% of the ammonia produced in the U.S. comes from four states—Louisiana, Oklahoma, Texas, and Iowa—due to large reserves of natural gas (NG). Subsequently, just over 71% of the urea produced in the U.S. comes from these same four states. See Figure 32 in the appendix for a full breakout of production by state.

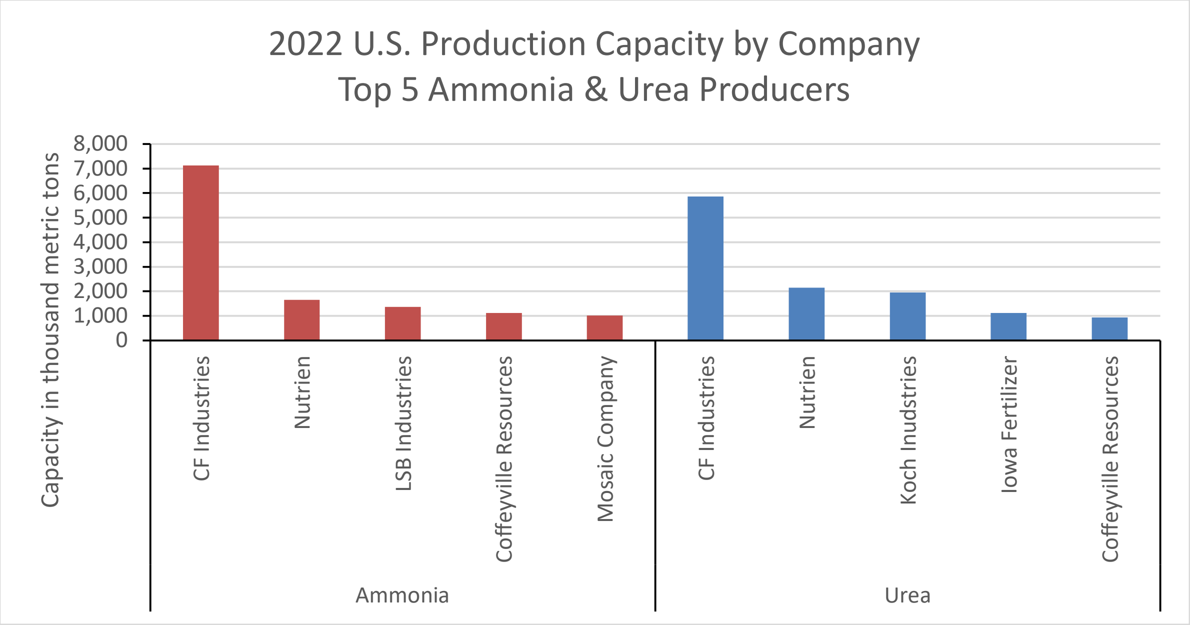


Figure 2. U.S. Ammonia and urea producers by capacity [5].

The major contributing factor to market dynamics and a company's ability to enter a given market is the cost to produce the product and the price at which ammonia and urea can be sold given market demand.

Figure 3 plots the changes in nitrogen fertilizer prices between 2007 and 2022. The two biggest variations in price come first in 2008 during the great recession, and second shortly after the SARS--CoV-2 virus global spread began. It is worth noting that ammonia and urea have different nitrogen contents. Anhydrous ammonia fertilizer has a higher nitrogen content than urea fertilizer, with nitrogen accounting for up to 82% of its weight. Urea fertilizer, on the other hand, typically contains around 46% nitrogen. In Figure 3 price is represented both as USD per metric tonne and USD per pound of nitrogen. Excluding the outlier events, the average global price per metric tonne (USD per pound of nitrogen) in that time period was $279 ($0.30) for urea and $383 ($0.23) for ammonia. During the said period the maximum price was $846 ($0.92) for urea and $1,076 ($0.66) for ammonia, and the minimum price was $181 ($0.20) for urea and $249 ($0.15) for ammonia.

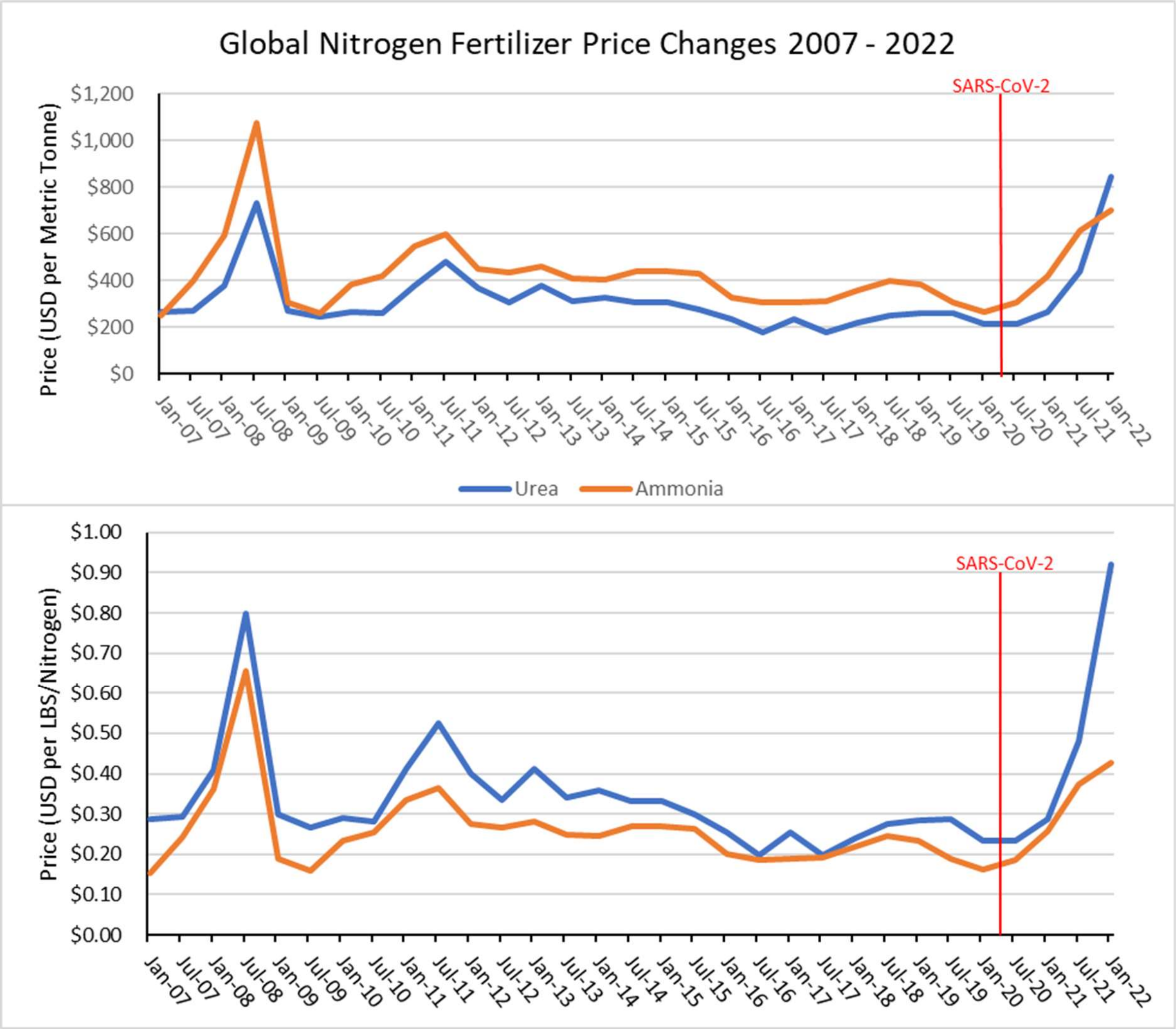


Figure 3. Historical Global Nitrogenous Fertilizer Prices. Source: Bloomberg.

Prices in the United States have behaved similarly, but more recent data looks at how the Russian invasion of Ukraine, which lead to significant U.S. sanctions, has extended the SARS-Cov-2 driven price inflection. Figure 4 shows the U.S. nitrogenous fertilizer price index between 2015 and 2023[b]. In it, red lines are used to show the start of the SARS-Cov-2 pandemic as well as the beginning of the Russian sanctions. According to a Reuters article from 2022, before sanctions Russia accounted for 22% of ammonia and 14% of urea exports globally. Another major contribution to ammonia and urea prices is the price of NG. Due to its role as primary a feedstock (hydrogen production via SMR using NG), the rise and fall of NG will also play a significant role in the price of nitrogenous fertilizers[c].

---

[b] Nitrogenous fertilizers in this data includes synthetic ammonia, nitric acid, ammonium compounds, and urea

[c] 95% of hydrogen in the United States is produced via natural gas steam methane reforming

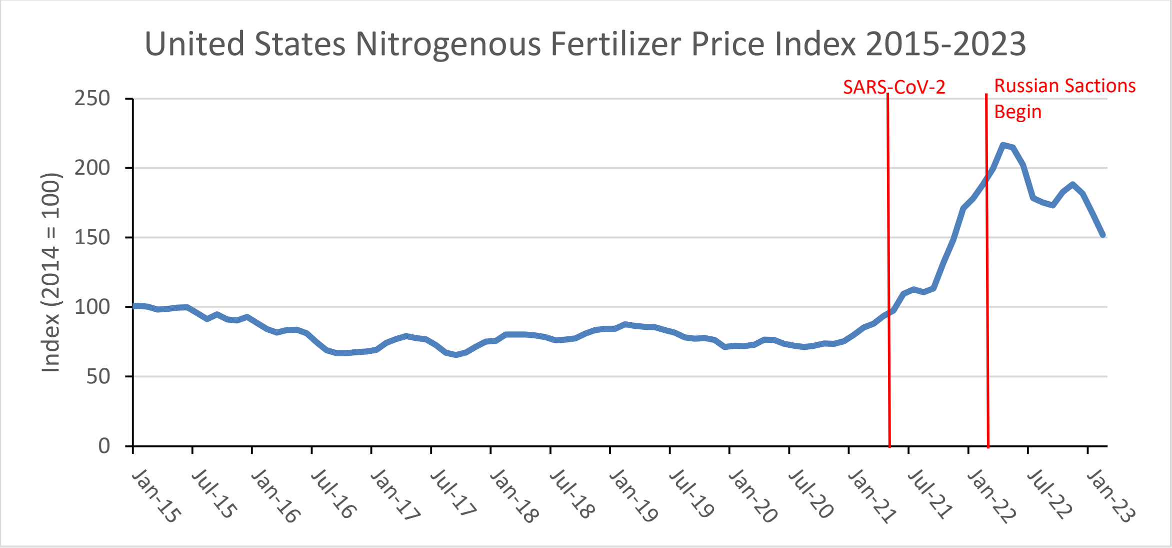


Figure 4. U.S. nitrogenous-fFertilizer price index.[6]

Transportation from ammonia production hubs to demand centers can also impact the cost. As mentioned previously, the existing ammonia production facilities are located almost exclusively where NG supplies and geological storage facilities for both NG and hydrogen are abundant. Figure 5 gives a map showing the regional locations and scale of U.S. ammonia production.

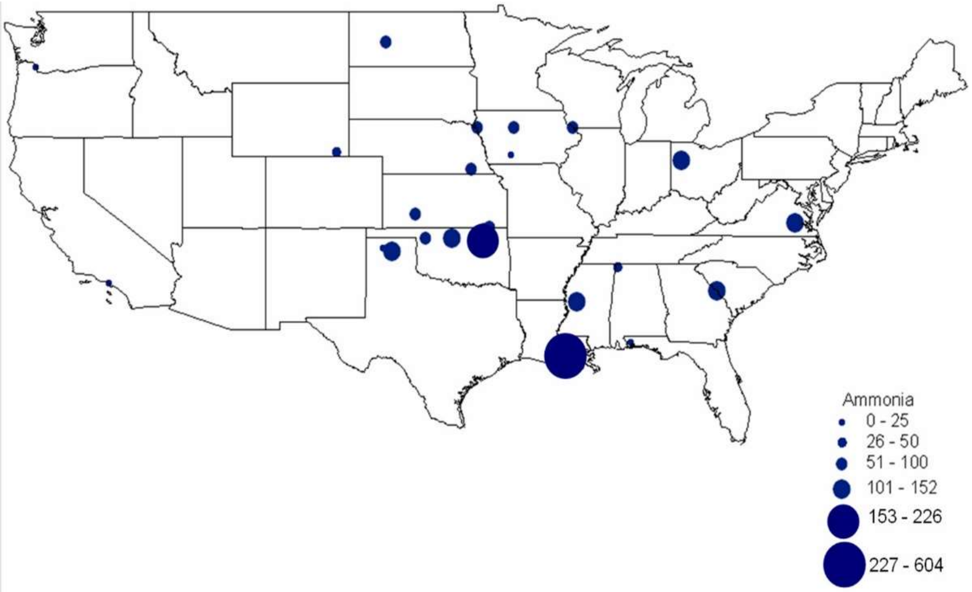


Figure 5. U.S. ammonia production by regional location and scale.[8]

Envision ammonia production by coupling with an NPP and HTSE allows the production of ammonia to be decoupled from NG in both location and price. Placing ammonia production in locations close to demand but far from the existing supply, reduces transportation costs and facilitates additional cost savings. Table 2 presents ammonia transportation costs from different sources. Not included in the table is transportation via pipeline. This method is highly limited; that is, the U.S. ammonia pipeline network is limited.

Table 2. Ammonia transportation costs [9]. Source: National Hydrogen Roadmap.

Ammonia Transportation Costs by Type	
Method	**Cost ($/Tonne-kilometer)**
Truck	$0.33
Rail	$0.04
Shipping	$0.03

It should also be noted that both ammonia and urea, have alternative uses apart from fertilizers. As mentioned previously, these represent a minority share of consumption for both, but shifts in demand in these markets also have the potential to impact prices. Demand shifts in non-fertilizer markets will likely be minimal because usage is predominantly driven by the agricultural industry. It is also possible that demand and prices could shift if ammonia were to be used in new markets. For example, a 2021 article in Chemical Engineering News details the potential for ammonia to be used as a fuel. The article explains that while it is hypothetically possible to use ammonia in marine engines, none are presently capable of using the fuel, and the technology is still far from a broad application. Should such engines be developed, demand for ammonia could increase significantly. It is in cases like this that additional producers would be needed.

Factors to consider when opening new ammonia production near NPPs are similar to those seen in the construction of any greenfield production facility:

- What is the cost to produce the product, and the likely selling price? Is there enough margin between the two for an acceptable return on investment?
- What scale of demand exists for the product?
- What level of existing or forecasted competition exists in the current market?

With the above analysis as context, the following can be concluded about the ammonia and urea markets. Prices appear to be relatively stable, outside of extraordinary events such as recession, war, and pandemics. Thus, producers must be able to manufacture both at or historical averages to be competitive, assuming prices continue to fall to normal pre-pandemic and war levels. Demand for both ammonia and urea are not expected to see substantial gains in the near future. Growth is projected to be slow and steady, and barring any technological developments that open new markets, major swings are not expected in the next 25 years. Finally, competition in both markets is strong. As noted previously, in the U.S. ammonia is produced by 17 firms, with a single firm dominating the national plant capacity. Urea faces even stronger competition with only 10 producers nationally, and the same firm dominating production. Companies looking to enter the ammonia market will likely face some competitive barriers due to monopolistic forces.

