

Outlook on Industrial Requirements for Incorporating Nuclear Energy into Industrial Processes

September | 2023

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Idaho National Laboratory



IES

Integrated Energy Systems

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EXECUTIVE SUMMARY

There is an increasing interest globally and in the U.S. in decarbonizing heavy industrial processes which have large demands for heat and power. Currently these industries primarily use fossil fuels to meet these demands and they include: oil & gas, petroleum refining, chemicals and derivative products manufacturing, iron & steel production, polymers, ammonia and fertilizers, etc. The U.S. DOE Integrated Energy Systems (IES) program seeks to identify and analyze opportunities for integrating and substituting nuclear energy to fulfil these large heat and power demands in a cost competitive and sustainable manner while reducing carbon emissions of the processes by using clean nuclear power. Figure ES1 shows the concept of operations for the nuclear integrated energy system. Presently various representatives from a subset of these industrial companies have expressed interest in evaluating the options of integrating future advanced nuclear small modular reactors with their industries. This report is a scoping study to provide an outlook of industrial energy demands and the potential nuclear energy substitution potential. Future work will analyze in a more detailed manner the potential designs for coupling advanced nuclear reactors with various industries.

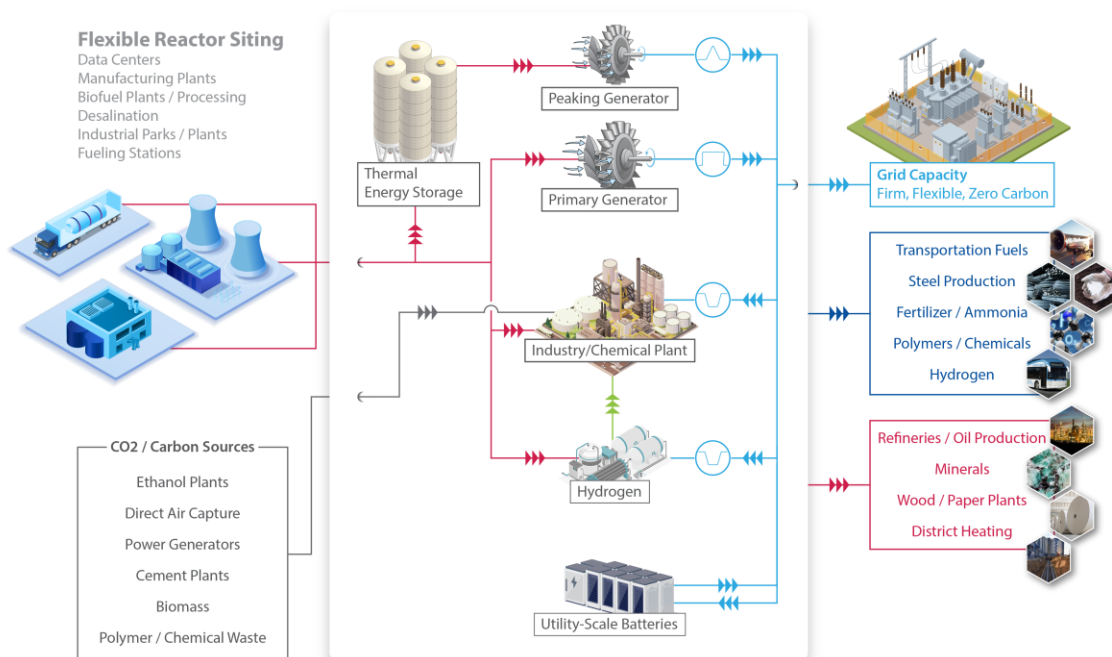


Figure ES1. Concept of operations (CONOPS) for integrated energy systems showing potential energy flows from nuclear energy to various industries to decrease carbon emissions competitively and sustainably.

A survey was developed and distributed directly to various industry representatives, with the goal of receiving feedback on the interest in nuclear power integration and understanding the needs of industrial heat and power users. A link to the survey is still live and responses can continue until a broad representation of the chemical and manufacturing industries have responded. A summary of the results of the survey is included in the report and the full survey is included in the Appendix.