2.1.2 Theoretical Heat Available from Ammonia Production

Ammonia is traditionally produced through the Haber-Bosch process. This involves combining purified nitrogen and hydrogen gases under high-pressure and temperature, using a catalyst to promote the reaction between the two gases. The net reaction is shown below:

$$3H_2 + N_2 \leftrightarrow 2NH_3;\ \Delta H\ (500°\mathrm{C}) = -109 \frac{kJ}{mol\ N_2}$$

Per the reaction, there are four mols of reactant for every two mols of product, thus higher pressures favor products and not reactants from an equilibrium perspective. Ammonia is conventionally produced using very high-pressure (~300atm). The reaction is exothermic thus increasing the temperature of the reaction is unfavorable towards producing ammonia from an equilibrium perspective, but the higher temperatures of reaction in the range of 400–500°C are optimal for catalyst activity and also for the overall reaction yield and rate. The exothermic heat from the reaction is usually extracted in various reactor stages to maintain the temperature for optimal catalyst activity without inhibiting the reaction by equilibrium with higher temperatures. This interstage heat extracted between serial reactors can be used within the plant or used for external purposes such as generating electricity or in the case discussed in this report, for use in the production of hydrogen via HTSE. On the basis of ammonia and from the reaction above, 218 kJ/mol of heat are theoretically available. This equates to 3.23 MW_{th}-hr. / ton of ammonia.

For an ammonia plant with a capacity of 3360 ton/day of ammonia production, 451.6 MW_{th} of heat is theoretically available from the ammonia reactors. A portion of this heat is necessarily used in feed preheat.

2.1.3 Ammonia Production: Existing Plant Layouts, Technology, Design

The preparation of nitrogen and hydrogen as feed gas has multiple variations that include steam methane and autothermal reforming followed by a water-gas shift step.[6] A simple generalized BFD of ammonia-synthesis is shown in Figure 6. In this BFD NG is used as the source of hydrogen and combustion with air is the source of nitrogen.

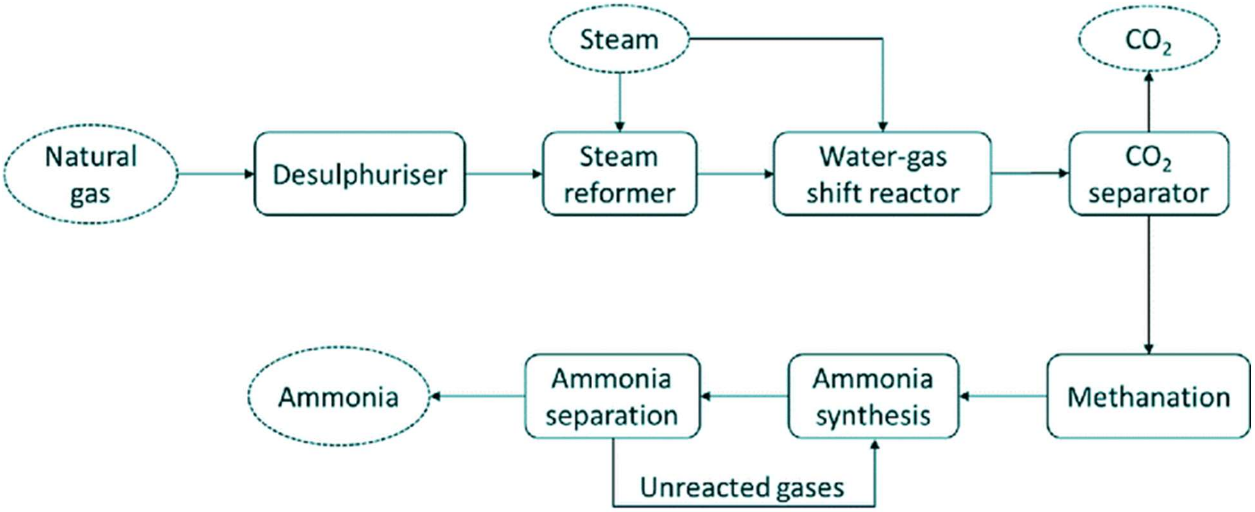


Figure 6. Simplified and generalized BFD of ammonia-synthesis.

The process steps to produce ammonia include the desulfurization of NG; NG is used as feedstock and fuel for the ammonia plant and is supplied from the NG pipeline network. The NG for process feed is directly delivered to the ammonia plant battery limit for use as the ammonia feedstock, and combustion for the feedstock preheater, primary reformer, auxiliary superheater and start-up heater in the ammonia plant. Feed gas goes through a desulfurization step for sulfur removal, prior to conversion to synthesis gas for ammonia production. Figure 7 shows an example of a full process flow diagram (PFD) for ammonia-synthesis.

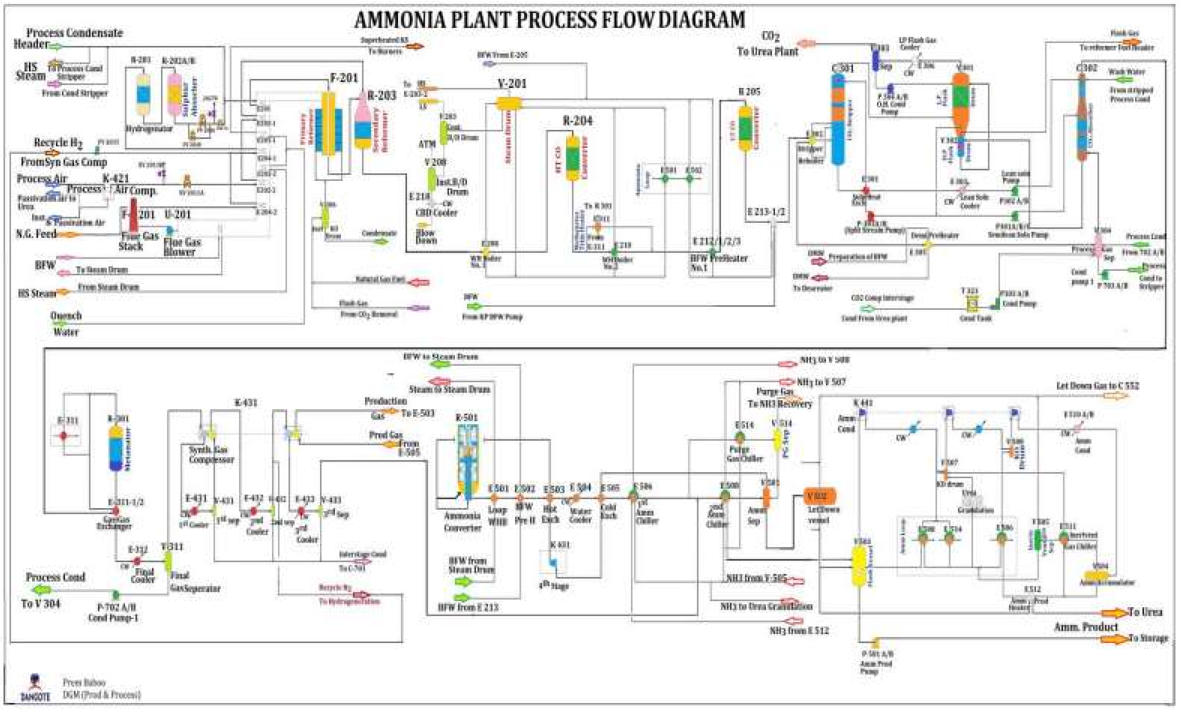


Figure 7. PFD for a typical ammonia plant [7].

NG contains sulfur compounds used to odorize the NG in the pipeline, but which harm the catalyst in the reforming reactor and other reactor systems. These compounds consume hydrogen by undesired side reactions. A packed bed reactor of zinc oxide catalyst is used to remove sulfur. The carbon and hydrogen content of the NG feedstock is converted to carbon-dioxide and hydrogen using steam at high-temperature with a nickel-based catalyst. CO which is formed in the previous process is converted to carbon-dioxide by using steam which results in a shift reaction producing more hydrogen. High and low-shift reactors are arranged for this conversion process.

All the CO_2 carbon-dioxide produced is removed by a liquid absorption process with a series of absorption and stripping towers to recover most of the CO_2 which is used in the production of urea. Any traces of CO_2 and unreacted CO are converted to methane by reacting hydrogen with the carbon oxides using a nickel catalyst in a methanation reactor. Heat is produced in this exothermic reaction. The hydrogen stream is reacted with nitrogen in a series of reactors to produce ammonia. The reactors contain catalysts and operate at high-temperature and pressure for the formation of ammonia.

The ammonia process has high-temperature exothermic reaction systems that are sources of heat energy. Steam is generated from multiple sources. High-pressure steam is generated from heat recovery from the SMR furnace effluent and heat exchange with the ammonia-synthesis reactor. Medium-pressure steam is produced from the heat exchange with shift convertor reactor effluent and the ammonia-synthesis reactor effluent. Table 3 show typical steam quality and quantity generated from the ammonia-synthesis reactors for an ammonia plant production of roughly 3,360 MT/D.

Table 3. Heat quality generated from a typical ammonia reactor assuming integration with an NPP and an HTSE plant for the hydrogen source (no SMR unit).

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Nitrogen generator Ammonia Rx	1,815,000 lb/hr.	1,515 psi, 598°F (saturated)
Medium Pressure Steam	Ammonia Rx Let down turbines System heat integration	605,000 lb/hr.	165 psi, 366°F (saturated)
Low-Pressure Steam	System heat integration	524,000 lb/hr.	30 psi, 250°F (saturated)

Table 4. Heat quality is generated from a steam methane reformer for hydrogen production from natural gas and a typical ammonia reactor.

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Natural gas steam methane reformer Ammonia Rx	734,000 lb/hr.	1,515 psi, 598°F (saturated)
Medium Pressure Steam	Ammonia Rx Let down turbines System heat integration	755,000 lb/hr.	165 psi, 366°F (saturated)
Low-Pressure Steam	System heat integration	549,000 lb/hr.	30 psi, 250°F (saturated)

2.2 Synthetic-Fuels

Among the commonly researched synthetic-fuels processes, FT synthesis is one of the most developed, having development roots during World War II. FT synthesis produces naphtha/gasoline, jet, diesel, and wax. The wax can be upgraded to lube oils. FT fuels are particularly attractive for transportation applications because of their ‘drop in’ compatibility with existing infrastructure and ground and air transportation uses as well as compatibility with conventional petroleum fuels for blending. Fuels are produced via the FT reaction from syngas (a mixture of CO and H_2), which is produced from converting a carbon source such as CO_2 or organic material and H_2. For this report, syngas will come from HTSE to produce the hydrogen and a CO_2 source with reverse water-gas shift (RWGS) will be used to provide the right mixture of CO and H_2 syngas for the FT reaction.

Various feedstocks and process steps can be used to supply H_2 for the synthesis. NG and light hydrocarbons can be reformed through a SMR unit to produce the hydrogen required for the process. This pathway also yields the CO component in the syngas stream which is a key ingredient for the FT process.

Also, a near-zero carbon pathway for hydrogen production could be achieved with water electrolysis that uses a near-zero carbon electricity source such as nuclear power. The CO component required for the FT reaction could be sourced from the conversion of CO_2 in the RWGS reaction. CO_2 can be provided from ethanol and ammonia plants in near-pure form; thus, CO_2 capture from these streams has both a low energy penalty and a low cost. The resultant syngas of H_2 and CO is converted to hydrocarbons with carbon chains ranging from C1–C30, via the FT reaction.

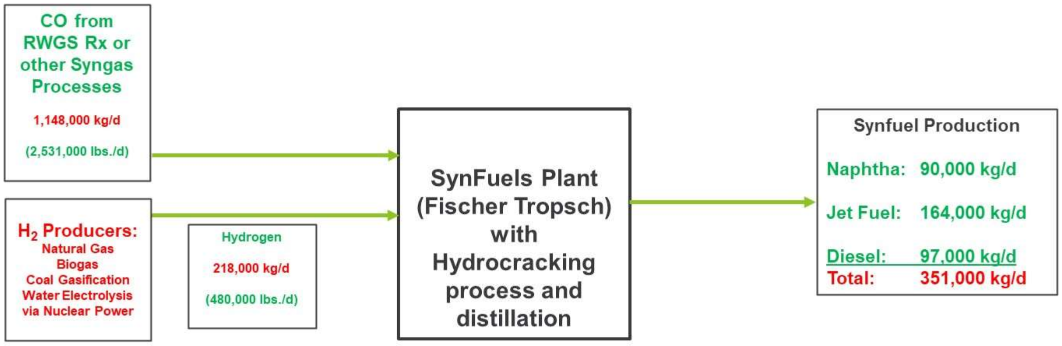
The conversion of hydrogen and CO to higher hydrocarbons in the FT process is very exothermic. Products are synthesized through the following net chemical equation:

$$(2n+1)H_2 + n\,CO \rightarrow C_nH_{(2n+2)} + n\,H_2;\ \Delta H = -165\ \text{kJ/mol of CO}.$$

Product yield is expressed as the number of moles of CO (n) combined in the catalytic process.

Through distillation, liquid hydrocarbons (C4-C20 for naphtha, jet fuel and diesel) are separated and collected as the final product. The heavier portion (C20-C30) is further processed with additional hydrogen via a hydrocracking reaction, and the resultant products are distilled into different carbon chain lengths to blend with existing gasoline, jet and diesel fuels.

Figure 8 shows a simplified BFD of the synfuels process.



Source: ANL/ESD-22/1 "The Modeling of Synfuel Production Process ASPEN Model of FT production with electricity demand provided at LWR scale"

Generated process heat/ source	Quantity
Direct heat from waste gas boiler	105.6 GJ/hr.
Fischer Tropsch reaction heat	202 GJ/hr.

Figure 8. Simplified BFD of synthetic-fuels production.

Figure 9 shows a hypothetical synfuels process designed in [10]. This design uses a highly pure CO_2 source from an ethanol plant, H_2 from HTSE and the FT synthesis process from the syngas. In stream (1), hydrogen is produced from electrolysis or from SMR and is charged to the FT reactor and the hydrocracking process to upgrade heavy waxy products. CO_2 (2) is charged to a Reverse Water-Gas Shift (RWGS) to convert the stream to CO, a key component for the FT process to produce FT products which are alkanes. The CO and H_2 streams are combined to form the syngas stream to the FT reactor (3). The resultant FT product (4) is sent to degassing/separation.

Separated/unreacted H_2, streams (6) and (11), are compressed and recycled to the inlet of the FT reactor. Heavier separated components are sent to the boiler for combustion and steam generation. The raw synfuel product feed to the distillation section (14) and is separated by boiling point to naphtha (17), jet fuel (18) and diesel (19). Heavy waxy FT product (13) is combined with hydrogen (15), and upgraded in a hydrocracking reactor, and sent to the distillation section to be separated into synthetic products.

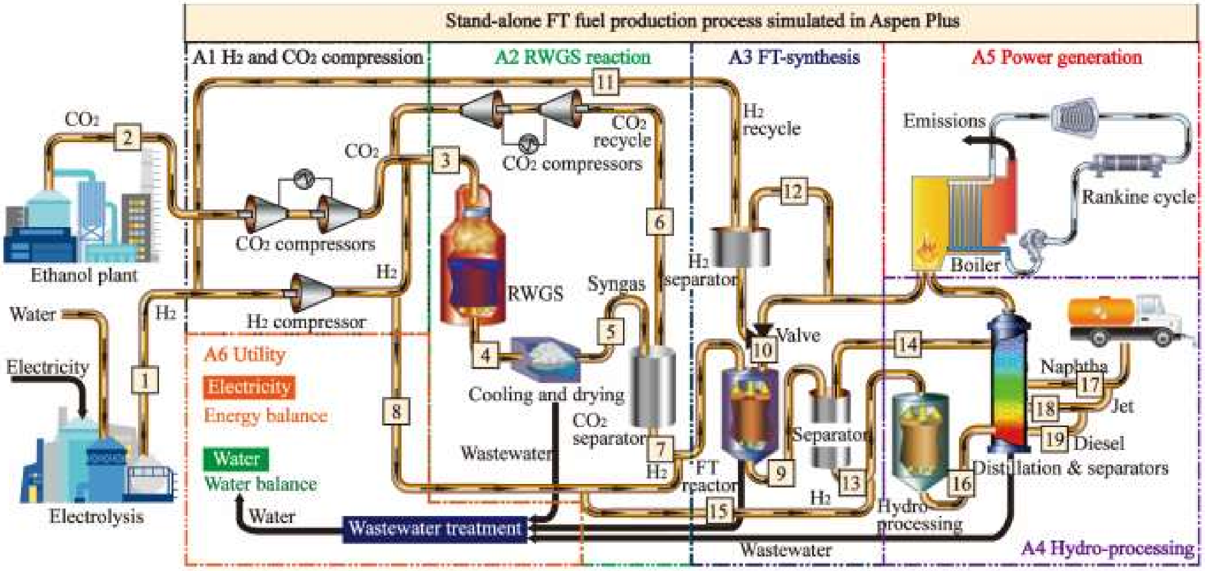


Figure 9. Hypothetical synfuels PFD [10].

Table 5 gives the projected prices for synthetic-fuels which are at a premium above petroleum fuel prices. These prices are limited to snapshots and do not take into account any recent developments in synthetic-fuels processes. The synthetic product pricing reflects estimates for current markets [11, 12, 13].

Table 5. Projected synthetic fuel prices.

Fuel	Prices
Synthetic gasoline	\$7.6/gal.
Synthetic jet fuel (SAF)	\$8.7/gal.
Synthetic diesel	\$5.2/gal.

Table 6 shows the quality and quantity of steam-generated from the FT synthetic-fuels process. This energy information is based on an FT plant capacity of ~351,000 kg/d of combined synthetic naphtha, jet fuel and diesel production [16].

Table 6. Quality and quantity of steam available from an FT synthetic-fuels process.

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Waste-gas boiler	35,000 lb/hr.	1,515 psi, 940°F (superheated)
Low-Pressure Steam	FT Reactor	35,000 lb/hr.	75 psi, 300°F (saturated)

2.3 Refineries

Crude oil is refined in petroleum refineries and converted to usable products such as transportation and heating fuels, chemicals, chemical feedstocks, and asphalt. The refining process of crude oil includes fractionation, conversion and blending to yield these products.

Petroleum refineries vary in complexity but include these basic steps to produce these products. In general, refining is an energy-intensive process. Though some conversion and upgrading steps in the process are exothermic, because of the large internal heat demands within the refinery, the opportunities for exporting thermal energy without incurring an opportunity cost are low. The process steps are included for information and they are described as to whether they are exothermic and how much heat is theoretically produced. A table of refining operations and their respective operating conditions are provided in Table 7.

Table 7. Operating conditions for selected refinery unit operations.

Process	Temperature	Pressure	Heat of Reaction	Reaction Type
Hydrotreating	300 – 425*C	735 – 1,500 psi		Exothermic
Hydrocracking	375 – 500*C	1,200 – 3,000 psi	-5-12 kJ/mol of H_2 consumed	Exothermic
Fluid Catalytic Cracking	480 – 550*C	10 – 20 psi		Endothermic
Coking	485 – 505*C	10 – 30 psi		Endothermic

A map of rough locations and sizes of U.S. refineries is shown in Figure 10.

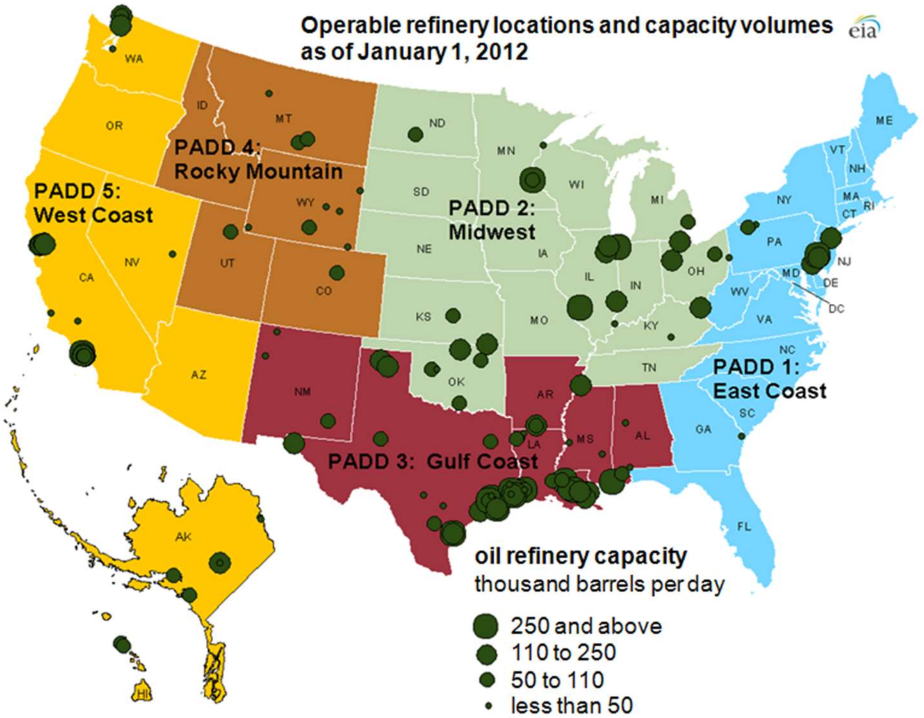


Figure 10. Map of existing U.S. refinery locations and scale.

Historical and projected petroleum fuel prices are provided in Figure 11 for comparison with some projected costs for synfuels.

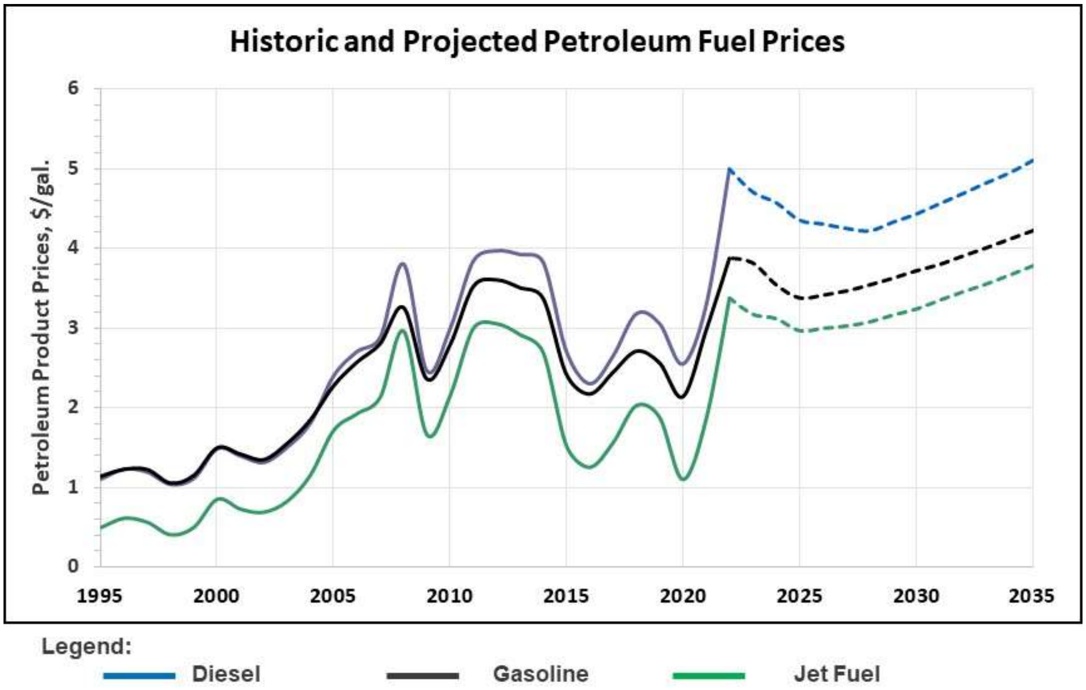


Figure 11. Historical and forecasted fuel prices.

Note the following in relation to Figure 11:

- Solid lines are the historic petroleum prices. Dashed lines illustrate the projected price for petroleum product.
- Petroleum prices include distribution, marketing, and taxes [16]. The energy demand ranges for a typical refinery per barrel are illustrated in Table 8:

Table 8. Energy demands for a typical petroleum refinery.

Source	Value
Energy use, MJ/bbl	5,930 – 6,000
Steam, MJ/bbl	35 - 40
Heat, MJ/bbl	350 - 400

A simplified BFD and PFD of generalized refinery operations are shown in Figure 12 and Figure 13

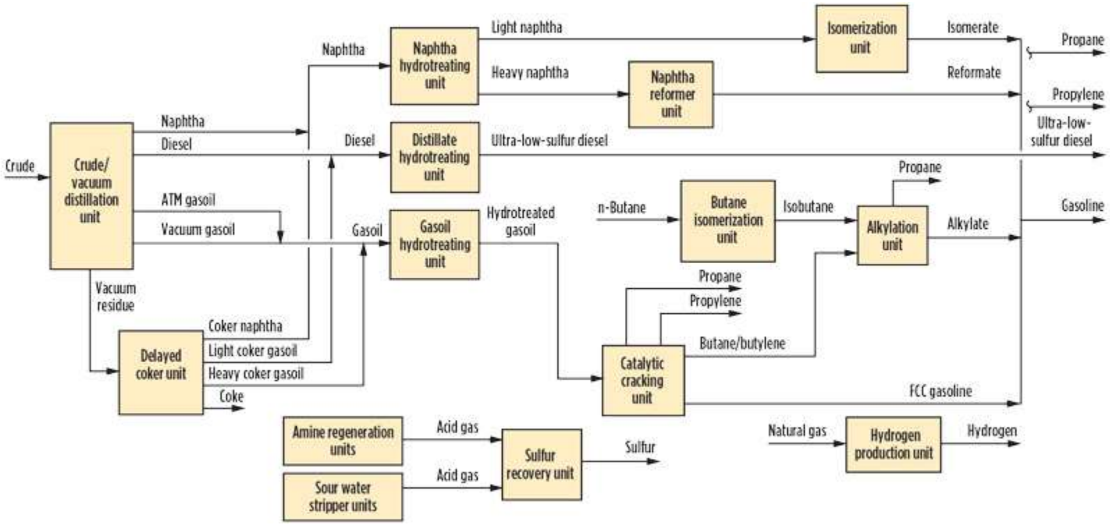


Figure 12. Simplified generalized refinery BFD.

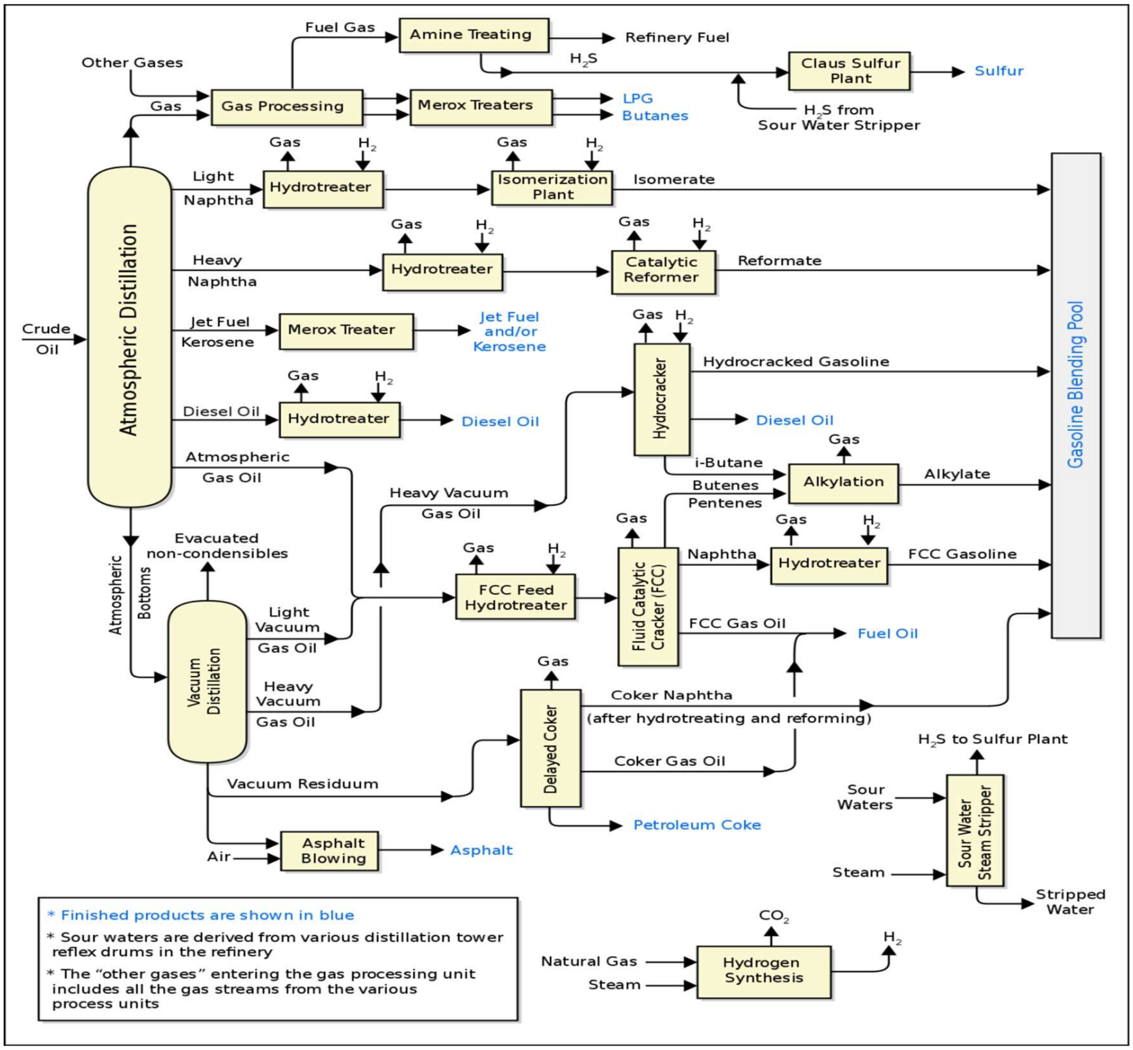


Figure 13. Typical refinery PFD showing the various process operations [17].