For background, an overview of the developing range of advanced nuclear reactor technologies is summarized with the details being provided in the Appendix. This review is intended to be an introductory overview providing a general description of the operating principles, reactor coolant core outlet temperature, and reactor size.

The industrial processes of oil refining, methanol production, pulp and paper, ammonia and chlorine-alkali are described focusing on how heat and power is used within the facilities in the context of identifying nuclear substitution opportunities. The aim is to provide reliable, competitive, and sustainable energy that is clean while reducing carbon emissions and other environmental impacts such as water withdrawals, consumption, and contamination. A brief summary of the industries of oil refining, methanol, pulp and paper (P&P), ammonia and chlor-alkali is included as follows.

The **refining** industry exhibited in Figure ES2 is a leading consumer of fossil-fuel based heat, power and hydrogen in the U.S. industrial sector, resulting in over 238 million metric tonnes of CO₂ emissions in 2022. (reference: EIA 2023 AEO) The overall mass and energy for an average complex refinery in the US is exhibited in Figure ES2 and provides the energy metrics that could integrate with a nuclear power plant.

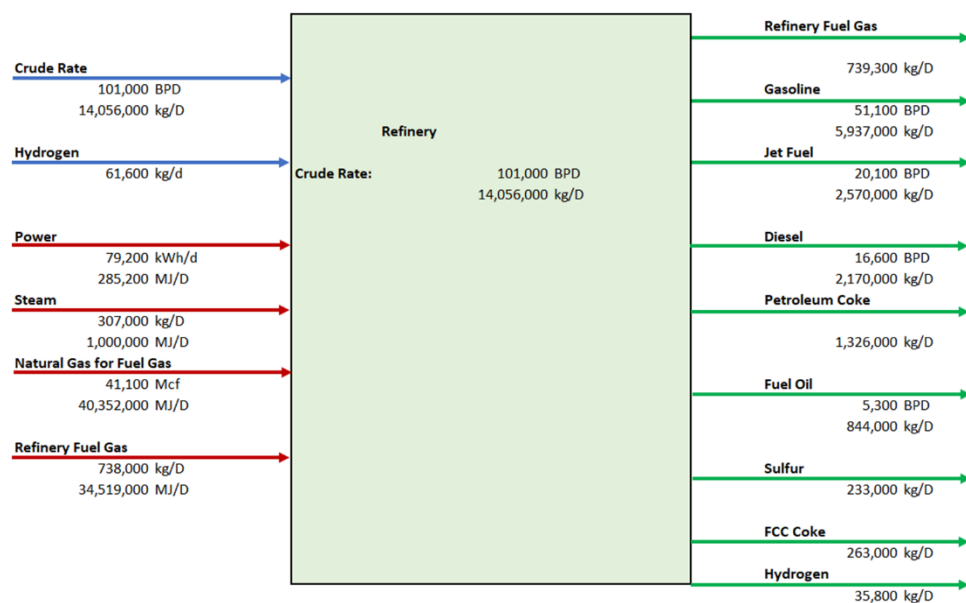


Figure ES2. Refinery Mass and Energy Balance

The operating conditions and resultant energy products of nuclear power plants, especially advanced reactors, are complimentary with refinery energy systems. Fractionation, alkylation, reforming, hydrotreating, hydrocracking, coking, isomerization, and fluid catalytic cracking all occur at temperatures below possible advanced reactor core outlet temperatures (all at less than 600°C). Through the integration of nuclear heat with the refining sector, these reactors can supply sustainable, zero-carbon energy to the U.S. refineries and significantly reduce the associated CO₂ emissions.

Methanol is a chemical with versatile applications across a variety of industries, both as a feedstock and as a stand-alone product. The major downstream products derived from methanol are acetic acid, formaldehyde, and dimethyl-ether. The derivative chemicals are used to produce plastics, adhesives, olefins such as ethylene and propylene, and for production of synthetic fuel such as gasoline, diesel, and jet fuel. The annual methanol demand in the U.S. is forecasted to reach 8.4 million metric tonnes by the year 2027. A confirmed storage of 1.54 million metric tonnes can be leveraged towards methanol export to fulfill growing global demand. Lastly, as a potential precursor to synthetic fuel, methanol to gasoline production is a mature and investigated pathway for a potential integration with small-modular nuclear reactors. Nuclear-integrated methanol production can enable decarbonization within industrial and transportation sectors.