2.3.1 Fractionation

Fractionation is a refining step that separates components by their boiling temperature i.e., crude oil and other intermediate streams in fractionation and distillation columns. Heat is supplied to the columns with fired furnaces to enable the separation of lighter components from heavier boiling fractions. These streams are sent as component streams for product blending or further conversion and upgrading in other refining units. The first step in all refineries requires atmospheric distillation units for the initial stream separation. In more complex refineries, a vacuum-distillation column may be included to remove and upgrade heavier petroleum fractions in the refinery to higher-value products.

2.3.2 Upgrading and Conversion

Following the fractionation step, heavy, lower-value distillation fractions can be processed further into lighter, higher-value products such as gasoline, diesel fuel and other finished products.

The most widely used conversion method is called cracking because it uses heat, pressure, catalysts, and sometimes hydrogen to crack and reduce heavy hydrocarbon molecules into lighter ones. Cracking processes are employed to upgrade these lower-value streams to lighter components that can be blended to meet the product specifications. These processes use combinations of high temperatures, pressures and catalysts to accomplish these refining steps. Also, some cracking processes use hydrogen to catalytically reduce the heavy hydrocarbon streams. Complex refineries can use fluid catalytic cracking, coking and hydrocracking/hydrocracker units for the cracking process. The heat energy generated in these cracking units is recovered by integrating the heat with preheat heat exchange systems and steam-generating. A cracking unit consists of one or more tall, thick-walled, rocket-shaped reactors and a network of furnaces, heat exchangers, and other vessels.

Cracking is not the only form of crude oil conversion; other refinery processes rearrange and combine molecules rather than splitting them to add value.

Alkylation, for example, is an exothermic process that makes gasoline components by combining some of the smaller gaseous byproducts of cracking to higher-carbon-number molecules in the range of fuel blendstock. The process takes place in a series of large, horizontal vessels and tall, skinny towers. Alkylation makes gasoline components by combining light hydrocarbons in the presence of sulfuric or hydrofluoric acid.

Reforming is an endothermic process that uses heat supplied by fired furnaces, moderate pressure, and catalysts to turn naphtha, a light, relatively low-value fraction, into high-octane gasoline components.

2.3.3 Contaminant Removal

Crude oil contains contaminants such as sulfur and nitrogen. These contaminants need to be removed from the resultant component streams before they can be blended into the ultimate products. Hydrotreating and hydroprocessing processes are employed for this purpose which uses high-temperature and pressure in the presence of hydrogen and catalysts. These processes are exothermic and generate excess heat. The heat energy is recovered from the hydroprocessing units and efficiently used throughout the process and or integrated with other refining units to conserve energy.

2.3.4 Blending

The component streams from the refining units are combined to meet the specifications for gasoline, jet, and diesel fuel products.

2.3.5 Heat Recovery

Refineries use high-temperature systems throughout the refinery. Fired furnaces are used to supply preheat to hydroprocessing units and reboil heat to distillation columns. Also, many refining units operate at high temperatures ranging from 400 to 1,500°F. Heat is efficiently recovered from these systems to generate various levels of steam and system preheat.

Steam-generated heat recovery or combustion of excess light-hydrocarbon gases is used for power generation. Depending on the steam conditions of pressure and temperature, power generation from a steam-extraction system could require 30–80 lb/hr./kW of power generation. Another power generation mode uses a condensing turbine which generates power by reducing the inlet steam pressure to a low-temperature via condensing the outlet steam to condensate. This power generation method requires 20–30 lb/hr. of steam/kW of power generation.

2.4 Methanol

Methanol is a chemical that can be used as a transportation fuel and a basic building block for multiple chemicals. It can be produced from coal, heavy oil, naphtha, biogas, and NG feedstocks. These feedstocks are pretreated to remove contaminants such as sulfur, nitrogen and other catalysts and process poisons before further processing.

The treated feedstocks are converted by gasification, steam methane and autothermal reforming to produce a synthesis gas feedstock for methanol production. The reforming units operate at temperatures of 1,500–1,800°F and a pressure range of 200–300 psi. The resultant synthesis gas contains H_2, CO and

CO_2 which are compressed and fed into a methanol-synthesis reactor. The reactions for the formation of methanol are shown below.

Syngas is compressed to 1,090 psi and preheated to a reactor temperature of 422°F prior to introduction into the methanol conversion reactor. The methanol-synthesis reaction is an exothermic reaction that will produce a large amount of steam. The synthesis reactions are shown below:

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

$$CO + 2H_2 \rightarrow CH_3OH$$

The heat of formation for methanol is (-240) kJ/mol of methanol. The optimum concentrations of the components of the syngas are defined by a syngas module (M) [18]. The module is shown below:

$$M = (H_2 - CO_2)/(CO + CO_2) = 2.0 \text{ to } 2.1$$

The raw methanol produced in the methanol-synthesis reactor is refined through a series of distillation columns to purify the ultimate methanol product.

Near-zero carbon pathway for hydrogen production could be achieved with water electrolysis that uses a near-zero carbon electricity source such as nuclear power. The CO component required for the methanol reaction could be sourced from the conversion of CO_2 in the RWGS reaction. CO and CO_2 can be provided from streams from ethanol plants and ammonia plants in near-pure form; thus, CO_2 capture from these streams has both a low energy penalty and consequent cost. The resultant syngas of H_2, CO_2 and CO is converted to methanol. A simplified diagram of a typical ammonia plant is shown in Figure 14.

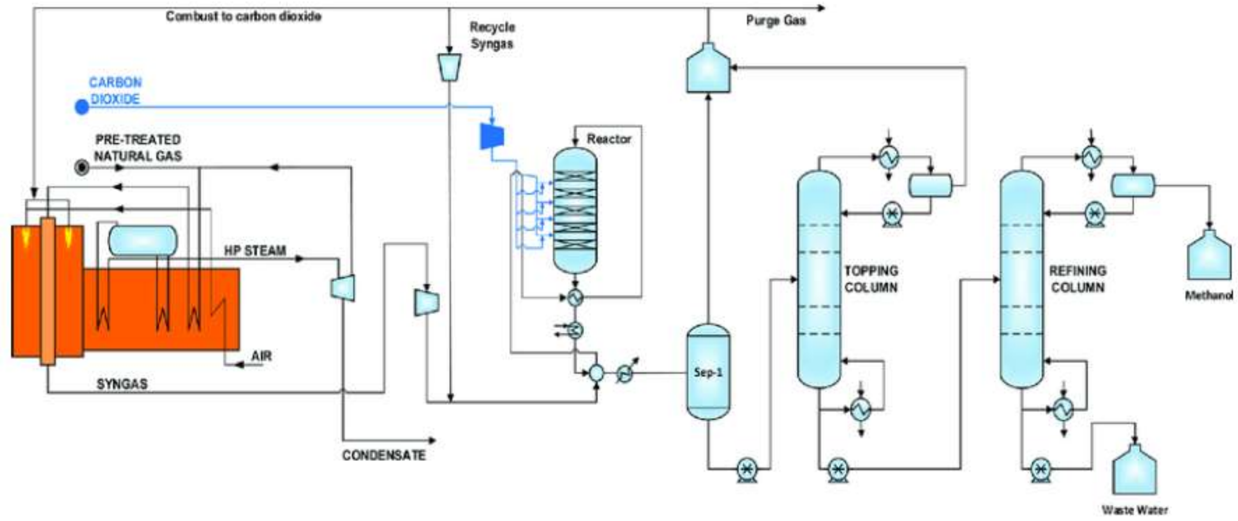


Figure 14. Simplified generalized methanol production plant [17].

Methanol is produced in the U.S. predominantly around the Gulf Coast in proximity to the abundant of NG supply shown in Figure 15. Other methanol production sites are located near coal–gasification and other NG supply fields.

Figure 15. US Methanol plants [16].

2.5 Nuclear Power Plant Heat Extraction

Several studies have been carried out at INL on the topic of heat extraction for existing light water reactors (LWRs) to support hydrogen production via HTSE. One of the studies conducted a detailed techno-economic analysis of hybrid configurations to optimize the total system in a regulated market specific to the Monticello and Prairie Island LWR NPPs located in the greater Minneapolis area and operated by Xcel Energy[1]. Hydrogen production via HTSE process was extensively modeled and evaluated, including the design and analysis of the SOEC stacks, balance-of-plant (BOP), and a very limited assumption on NPP thermal tie-in capital expenses (CAPEX), operating expenses (OPEX) including utility and energy consumption, design and performance assumptions, current versus future *n*th of-a kind (NOAK) technology—using an assumed learning rate—and operating modes.

A thermal extraction system was designed to enable the integration of an NPP with a flexible industrial process. This allowed heat and electricity from the NPP to be stored or used by a nearby industrial process during periods of grid overgeneration. As a result, additional revenue could be generated for the LWR integrated system while supporting the decarbonization of both the power and industrial sectors. Figure 16 shows a schematic of the integrated system.

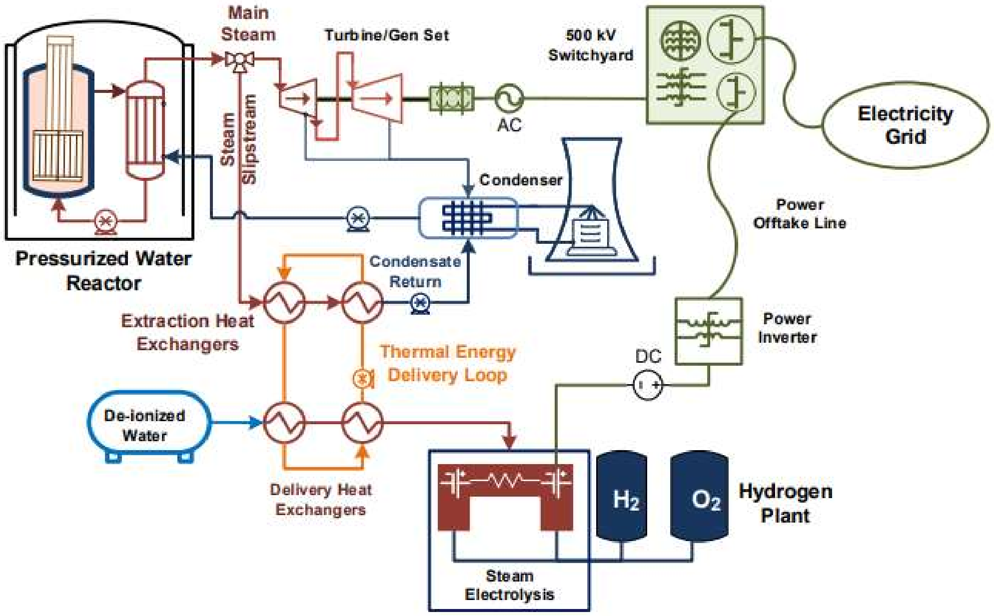


Figure 16. Thermal extraction system to allow integration between NPP and HTSE system.

To estimate the costs of the components required for integration, along with the costs for the HTSE system, models were developed and appropriately sized in Aspen HYSYS. This was followed by the estimation of installed costs using Aspen Process Economic Analyzer. The cost estimates were modified based on whether the components were modular or scalable, and whether a learning curve was applicable to the system or not. Details of the modeling and cost estimation analysis are available in [1]. This study also included a levelized cost of hydrogen (LCOH) analysis for the nuclear-integrated HTSE system, which was compared to the LCOH of an SMR system. It was determined that the LCOH for the base case HTSE system was \$1.93/kg- H_2, whereas that of the SMR was \$1.03/kg- H_2. However, this difference could be reduced with improvements in HTSE stack performance and a reduction in stack costs. Additionally, carbon taxes on systems like SMR and the paradigm shift in the energy market towards carbon-free energy sources would make green hydrogen more attractive.

Another study conducted at INL in collaboration with Sargent & Lundy focused on developing a preconceptual design for coupling LWRs to HTSE systems at 100 MWe and 500 MWe scales. The study assessed the technical feasibility of diverting thermal and electrical energy from NPPs and high-voltage generators to HTSE systems for hydrogen production. Three designs were initially selected for evaluation based on their methods for producing process steam for the HTSE plant. Design 1 incorporated an auxiliary steam feature that could extract the main steam, while Design 2 considered cold reheat extraction after the high-pressure turbine. Design 3 did not use steam from the BOP but instead utilized an electric boiler to generate the process steam. Design 2 was analyzed for the 100 MWe HTSE case, while Designs 1 and 2 were assessed for the 500 MWe HTSE case. Design 3 was not given detailed analysis due to its lower efficiency, which would result in higher operating costs compared to the other designs. A schematic of Design 2 whose technical analysis would be applicable to most of the existing LWRs within the nation is Figure 17.

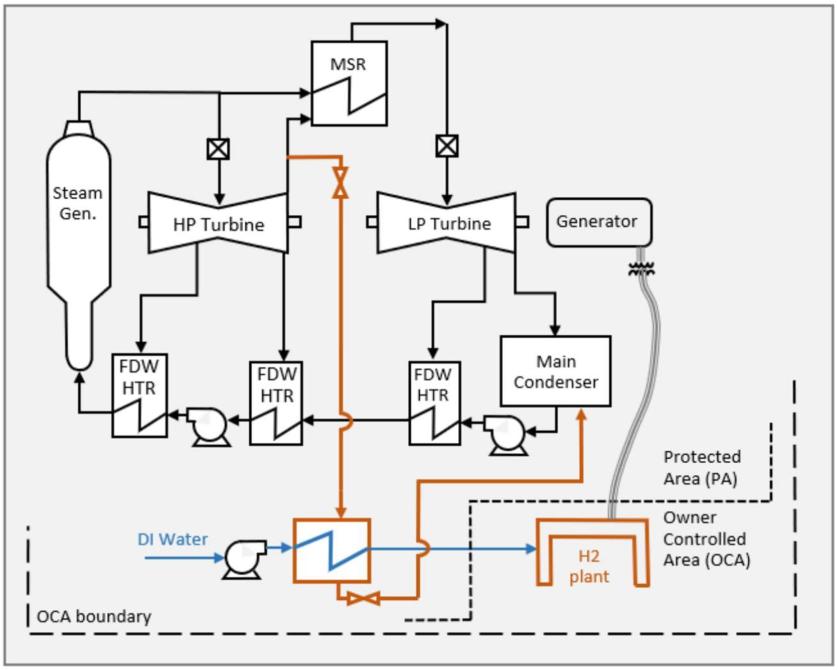


Figure 17. Steam-extraction from the secondary loop, downstream of the high-pressure turbine.

The impact of thermal energy extraction on the nuclear BOP was analyzed in detail by using a steady-state analysis tool called PEPSE. For cost analysis, the 100 MWe and 500 MWe HTSE facilities were assumed to be at distances of 250 m and 500 m away from the NPP. The proposed 100 MWe hydrogen production facility uses a portion of the turbine cycle steam to extract approximately 25 MW of thermal energy to generate steam for the H_2 plant. Its effect on the system performance is provided in Table 9.

Table 9. Parameter values for 25 MWt extraction to support a 100 MWe HTSE system.

Parameter	Unit	Extraction Amount		Change
		0 MWt	25 MWt	
Reactor Thermal Power	MWt	3659	3659	-
Generator Output	MWe	1239.6	1234.3	-5.3MWe
Main Steam Flow	Mlb/hr.	16.28	16.28	0.00%
Cold Reheat Flow	Mlb/hr.	12.73	12.72	-0.05%
25 MWt Thermal Extraction Flow	lb/hr.	0	85,238	-
Extracted Steam Fraction of Cold Reheat Flow	%	0	0.67	0.67%
Remaining Steam to MSRs	Mlb/hr.	12.73	12.64	-0.67%
Hot Reheat Flow	Mlb/hr.	11.26	11.17	-0.76%
Heater Drain Forward Temperature	◦F	339.7	339	-0.7 °F
HP FWH Cascading Drain Flow	Mlb/hr.	1.39	1.39	-0.23%
LP FWH Cascading Drain Flow	Mlb/hr.	2.42	2.41	-0.41%
Heater Drain Tank Pressure	psia	185.5	184	-1.5 psi

Similarly, for the 500 MWe HTSE facility, thermal extraction via two trains was performed to total 105 MWt of steam diversion. Its effect on the system performance is provided in Table 10.

Table 10. Parameter values for 105 MWt extraction to support 500 MWe HTSE system.

Parameter	Unit	Extraction Level		Change
		0 MWt	105 MWt	
Reactor Thermal Power	MWt	3659	3659	-
Generator Output	MWe	1239.6	1217.2	-22.4 MWe
Main Steam Flow	Mlb/hr.	16.28	16.28	0.00%
Cold Reheat Flow	Mlb/hr.	12.73	12.7	-0.20%
105 MWt Thermal Extraction Flow	lb/hr.	0	355,193	-
Extracted Steam Fraction of Cold Reheat Flow	%	0	2.8	2.80%
Remaining Steam to MSRs	Mlb/hr.	12.73	12.35	-2.99%
Hot Reheat Flow	Mlb/hr.	11.26	10.9	-3.18%
Heater Drain Forward Temperature	◦F	339.7	337	-2.7°F
HP FWH Cascading Drain Flow	Mlb/hr.	1.39	1.38	-0.92%
LP FWH Cascading Drain Flow	Mlb/hr.	2.42	2.37	-1.72%
Heater Drain Tank Pressure	psia	185.5	179.5	-6.0 psi

An economic analysis was performed to estimate the cost of integrating the HTSE and NPP systems, enabling plant owners to better understand the capital costs involved in modifying the NPP to integrate with the 100 MWe and 500 MWe HTSE systems. A summary of the cost analysis is provided in Table 11 which provides a levelized cost estimate for the HTSE facilities at distances of 250 m and 500 m, at capacities of 100 MWe and 500 MWe.

Table 11. Cost Summary for integration of HTSE system with a NPP.

Description	100 MWe Design		500 MWe Design	
	500 m Separation	250 m Separation	500 m Separation	250 m Separation
Direct Costs				
Labor	2,075,247	1,457,099	3,596,659	2,558,137
Material	2,365,820	1,426,949	3,896,426	2,580,470
Subcontract	1,335,951	1,060,793	1,795,951	1,520,793
Construction Equipment	484,859	312,550	814,510	551,401
Process Equipment	1,161,540	1,161,540	2,956,660	2,956,660
Total Direct Cost	7,423,417	5,418,931	13,060,206	10,167,461
Indirect Costs				
Additional Labor	572,047	401,628	991,427	705,156
Site Overheads	1,455,759	1,022,074	2,523,010	1,794,501
Other Construction Indirect	2,952,085	1,982,403	5,069,187	3,558,192
Project Indirect	3,999,791	3,856,656	4,375,066	4,158,325
Total Indirect Cost	8,979,682	7,262,761	12,958,690	10,216,174
Contingency Costs				

Description	100 MWe Design		500 MWe Design	
	500 m Separation	250 m Separation	500 m Separation	250 m Separation
Contingency on Labor	349,098	225,036	586,447	397,009
Contingency on Material	1,664,354	1,003,859	2,741,136	1,815,361
Contingency on Subcontract	2,910,416	2,043,372	5,044,110	3,587,642
Contingency on Construction Equip.	667,976	530,397	897,976	760,397
Contingency on Process Equipment	609,809	609,809	1,552,247	1,552,247
Contingency on Project Indirects	1,999,896	1,928,328	2,187,533	2,079,163
Total Contingency Cost	8,201,549	6,340,801	13,009,449	10,191,819
Total Cost	24,604,648	19,022,493	39,028,345	30,575,454
Standardized Cost ($/kW)	246	190.2	78.1	61.2

3. EXAMPLE CASE SCENARIOS FOR INDUSTRIAL HEAT INTEGRATION WITH NPP-HTSE HYDROGEN PRODUCTION

The following example cases show simplified heat and energy balances and both BFDs and PFDs for hypothetical integrations of an ammonia plant and a synthetic-fuels plant with HTSE hydrogen production and nuclear power. These cases presuppose that as much heat as possible is taken from the ammonia and synfuels plants to use in HTSE.

3.1 Nuclear-Integrated Hydrogen Production

Various studies have quantified the heat and material balances for nuclear-integrated hydrogen production via HTSE. The following diagram is simplified from [20]. This diagram provides some metrics regarding the amount of electricity, feedwater, and thermal energy in the form of steam is required for a 1000 MWe HTSE system, which could produce green hydrogen at a rate of 774 MT/d. However, the goal of this analysis is to evaluate other potential heat sources to provide thermal input to the HTSE system.

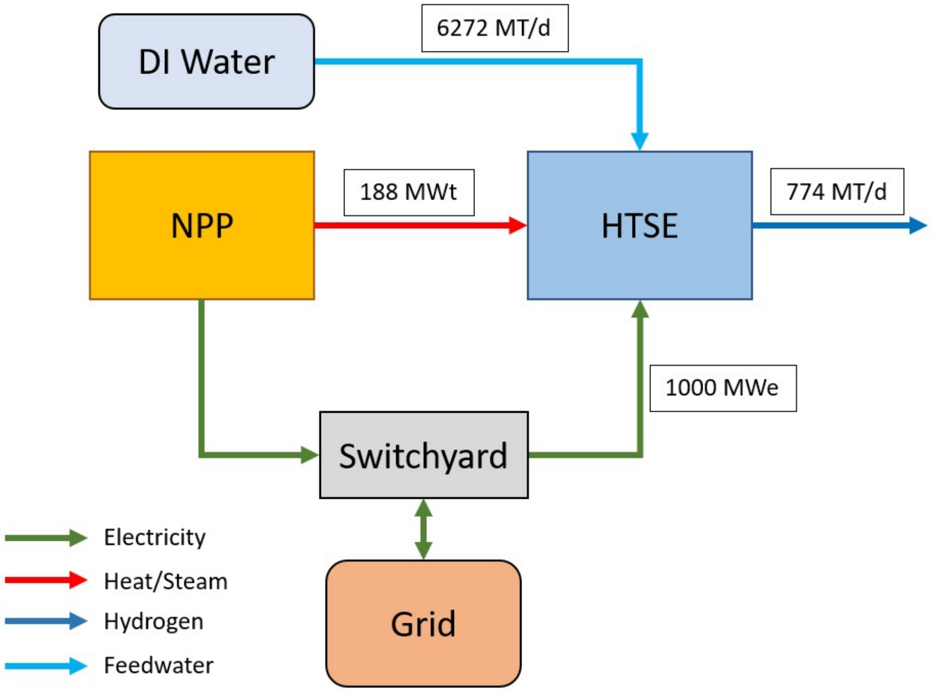


Figure 18. Simplified HTSE heat and material-balance adapted from INL-RPT-22-66117.

One potential advantage of using alternative heat sources, such as an ammonia-synthesis plant or synfuels production plant, is that it could reduce the reliance on extracting heat from NPPs for hydrogen production. By using these alternative heat sources, the NPPs could solely focus on generating electricity, which could then be used to power the HTSE process to produce hydrogen. This approach could simplify the process of nuclear-integrated hydrogen production and potentially make it more efficient and cost-effective.

By integrating hydrogen production with NPPs without the need to extract thermal energy, the development of nuclear-integrated hydrogen production could be accelerated. This could lead to a quicker and more efficient transition to a low-carbon economy, where hydrogen plays a crucial role in reducing greenhouse gas emissions. The extraction of thermal energy from NPPs and the associated regulation reviews could still take place at their own pace and be incorporated when ready, without impeding the progress of nuclear-integrated hydrogen production.

Thermal energy extraction from ammonia and synfuels production plants is discussed in the following sections.

3.2 Ammonia

Conventional ammonia production using the Haber-Bosch process, as introduced in Section 2 of this report, uses NG as a source of hydrogen to combine with nitrogen to form ammonia. The conventional process involves several steps, including the conversion of NG into hydrogen gas via SMR, and then combining the hydrogen gas with nitrogen in a high-pressure reactor vessel. The reaction between hydrogen and nitrogen results in ammonia, which is then cooled and condensed into a liquid form. While this process has been in use and optimized for over a century and is cost-effective due to the abundance of NG, it is not considered sustainable in the long term due to its dependence on fossil fuels and its significant carbon footprint.

A study conducted as a part of the Next Generation Nuclear Plant (NGNP) project evaluated the integration of a high-temperature gas-cooled reactor (HTGR) with conventional chemical processes such as ammonia and hydrogen production 15. The idea behind this analysis was to study the integration of heat from the high-temperature helium and steam from the HTGR to support the chemical processes, to reduce greenhouse gas emissions. This study has been leveraged herein to provide a background for the ammonia-synthesis process wherein hydrogen is produced via an SMR as well as an HTSE system, and nitrogen is produced via air-hydrogen combustion or a cryogenic air separation unit (ASU).

3.2.1 Design Using Combustion to Provide Nitrogen

Out of several ways to acquire nitrogen to combine with hydrogen, the two methods considered herein are combustion of air-hydrogen mixture to produce nitrogen, and cryogenic separation of nitrogen from the air in an ASU. In the air-hydrogen combustion process, high-temperature and pressure causes the nitrogen and oxygen in the air to react and the resulting nitrogen oxides can then be reduced using urea or ammonia to comprise the exhaust gases. These reducing agents cause nitrous oxide (NO_X) to convert into nitrogen gas and water vapor. The water vapor can be condensed out of the mixture while the nitrogen can be combined with hydrogen for ammonia-synthesis.

3.2.1.1 Hydrogen provided by SMR

SMR is the most common method of producing hydrogen. It involves reacting NG or other hydrocarbons with steam at high temperatures in the presence of a catalyst to produce H_2 and CO. The CO gas can be reacted with steam in a water-gas shift reaction to produce additional H_2 and CO_2. In the NGNP study mentioned previously, an ammonia-synthesis plant that would produce about 3,360 MT/d of ammonia would require 546 MT/d of hydrogen. This, in turn, requires 3,984 MT/d of NG (166 klb/hr.) and 11,016 MT/d of steam (459 klb/hr.). A simplified BFD is shown in Figure 19.

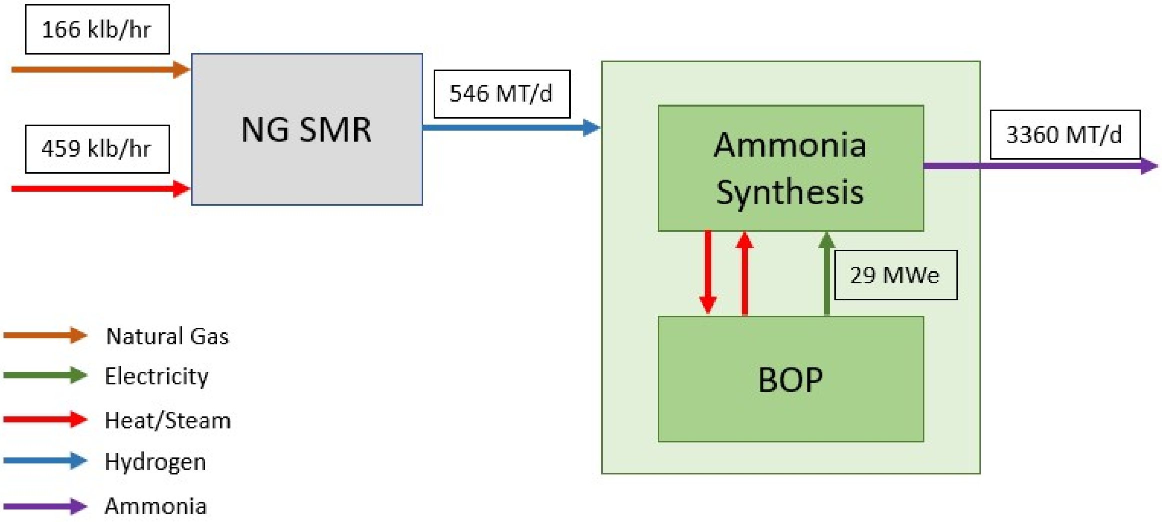


Figure 19. Simplified BFD of a conventional NG-to-ammonia process plant.

3.2.1.2 Hydrogen provided by HTSE

A second option presented in [15] looks at hydrogen production from an HTSE plant and N_2 generation from hydrogen-air combustion. Because the focus of this work is primarily on how heat from the ammonia-synthesis process can be diverted to support HTSE, details of other operations and products such as CO_2 generation via oxy-combustion of NG, CO_2 compression, nitric acid-synthesis, ammonium-nitrate synthesis, and urea synthesis are not included in the following discussion. Figure 20 shows a simplified BFDs of the hydrogen-to-ammonia process, wherein thermal and electrical energy needed by the HTSE are provided by the NPP. The numbers for the HTSE system requirements were acquired from[21].