The manufacturing of **pulp and paper** requires large amounts of low-pressure steam to digest and wash wood fibers for pulp and press and dry pulp into paper. Most of the low-pressure steam is generated from burning wood waste material; bark is burned in hog boilers, and lignin is boiled in the black liquor recovery boiler. In a typical integrated pulp and paper mill, 50–80% of the steam is produced from these sources, and additional steam is produced in a natural gas or fuel oil boiler. Steam is sent through turbines to lower the pressure and generate electricity for the plant. The other energy intense process in the plant is the lime kilns, which require high temperatures from natural gas combustion to convert compounds needed for the chemical recovery process. A nuclear power plant could replace steam and electricity generated from wood waste and natural gas allowing lignin and bark to be processed into bio-based chemicals or fuels.

Ammonia is the second largest manufactured industrial chemical. The most widely used process to synthesize ammonia is the Haber-Bosch process with steam methane reforming being used to produce the hydrogen while an air separation unit is most often used to produce the nitrogen that is fixed by the hydrogen. The Haber-Bosch process synthesizes ammonia under very high-pressure conditions. Both steam-methane reforming and high-pressure compression are energy intensive steps. However, the hydrogen-nitrogen reaction is highly exothermic and must be continuously cooled to manage the reaction efficiency. Hence the main role for nuclear energy is to provide power to the compressors and air separation plant. The advent of high-temperature, water-splitting electrolysis presents an opportunity to produce hydrogen using nuclear energy. In this case, the thermal energy generated by the Haber-Bosch reactors can also raise steam to feed to the electrolysis plant. Such a scheme can optimize the benefits of using a nuclear reactors to support ammonia production while eliminating the use of methane (or natural gas and other fossil-fuels) for the production of ammonia. Prior detailed process development has shown up to a 95% reduction in CO₂ emissions is possible when nuclear energy, water, and air are the only feedstocks for ammonia production.

Chlorine is a critical chemical in the production of many goods and disinfection of water supplies. Approximately 11 million metric tonnes were produced in the U.S. in 2021. Chlorine is primarily produced in an electrolysis process that requires large quantities of low temperature heat and electricity. Along with chlorine gas, sodium hydroxide is co-produced during electrolytic separation of sodium chloride, which is supplied in brine. As sodium hydroxide is alkaline, co-production with chlorine gives rise to the “chlor-alkali” name the industry is known by. All but one of 39 U.S. plants (as of 2021) utilize one of two types of electrolysis cells: diaphragm and membrane, with process temperatures ranging from 74°C to 105°C. Heat for the cell, for preprocessing of brine, and for concentration of sodium hydroxide are typically supplied by steam at 177°C and 820 kPa. If all heat is supplied by steam, the 2.7 TJ daily heat demand of an “average” plant (producing 828 tonnes of chlorine daily) may be met by approximately 576 tonnes of steam per day. Continuous electricity demand by the “average” plant is 141 MW, although this may be reduced by utilization of hydrogen, a byproduct of the cell, for on-site electricity generation. Potential reduction of carbon dioxide emissions by supplying all heat and electricity from a nuclear reactor is approximately 28.7 million tonnes in the U.S. annually or greater—735,000 tonnes or more, per plant, per year.