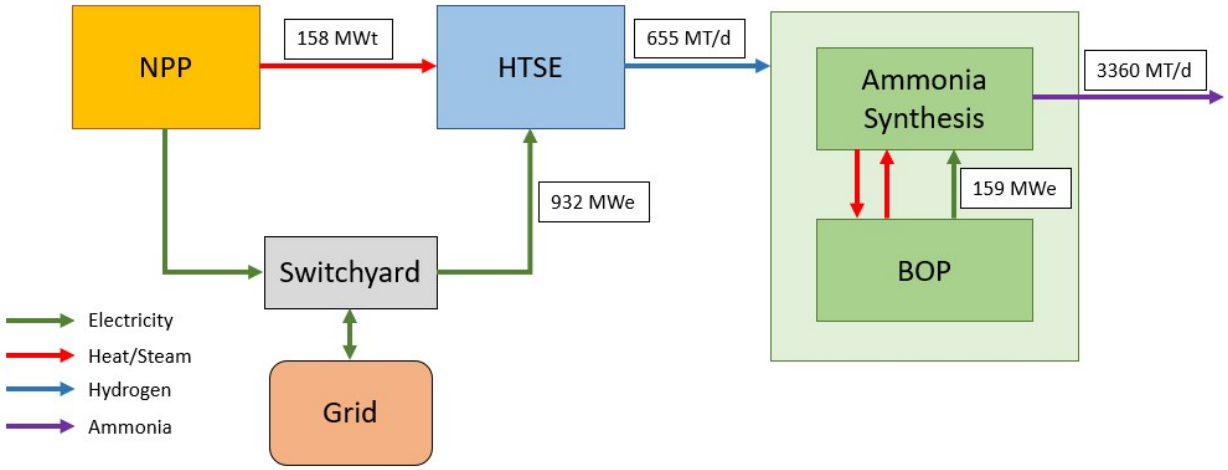
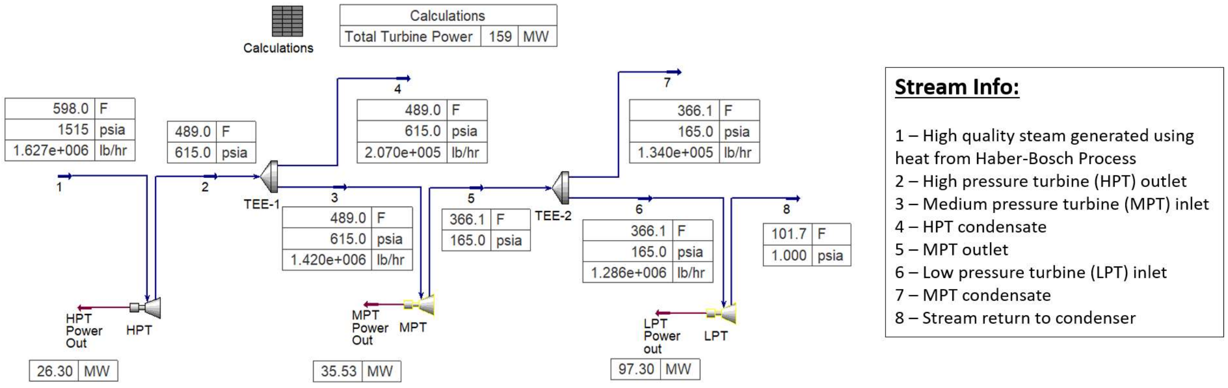


Figure 20. Simplified baseline BFDs for the hydrogen-to-ammonia process (without ASU) from the reference.

Ammonia plants include multiple reactors. The reactor feed composed of H_2 and N_2 is preheated usually using heat from the first reactor in the series. The heat generated by the exothermic reaction of ammonia-synthesis is usually removed at the outlet of each series reactor thus maintaining the optimal reactor conditions for the catalyst. From the second and subsequent reactors, excess heat is used to generate steam. This steam is diverted to the steam turbines for power generation in the baseline design described in the above-mentioned reference. This power is used by various components: pumps and compressors within subsystems such as CO_2 processing, cooling tower, water treatment facility, and urea synthesis.

To reduce the thermal dependency of the hydrogen production system on the NPP, some of the steam produced by the ammonia-synthesis process could be diverted from the ammonia BOP and sent to the HTSE system. This would allow the NPP to divert all its steam to its BOP to produce more electricity and sell it to the grid. To perform this analysis, a steady-state model of the existing BOP design in the ammonia production plant was developed in Aspen HYSYS, as is shown in Figure 21.



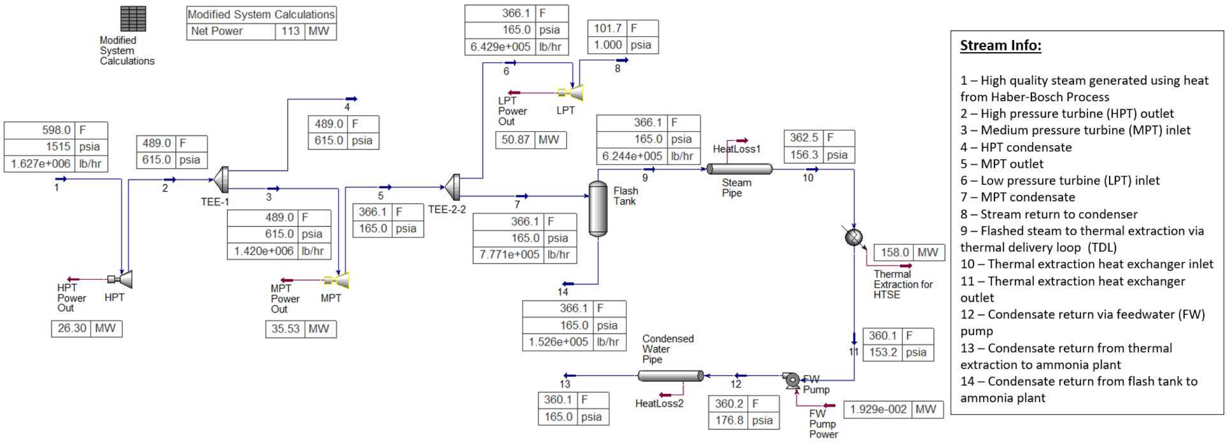
Stream Info:

1 – High quality steam generated using heat from Haber-Bosch Process
2 – High pressure turbine (HPT) outlet
3 – Medium pressure turbine (MPT) inlet
4 – HPT condensate
5 – MPT outlet
6 – Low pressure turbine (LPT) inlet
7 – MPT condensate
8 – Stream return to condenser

Figure 21. HYSYS-based BOP model for hydrogen-to-ammonia process (without ASU).

This model provides an overview of the stream conditions in and out of the turbine train, as well as extractions from the turbines for internal feedwater heating. The calculations block is an embedded spreadsheet that allows for calculating the sum of powers generated by the turbine train. The HYSYS model allows for convenient modifications to the BOP system and calculates the resulting change in the electrical output.

For the thermal extraction modification, it was assumed that the HTSE plant was located at a distance of 1 kilometer (km) from the ammonia production plant (heat source). To divert thermal energy from this BOP, the stream off TEE-2 (Stream 7) is sent to a thermal delivery loop (TDL). This TDL consists of a flash tank, two 1 km long pipes to transfer the heat to the HTSE facility and return the condensate, a heat exchanger to transfer heat between the utility steam and process steam, and a circulation pump. Figure 22 shows the modified BOP with the TDL.



Stream Info:

1 – High quality steam generated using heat from Haber-Bosch Process
2 – High pressure turbine (HPT) outlet
3 – Medium pressure turbine (MPT) inlet
4 – HPT condensate
5 – MPT outlet
6 – Low pressure turbine (LPT) inlet
7 – MPT condensate
8 – Stream return to condenser
9 – Flashed steam to thermal extraction via thermal delivery loop (TDL)
10 – Thermal extraction heat exchanger inlet
11 – Thermal extraction heat exchanger outlet
12 – Condensate return via feedwater (FW) pump
13 – Condensate return from thermal extraction to ammonia plant
14 – Condensate return from flash tank to ammonia plant

Figure 22. HYSYS-based modified BOP to allow for thermal extraction in hydrogen-to-ammonia process (without ASU).

The split-flow ratio was adjusted downstream of TEE-2 (shown as TEE-2-2 in Figure 22) therefore, the turbine performance upstream of the split is consistent with the unmodified BOP shown in Figure 20. The flow split ratio at TEE-2 was adjusted in a manner that the heat being extracted equals the 158 MW thermal requirement the HTSE plant. The pipe used to transfer the utility steam in the TDL is 1 km long, with an inside diameter of 28 in. and a wall thickness of 1 in. Similarly, the condensate return pipe has an inside diameter of 10 in.with a wall thickness of 1 in. The pipe diameters were chosen to ensure that vapor velocity was maintained on the steam side and the fluid remained subcooled on the condensate return side. Both pipes have a 5-in.insulation of urethane foam applied to their pipe walls to minimize heat loss to the environment which is assumed to be at 68°F.

Based on the modified Aspen HYSYS model, an updated BFD is presented in Figure 23. It is evident that all the 158 MWth heat required by the 932 MWe HTSE can be met by diverting thermal energy from the ammonia plant BOP. This, however, results in a 46 MWe (~29%) reduction in the electricity produced by the ammonia plant's BOP—from 159 to 113 MWe—which will have to be met by other sources such as an NPP. The heat reduction can be met by an NG boiler.

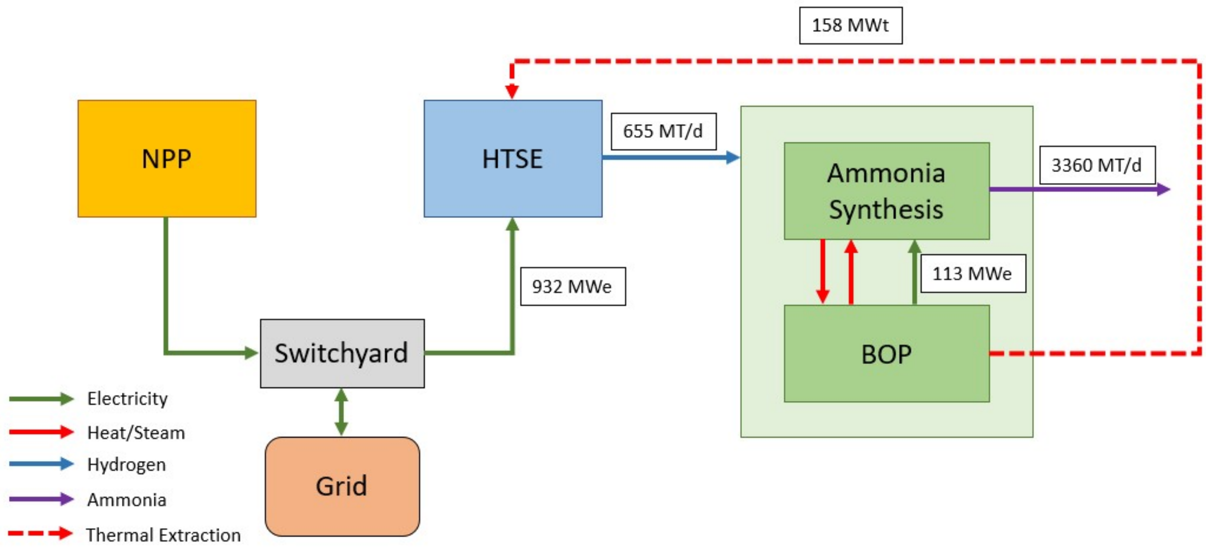


Figure 23. Modified BFD for hydrogen-to-ammonia process (nitrogen sourcing by H_2 combustion, not shown) from the reference.

3.2.2 Design Using Air Separation to Provide Nitrogen

A third option analyzed in [15] was a design that used the HTSE for hydrogen generation, and a cryogenic ASU for N_2 generation. Details regarding other operations and products such as CO_2 generation via oxy-combustion of NG, CO_2 compression, ammonia-synthesis, nitric acid-synthesis, ammonium-nitrate synthesis, urea synthesis, power production, cooling towers, and water treatment are outside the scope of this work and are therefore not included herein. A simplified version of the ammonia-synthesis process using cryogenic air separation is shown in Figure 24.

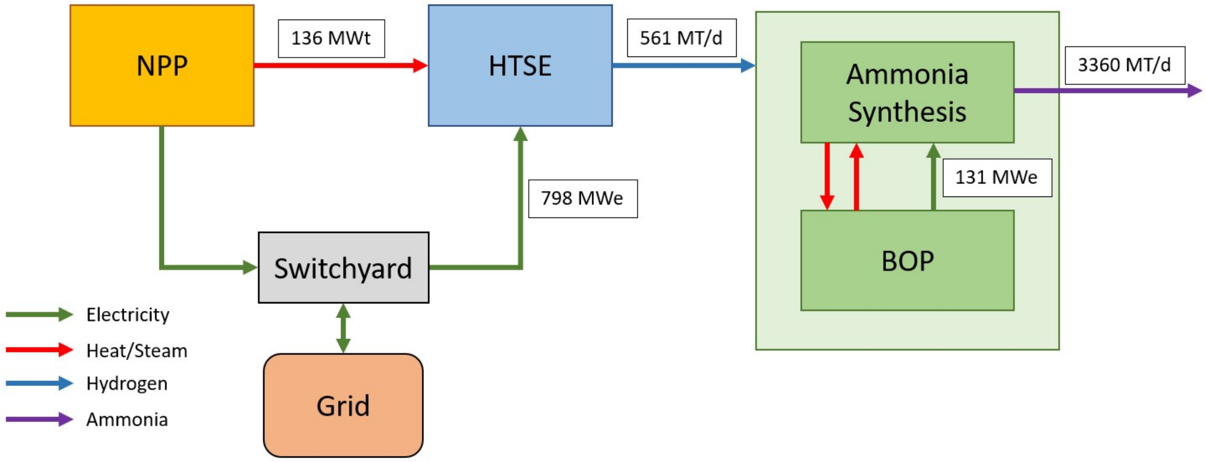
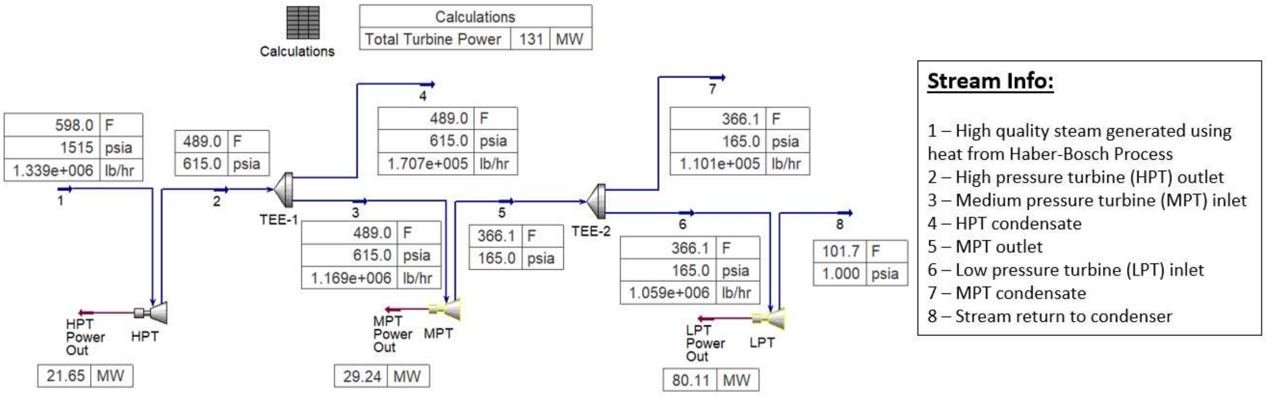


Figure 24. BFD for hydrogen-to-ammonia process (with ASU).

ammonia-synthesis A steady-state Aspen HYSYS model was developed for the BOP as shown in Figure 25.