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CONTENTS

EXECUTIVE SUMMARY	ii
ACRONYMS.....	xi
1. INTRODUCTION.....	1
2. INDUSTRIAL SURVEY	3
2.1 Industrial Survey Questions and Results.....	3
3. OVERVIEW OF ADVANCED REACTORS	5
3.1 High-Temperature Gas Reactors.....	7
3.2 Liquid Metal Fast Reactors	8
3.3 Molten Salt Reactors	9
3.4 Advanced Light-Water Reactors.....	10
4. INDUSTRIAL NUCLEAR INTEGRATION POTENTIAL	11
4.1 Oil Refining.....	11
4.1.1 Refinery Energy System	14
4.1.2 Fractionation	15
4.1.3 Upgrading and Conversion	15
4.1.4 Contaminant Removal.....	16
4.1.5 Stream Quality Improvement and Blending	16
4.1.6 Heat Recovery.....	16
4.1.7 Refining CO ₂ Emissions	17
4.2 Methanol	17
4.2.1 A Brief Overview.....	17
4.2.2 Methanol: Applications.....	18
4.2.3 Top Five Target Markets for Methanol.....	19
4.2.4 Methanol Production.....	21
4.2.5 Industrial Processes, Reformers, Exothermic Synthesis, Process Control and Optimization	24
4.2.6 Downstream Products	28
4.2.7 Major North American Methanol Producers and Port Storage Capacities	30
4.2.8 Nuclear-Integrated Methanol Production.....	31
4.3 Pulp and Paper	32
4.3.1 Process Description.....	33
4.3.2 Plant Load Data.....	37
4.3.3 Decarbonization Opportunities	39
4.4 Ammonia.....	43
4.4.1 Statistics: Production, Usage, Price, Location	43
4.4.2 Preparation of Feed Material for Ammonia Synthesis.....	46
4.4.3 Ammonia Synthesis: Haber-Bosch Process	50

4.4.4	Energy Consumption Analysis of the Process	55
4.4.5	Downstream Product and Process.....	59
4.4.6	Opportunity for Nuclear Reactor Integration.....	60
4.5	Chlor-Alkali	61
4.5.1	Market.....	61
4.5.2	Production Process.....	61
4.5.3	Energy Requirements and Opportunity for Nuclear Reactor Integration.....	63
4.5.4	Decarbonization Potential.....	63
5.	CONCLUSIONS.....	63
6.	ACKNOWLEDGEMENTS	66
7.	REFERENCES.....	67
	APPENDIX A.....	79
	APPENDIX B	82

FIGURES

Figure 1.	U.S. total energy Sankey Diagram (Lawrence Livermore National Laboratory and United States Department of Energy 2022).....	1
Figure 2.	Advanced Nuclear Energy Pathways by Sector.	2
Figure 3.	Areas of interest for industrial survey responders as of August 2023. Highest possible score is 100%.....	3
Figure 4.	Average weighted score of identified research area priorities.....	4
Figure 5.	Energy integration method priorities.	4
Figure 6.	Visual representation of a few industrial applications and how they correspond to several nuclear reactor types (IAEA, 2017).....	6
Figure 7.	Coolant outlet temperatures for some of the HTGR and VHTR designs (Chapin 2004).	7
Figure 8.	Schematic diagram of a VHTR (Buckthorpe 2017).	8
Figure 9.	Schematic diagram of an SFR (Buckthorpe 2017).	9
Figure 10.	Schematic diagram of an MSR (Buckthorpe 2017).....	10
Figure 11.	Schematic diagram of a supercritical ALWR, more specifically a SCWR (Buckthorpe 2017).....	11
Figure 12.	Locations and sizes of oil refineries in the United States.	12
Figure 13.	Refinery block flow diagram.....	12
Figure 14.	Typical refinery PFD showing various process operations.	13
Figure 15.	Refinery Mass and Energy Balance.....	13
Figure 16.	Typical refinery steam system.....	14

Figure 17. Methanol production in units of million metric tons in the U.S. during 2010–2019 (American Chemistry Council, 2020).....	17
Figure 18. Global methanol demand by application for the year 2021 (Methanol Institute n.d.).....	18
Figure 19. Global methanol end-use categorization (in MMT, Methanol Institute n.d.).....	19
Figure 20. Target markets for methanol based on end use (in MMT, Methanol Institute n.d.).....	19
Figure 21. Demand forecasts for light olefins in the U.S. (in MMT, Statista 2020b).....	20
Figure 22. Projected methanol market volume (MMT) in the U.S. by the year 2027 (Statista 2020a).....	20
Figure 23. Global monthly methanol prices (U.S. dollar per metric ton) by location and type (Methanol Institute, 2023).....	21
Figure 24. A high-level architecture of process flow for methanol production	22
Figure 25. A zoomed-in architecture of the process corresponding to syngas preparation.	22
Figure 26. Methanol synthesis pathways and characterization of classical reactors.....	23
Figure 27. Upgrading conditions contingent on end-product (Idaho National Laboratory, 2012, 2010; Zang et al. 2022; Matsukata et al. 2011; Maldonado et al. 2010)	23
Figure 28. Combined reforming process for syngas production.....	24
Figure 29. ICI process incorporating a GHR in conjunction with oxygen-blown secondary reformer.	25
Figure 30. Process-flow sequence for methanol production from coal or fuel oil.....	25
Figure 31. Carbon oxides’s equilibrium conversion to methanol based on (reformed) natural gas with a composition of 73% hydrogen, 15% carbon monoxide, 9% carbon dioxide, 3% methane.....	26
Figure 32. Process flowsheet for methanol synthesis.	27
Figure 34. Sawtooth temperature profile within a Quench reactor: A – equilibrium line, B – maximum rate line, C – quench line, and D – intra-bed line.....	28
Figure 35. Average case material balance summary for methanol production (based off natural gas as a feedstock) (McMillan 2016).....	29
Figure 36. Comparative figure contrasting material feedstock and energy requirements for coal-driven MTG pathway using conventional approach and with HTSE and HTGR. Comparison performed for similar daily production profiles of gasoline and liquefied petroleum gas (LPG).	29
Figure 37. Average material and energy balance summary for MTO pathway using conventional approach and with HTSE and HTGR, with similar output profile of olefins being produced.	30
Figure 38. North American ports with confirmed methanol storage capacities (in metric tons).....	31
Figure 39. Global pulp and paper market evolution (Berg and Lingqvist 2019).....	33
Figure 40. Pulp and paper mill block flow diagram.....	34
Figure 41. High-level overview of the stages of the kraft cycle (Tran and Vakkilainen 2012).....	34
Figure 42. Depiction of a continuous digester (Pougatch, Salcudean, and Gartshore 2006).....	35

Figure 43. Chemical reactions in the black liquor recovery boiler (Jarvinen 2016).	36
Figure 44. Chemical reactions occurring in the causticization cycle.	36
Figure 45. Depiction of a paper machine (Egmason 2010).	37
Figure 46. Model of a pulp and paper mill steam system (Worsham 2020).	38
Figure 47. Black Liquor Gasification Combined Cycle (BLGCC) process diagram with sulfur recovery (Larson, Consonni, and Katofsky 2003).	41
Figure 48. Chemrec process diagram (Chemrec 2011).	41
Figure 49. Ammonia production facilities in the U.S. and their capacity in metric kilotons per year (United States Geological Survey 2021).	44
Figure 50. Anhydrous ammonia price in Illinois (Schnitkey et al. 2022).	45
Figure 51. National gas and ammonia prices in last 2 years (Raghuv eer and Wilczewski 2022).	45
Figure 52. Conventional ammonia production process by thyssenkrupp (Uhde) and operating conditions (Asiri, Inamuddin, and Boddula 2020).	50
Figure 53. Modern commercial ammonia plant design: (top) KBR and (bottom) Haldor Topsøe (Venkat Pattabathula 2016).	51
Figure 54. Mole fraction of NH ₃ at equilibrium where inlet mole ratio of N ₂ :H ₂ = 1:3 calculated from Aspen plus model.	53
Figure 55. Ammonia separation (left) condensation, (right) adsorption.	55
Figure 56. Schematic of the Uhde process dual pressure ammonia synthesis (Brightling 2018).	55
Figure 57. Energy flow diagram for methane-fed ammonia synthesis [reprinted from (Soloveichik 2016, 2017)].	58
Figure 58. schematic material input and output and energy requirements for Haber-Bosch process.	58
Figure 59. Major downstream nitrogen compounds from natural gas in the U.S. 2020 (United States Geological Survey 2021).	60
Figure 60. Flow-through of a 1 mtpa production of ammonia by CORE POWER.	61
Figure 61. Process flow diagram for a chlor-alkali plant based on the diaphragm cell. From (McMillan et al. 2016), based on (Pellegrino 2000; Tilak V. Bommaraju 2002).	62