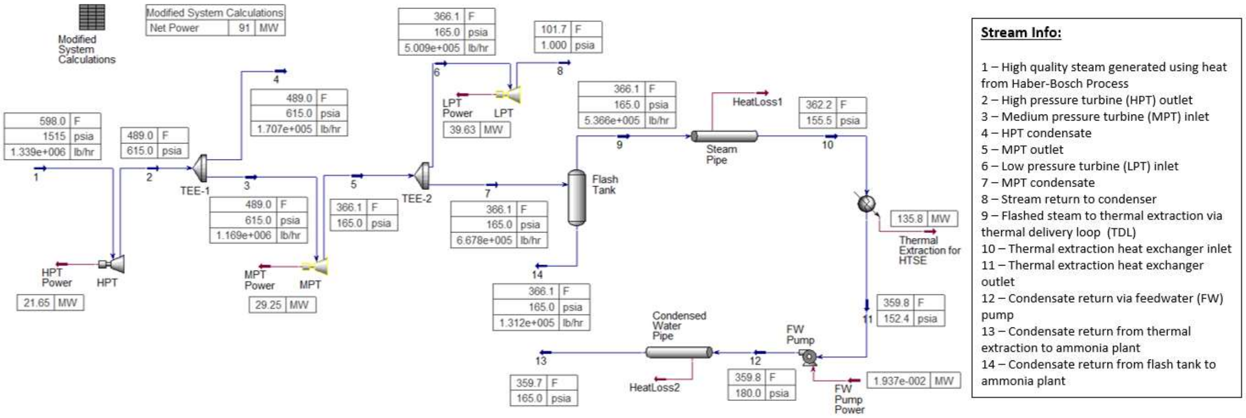


Stream Info:

1 – High quality steam generated using heat from Haber-Bosch Process
2 – High pressure turbine (HPT) outlet
3 – Medium pressure turbine (MPT) inlet
4 – HPT condensate
5 – MPT outlet
6 – Low pressure turbine (LPT) inlet
7 – MPT condensate
8 – Stream return to condenser

Figure 25. HYSYS-based BOP model for hydrogen-to-ammonia process (with ASU).

Thermal energy extraction can be achieved by diverting steam from downstream of TEE-2 (Stream 7) and using a TDL to transport the heat to the HTSE facility. A TDL similar to the one described in the previous example was designed for this purpose in HYSYS as shown in Figure 26.



Stream Info:

1 – High quality steam generated using heat from Haber-Bosch Process
2 – High pressure turbine (HPT) outlet
3 – Medium pressure turbine (MPT) inlet
4 – HPT condensate
5 – MPT outlet
6 – Low pressure turbine (LPT) inlet
7 – MPT condensate
8 – Stream return to condenser
9 – Flashed steam to thermal extraction via thermal delivery loop (TDL)
10 – Thermal extraction heat exchanger inlet
11 – Thermal extraction heat exchanger outlet
12 – Condensate return via feedwater (FW) pump
13 – Condensate return from thermal extraction to ammonia plant
14 – Condensate return from flash tank to ammonia plant

Figure 26. HYSYS-based modified BOP to allow for thermal extraction in hydrogen-to-ammonia process (with ASU).

Based on the modified Aspen HYSYS model for ammonia-synthesis with cryogenic air separation, a BFD indicating the thermal diversion to support the HTSE system is shown in Figure 27. For this TDL, a thermal extraction of 136 MW leads to a reduction in the electrical output of the BOP by 40 MWe (~31%) from 131 to 91 MWe. The lowering of thermal input back into the ammonia-synthesis supporting systems can be made up for using an NG boiler, and its corresponding reduction in electrical energy can be made up by the grid.

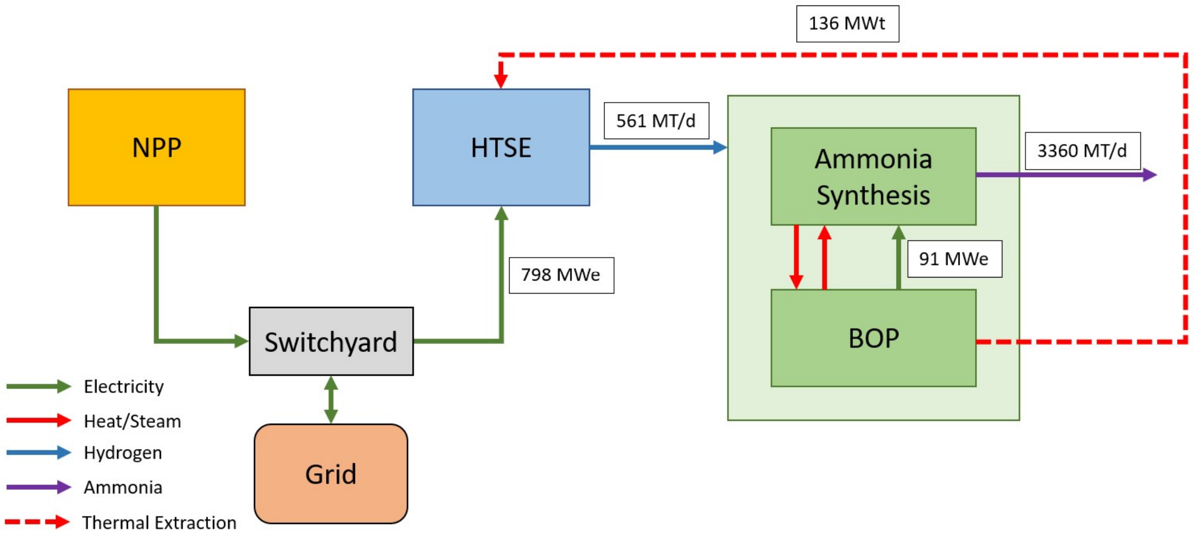


Figure 27. Modified BFDs for hydrogen-to-ammonia process (N_2 sourced from cryogenic ASU).

3.3 Synthetic-Fuels

3.3.1 Design Using Fischer-Tropsch Gas to Liquids

Synfuels are liquid or gaseous fuels produced from non-renewable resources such as coal, NG, oil shale, or directly from water and carbon dioxide. They are made by converting these raw materials through a chemical process into a fuel that can be used in place of conventional petroleum-based fuels such as gasoline or diesel. One common method for producing synfuels using H_2 is through gasification and then FT synthesis as previously described. In this process, the carbon-based feedstock is heated to produce a gas that is rich in CO and H_2. Syngas is then cleaned and processed to remove impurities, and the resulting hydrogen-rich gas is distilled and separated to produce several types of fuels e.g., naphtha, jet fuel, and diesel.

During the FT process, the catalysts break down the syngas into smaller molecules which then recombine to form long-chain hydrocarbons. The formation of these long-chain hydrocarbons is exothermic. The heat released during this process can be used to produce steam, followed by electricity generation using a steam turbine. Based on the information provided in [23], the small steam turbine efficiency in the FT process is ~17% which is very low when compared to the thermal-to-electrical efficiency of an NPP-BOP of about 33%. This analysis shows the alternative where the heat generated by the FT process can instead be used to support HTSE that produces H_2 as its feedstock for the FT process.

A baseline design for the FT process wherein thermal and electrical input is provided by the NPP is shown in Figure 28. Based on the presented design, 54 MWth and 317 MWe are needed to produce 223 MT/d of hydrogen. This H_2 is used as feedstock for synfuels synthesis. In addition to the 16 MWe generated by the BOP, synfuels production requires an additional 4 MWe to produce 90 MT/d naphtha, 164 MT/d jet fuel, and 97 MT/d diesel. This additional electricity will have to be sourced from the grid.

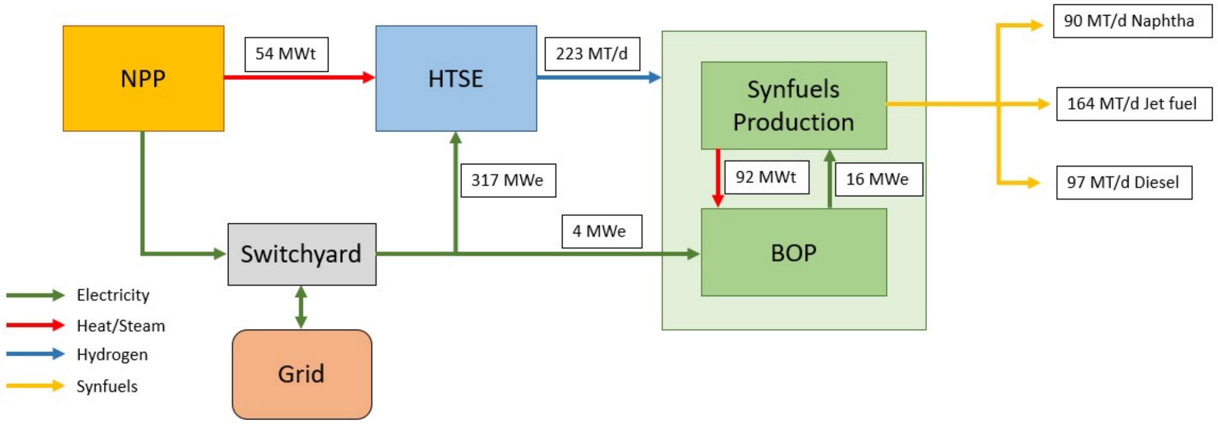


Figure 28. Baseline synfuels production process with thermal and electrical integration for HTSE.

Details regarding other operations beyond just the syngas and FT synthesis unit operations—such as H_2 and CO_2 compression, RWGS reaction, syngas production, FT synthesis, and hydroprocessing—are not included in the simple material and energy balance figures. An Aspen HYSYS model was not developed for the synfuels production case since stream conditions were not readily available. However, the information provided in the report already referenced was enough to calculate the effects of energy diversion from one process to another.

A modification to divert heat from the FT synthesis to the HTSE system is shown in Figure 29. It is shown that all the heat required by the HTSE can be met by the synfuels production process. A thermal extraction of 54 MWth lowers the heat input into the synfuels-coupled BOP from 92 MWth to 38 MWth. This consequently leads to a reduction in the electrical output of the BOP by 9 MWe (~56%) from 16 MWe to 7 MWe. This drop in electrical-power generation can be made up by the more–efficient grid electricity.

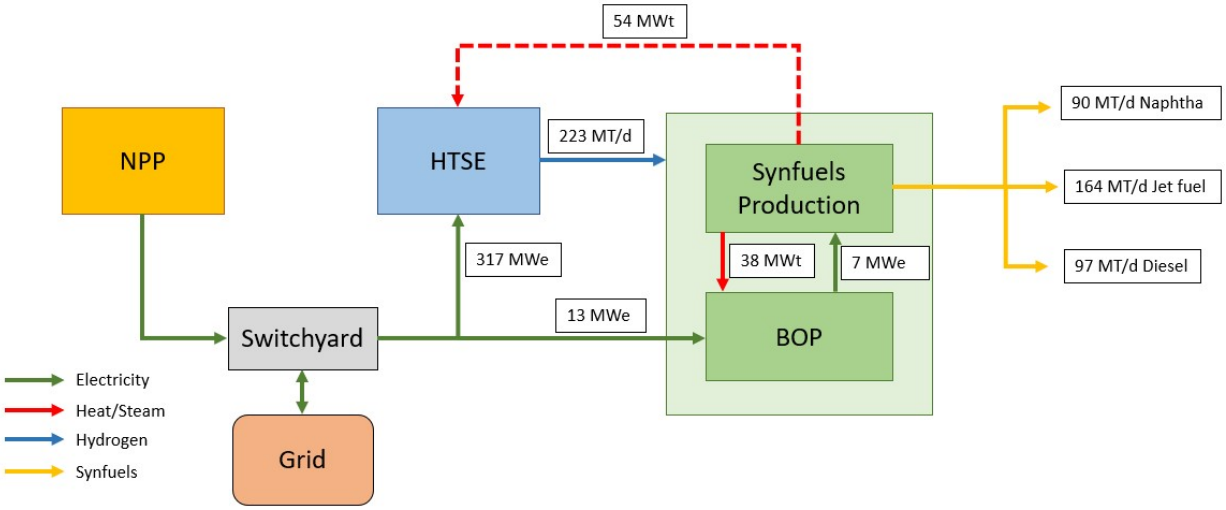


Figure 29. Modified synfuels production process with thermal extraction from FT synthesis to support H_2 production via HTSE.

This is one method of making a synfuels-production system more efficient. Another study presented in [24] proposes to use combustion exhaust gases to produce steam to aid separation via distillation and indicates that the steam produced could be used to preheat feedwater for the HTSE process.

It is evident that there are ways to make the synfuels production system more efficient by using the internally generated heat to support the HTSE system that provides one of its primary feedstocks. This would allow the NPP to eliminate steam diversion to the HTSE system, and utilize it to produce electricity which is needed by the HTSE system and at several compression stages within the fuel production process.

4. SUMMARY

In summary, this report has surveyed an array of industries with large industrial exothermic processes that could have heat available for use in HTSE H_2 production. The quality and quantity of heat available were normalized to the scale of the plants. Various designs of existing ammonia plants were summarized and a hypothetical synfuels plant was also used as an example. Specific scaled examples of these plants paired with NPP-HTSE H_2 production were conceptualized to show the heat and material-balances and how much H_2 and ammonia synfuels could be produced. These examples also show the available surplus or deficit of H_2 and heat. This study provides a baseline of comparison when considering alternative heat sources as options to provide heat to HTSE versus extracting the heat from an NPP.

4.1 Ammonia Market

Ammonia prices appear to be relatively stable, outside of extraordinary events such as recession, war, and pandemics. Thus, producers must be able to manufacture near historical averages to be competitive, assuming prices continue to fall to normal pre-event levels. Demand for both ammonia and urea are not expected to see substantial gains in the near future. Growth is projected to be slow and steady, and barring any technological developments that opens any new markets. Finally, competition in both markets is strong. In the United States, ammonia is currently produced by 17 firms, with a single firm dominating the national plant capacity. Urea faces even stronger competition with only ten producers nationally with the same firm dominating production. Companies looking to enter the ammonia market will likely face some competitive barriers due to monopolistic forces.

4.2 Ammonia and Synfuels HTSE Integration

For an ammonia plant with a capacity of 3,360 ton/day of ammonia production, 451.6 MWth of heat is theoretically available from the ammonia reactors. A portion of this heat is necessarily used in feed preheat. Table 12 and Table 14 show the quantity and quality of heat available from typical ammonia reactors and FT synfuels processes. Some of this heat is used for feed preheat and other internal uses while the remainder can be exported for use in HTSE.

Table 12. Heat quality generated from typical ammonia reactors and integration of a water-splitting electrolyzer with an NPP.

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Nitrogen generator Ammonia Rx	1,815,000 lb/hr.	1,515 psi, 598°F (saturated)
Medium Pressure Steam	Ammonia Rx Let down turbines System heat integration	605,000 lb/hr.	165 psi, 366°F (saturated)

Heat Type	Source	Quantity	Quality
Low-Pressure Steam	System heat integration	524,000 lb/hr.	30 psi, 250°F (saturated)

Table 13. Heat quality generated from a natural gas steam methane reformer for H_2 production and typical ammonia reactor.

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Natural gas steam methane reformer Ammonia Rx	734,000 lb/hr.	1,515 psi, 598°F (saturated)
Medium Pressure Steam	Ammonia Rx Let down turbines System heat integration	755,000 lb/hr.	165 psi, 366°F (saturated)
Low-Pressure Steam	System heat integration	549,000 lb/hr.	30 psi, 250°F (saturated)

Table 14. Quality and quantity of steam available from an FT synthetic-fuels process.

Heat Type	Source	Quantity	Quality
High-Pressure Steam	Waste-gas boiler	35,000 lb/hr.	1,515 psi, 940°F (superheated)
Low-Pressure Steam	FT reactor	35,000 lb/hr.	75 psi, 300°F (saturated)

Based on the modified Aspen HYSYS models presented in this report integration of HTSE with both ammonia and synfuels plants was done. A BFD of an ammonia plant integrated with HTSE and an NPP is presented in Figure 30. This analysis shows that all of the 158 MWth heat required by the 932 Mwe / 655 MT/d-H_2 HTSE can be met by diverting thermal energy from the ammonia plant BOP. This, however, results in a 46 Mwe (~29%) reduction in the electricity produced by the ammonia plant's BOP from 159 Mwe to 113 Mwe, which will have to be taken from the grid.

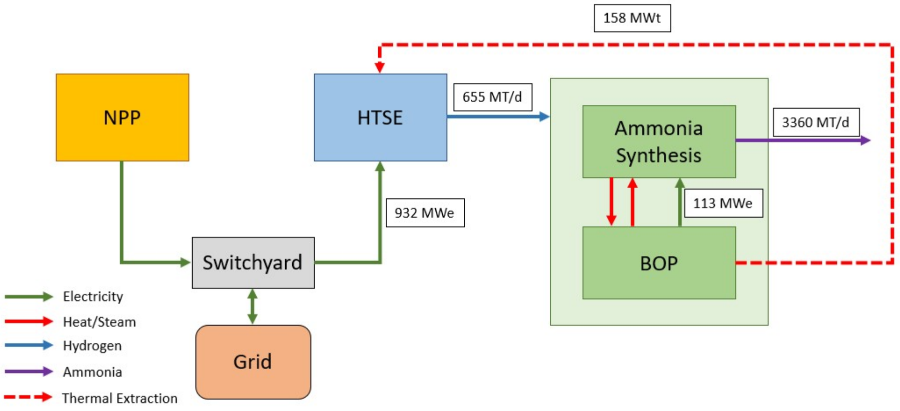


Figure 30. Simplified baseline BFD for hydrogen-to-ammonia process (without ASU).

Similarly, a BFD for a modified synfuels production plant is presented in Figure 31. From this analysis, it is evident that all the 54 MWth heat required by the 317 Mwe / 223 MT/d-H_2 HTSE plant can be met by diverting thermal energy from the BOP coupled with the FT process. This, however, results in a 9 Mwe (56%) drop in electricity produced by the BOP (from 16 Mwe to 7 Mwe) which can be made up for by using electricity from the grid.

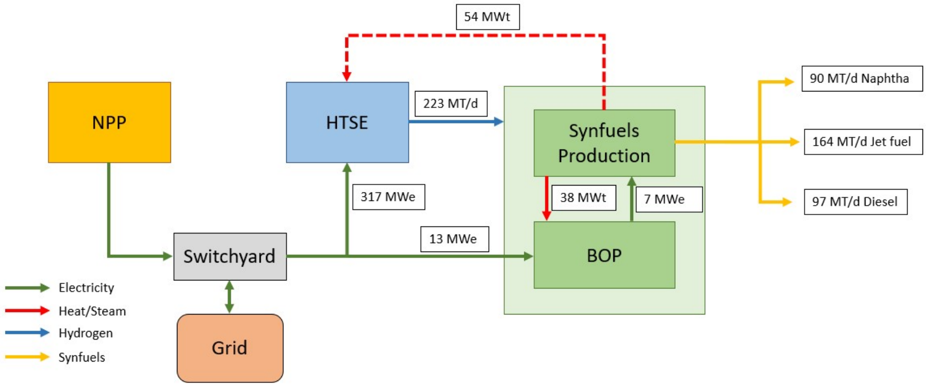


Figure 31. Simplified baseline BFD for synfuels integrated HTSE H2production.

4.3 Future Work

Future work in this area should involve more detailed techno-economic modeling around the example cases presented. A wider variety of scaling could be examined but more importantly, these concepts could be process modeled in detail. The CAPEX, OPEX, and LCOH and cost of ammonia and synfuels should be determined. The models could then be optimized with differences in heat integrations and pinch-point analysis to determine the optimum overall configurations and integrations.

5. REFERENCES

1. Knighton, Lane T, Wendt, Daniel S, Richards, James D, Rabiti, Cristian, et al *Techno-Economic Analysis of Product Diversification Options for Sustainability of the Monticello and Prairie Island Nuclear Power Plants*. United States: N. p., 2021. Web. doi:10.2172/1843030.
2. Knighton, Lane T, A. Shigrekar, Wendt, Daniel S, June 2020, *Markets and Economics for Thermal Power Extraction from Nuclear Power Plants Aiding the Decarbonization of Industrial Processes,* INL/EXT-20-58884, Rev 1, Idaho National Laboratory, Idaho Falls, ID.
3. Statista. (2021). Ammonia plant capacities in the United States from 2017 to 2020. https://www.statista.com/statistics/1266392/ammonia-plant-capacities-united-states/, (Accessed April 17, 2023).
4. Richards, J. D., Rabiti, C., Abou Jaoude, A., Westover, T. L., & Ramler, B. (2021). *Techno-Economic Analysis of Product Diversification Options for Sustainability of the Monticello and Prairie Island Nuclear Power Plants* (INL/EXT-21-62563, Rev 1). Idaho National Laboratory, Idaho Falls, ID (United States).
5. Nutrien. (2022). Nutrien 2022 Fact Book. Saskatoon, SK: Nutrien.
6. Federal Reserve Bank of St. Louis. (n.d.). Producer Price Index by Industry: Plastics Material and Resins Manufacturing (PCU325311325311). FRED Economic Data. Retrieved April 18, 2023, from https://fred.stlouisfed.org/series/PCU325311325311, (Accessed April 18, 2023).
7. Baboo, Prem Ammonia Plant Material Balance May 2021, Retrieved April 18, 2023, from https://www.researchgate.net/publication/351980089_Ammonia_Plant_Material_Balance.
8. Argonne National Laboratory. (n.d.). Hydrogen Markets. Center for Energy, Environmental, and Economic Systems Analysis. Retrieved April 18, 2023, from https://ceeesa.es.anl.gov/news/HydrogenMarkets.html.
9. National Hydrogen Roadmap. (2018). Australian Renewable Energy Agency. https://arena.gov.au/assets/2018/08/National-Hydrogen-Roadmap.pdf. (Accessed April 18, 2023).
10. Zang, G., Sun, P., Elgowainy, A. (2021). *The Modeling of Synfuel Production Process: ASPEN Model of FT production with electricity demand provided at LWR scale* (ANNL/ESD-22/1). Argonne National Laboratory, Argonne, IL.
11. DOE Alternative Fuels Data Center. (n.d.). Diesel prices. https://afdc.energy.gov/fuels/prices.html, (Accessed April 18, 2023).
12. Singh, S., & Joshi, G. (October 2022). *How SAF can become cost competitive against conventional fuel. Simple Flying*. https://simpleflying.com/saf-cost-competitive-jet-fuel/#:~:text=In%202020%2C%20the%20overall%20cost,price%20of%20conventional%20jet%20fuel., (Accessed April 18, 2023).
13. Bhadra, A. (2021, October 19). *What is synthetic e-fuel? A view into the market-changing alternative power source*. Evo India. Retrieved from https://www.evoindia.com/features/what-is-synthetic-e-fuel-a-view-into-the-market-changing-alternative-power-source, (Accessed April 18, 2023).
14. Enggyd. Block Diagram of Ammonia Production [Blog post]. Retrieved from http://enggyd.blogspot.com/2009/09/block-diagram-of-ammonia-production.html, (Accessed April 17, 2023).
15. Wood, R.A., & Boardman, R.A. (2010). TEV-666 Nuclear-Integrated Ammonia Production Analysis. Idaho Falls, ID: Idaho National Laboratory.

16. Elgowainy, A., Mintz, M., Lee, U., Stephens, T., Sun, P., Redds, K., Zhou, Y., Zang, G., Ruth, M., Jadun, P., Connelly, E., and Boardman, R. (2020). *Assessment of Potential Future Demands for Hydrogen in the United States* (ANL-20/35). Argonne National Laboratory, Argonne, IL.
17. Al-Moubaraki, Aisha & Obot, Ime. (2021). *Corrosion Challenges in Petroleum Refinery Operations: Sources, Mechanisms, Mitigation, and Future Outlook*. Journal of Saudi Chemical Society. 25. 101370. 10.1016/j.jscs.2021.101370.
18. Gohna, H. (1997, December 8-10). Concepts for modern methanol plants [Conference session]. Paper presented at the 1997 World Methanol Conference, Tampa, FL.
19. Alarifi, A., Al-Sobhi, S. A., Elkamel, A., & Croiset, E. (2014). *Multiobjective Optimization of Methanol Synthesis Loop from Synthesis Gas via a Multibed Adiabatic Reactor with Additional Interstage CO_2 Quenching. Energy & Fuels*, doi: 10.1021/ef5018379.
20. Wendt, D. S., & Knighton, L. T. (2022). High Temperature Steam Electrolysis Process Performance and Cost Estimates (INL/RPT-22-66117). Idaho National Laboratory, Idaho Falls, ID.
21. Knighton, L. T., Shigrekar, A., Yang Hui Otani, C. M., Casteel, M. J., Wendt, D. S., & Westover, T. L. (2022). *Preliminary Reversible Solid Oxide System Specification* (INL/RPT-22-69974). Idaho National Laboratory, Idaho Falls, ID.
22. Westover, T., Boardman, R. Idaho National Laboratory, Sargent & Lundy. Aughafah, H., Amen, G. R., Fidlow, H. R., Garza, I. A., Hope, E. M., Klemp, C., Kut, P., Rennels, C. L., Ross, M. M., Miller, J., & Wilson, A. J. (2023). Pre-Conceptual Designs of Coupled Power Delivery between a 4-Loop PWR and 100-500 MWe HTSE Plants. INL/RPT-23-71939.
23. Zang, G., Sun, P., & Elgowainy, A. (2021). *The Modeling of Synfuel Production Process: ASPEN Model of FT production with electricity demand provided at LWR scale* (ANL/ESD-22/1). Argonne National Laboratory, Argonne, IL.
24. Zang, G., Sun, P., Delgado, H. E., Cappello, V., Ng, C., & Elgowainy, A. (2022). *The Modeling of the Synfuel Production Process: Process models of Fischer-Tropsch production with electricity and hydrogen provided by various scales of nuclear plants* (ANL/ESD 22/8). Argonne National Laboratory, Argonne, IL.

Page intentionally left blank

Appendix A
U.S. Ammonia Production Capacity

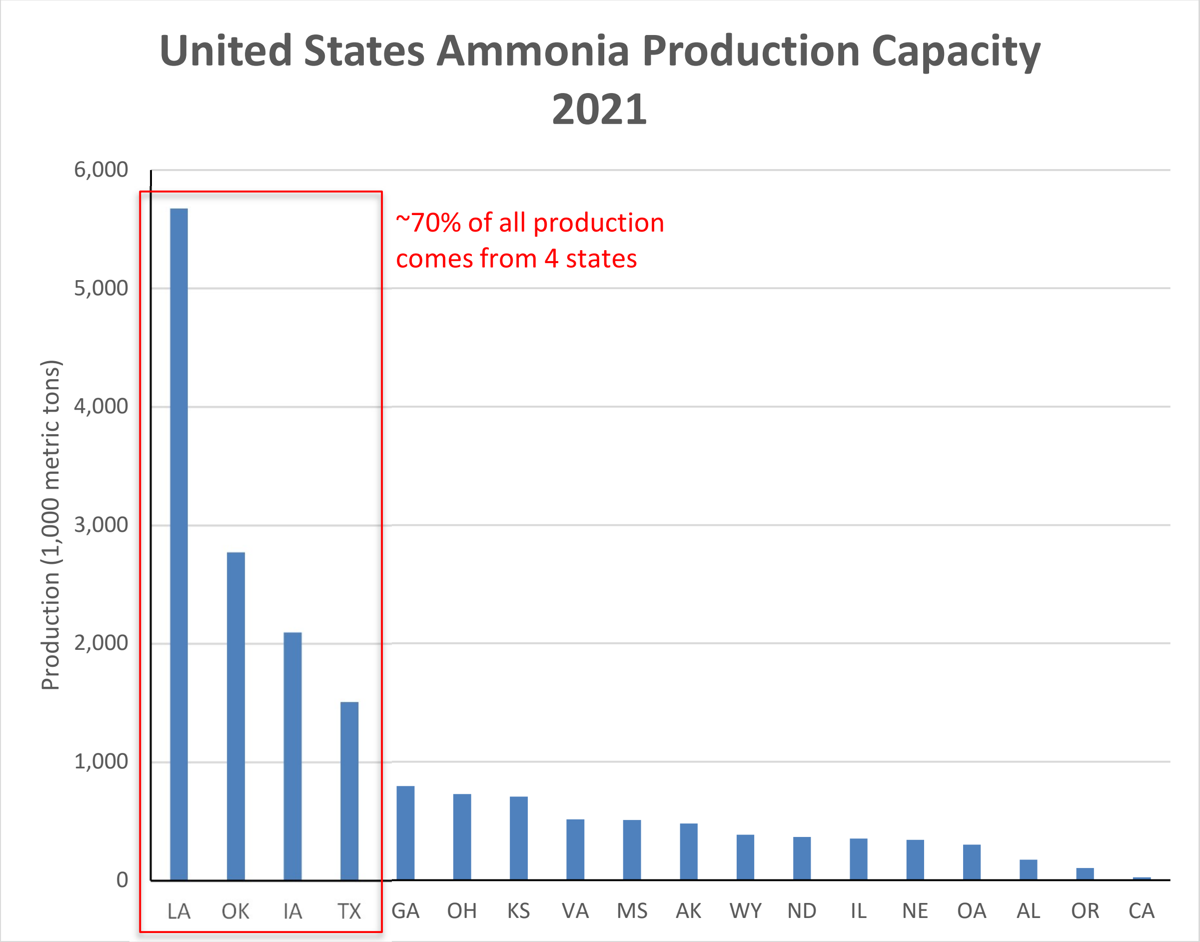


Figure 32. U.S. ammonia production capacity.[5].