TABLES

Table 1. Classification of advanced NPPs, based on their operating temperature ranges and thermal outputs.	6
Table 2. Operating conditions for selected refinery unit operations. The numbers correspond to the reference numbers seen in Figure 14.	15
Table 3. Summary of chemical reactions for downstream product upgrading with methanol.	28
Table 4. Plant steam sources (Worsham 2020).	38
Table 5. Turbine Electricity Generation (Worsham 2020).	38
Table 6. Plant steam demands (in terms of mass and energy) (Worsham 2020).	39
Table 7. Non-steam producing heat sources (Worsham 2020).	39
Table 8. Emissions from the pulp and paper industry.	40
Table 9 Electrolysis type: electrolyte, ion transport and reactions.	47
Table 10. Hydrogen production cost associated with different sources and processes.	48
Table 11. Energy consumed in Haber-Bosch process (Dybkjaer 1995).	56
Table 12. Energy flows in an ammonia production plant (Barton 2001).	57
Table 13. Energy requirement in methane-fed Haber-Bosch process (Smith, Hill, and Torrente-Murciano 2020)	57
Table 14. Energy requirements for ammonia synthesis in different feedstock and process [reprinted from (International Renewable Energy Agency and Ammonia Energy Association 2022; Smith, Hill, and Torrente-Murciano 2020)].	59
Table 15. Summary of identified industry CO ₂ emissions and process conditions.	64

ACRONYMS

ABWR	advanced boiling water reactor
AHWR	advanced heavy-water reactor
ALWR	advanced light-water reactor
APWR	advanced pressurized water reactor
BASF	Badische Anilin und Soda Fabrik
BLG	black liquor gasification
BLGCC	black liquor gasification combined cycle
CCS	carbon capture and sequestration
DC	direct current
DOE	department of energy
EPA	environmental protection agency
FCC	Fluid Catalytic Cracking
FORCE	Framework for the Optimization of Resources and Economics
FT	Fischer-Tropsch
GCFR	gas-cooled fast reactor
GCR	gas-cooled reactor
GHR	Gas-heated reformer
GIF	Generation IV International Forum
HERON	holistic energy resource optimization network
HP	high pressure
HTGR	high-temperature gas-cooled reactor
HTSE	high-temperature steam electrolysis
ICI	Imperial Chemical Industries
IES	integrated energy system
IMSR	Integral Molten Salt Reactor
LFR	lead-cooled fast reactor
LP	low pressure
LMFR	liquid metal fast reactor
LWR	light water reactor
MMT	million metric tons
MP	medium pressure
MSR	molten salt reactor
MTG	methanol-to-gasoline

MTO	methanol-to-olefins
NPP	nuclear power plant
PBMR	pebble bed modular reactor
PEM	proton exchange membrane
PFD	process flow diagram
PSA	pressure swing adsorption
PV	photovoltaic
SCWR	supercritical water-cooled reactor
SFR	sodium-cooled fast reactor
SMNR	small modular (nuclear) reactor (nominally SMR, 'N' added to avoid conflict with steam methane reforming)
SMR	steam methane reforming (may be small modular reactor in context of specific nuclear small modular reactor design names)
SOEC	solid oxide electrolyzer cell
TES	thermal energy storage
VHTR	very high-temperature reactor
WGS	water gas shift reaction

Outlook on Industrial Requirements for Incorporating Nuclear Energy

1. INTRODUCTION

Integrating nuclear generation into industrial processes is proposed as a pathway to introduce reliable, dispatchable, non-emitting energy into large industrial processes. Of the many anticipated challenges for integrating nuclear reactors into industrial processes, this report focuses on determining the specific opportunity for nuclear energy. Plant-wide or even high-level process information may not appropriately characterize the actual

The United States has incentivized and formally declared various climate change mitigation policies which will require significant energy consumption changes across the United States energy profile. Non-renewable carbon sources account for around three-quarters of all domestic energy consumption, as noted in Figure 1. The two primary decarbonization targets of the United States include a 50% reduction in carbon emissions by 2030 (relative to 2005 levels) and full decarbonization by 2050 (United States Department of State and United States Executive Office of the President 2021). Replacing the energy source or offsetting the emissions of nearly 77 Quads (81.2 Exajoules, or an average load of about 2.6 TW) is a significant challenge that will require multiple simultaneous solution approaches including non-emitting power generation, electrification, and innovative process development. Less than 40% of the domestic energy consumption was used in electricity generation in 2021. Decarbonizing heat use is needed to achieve the aggressive goals put forward by the United States.

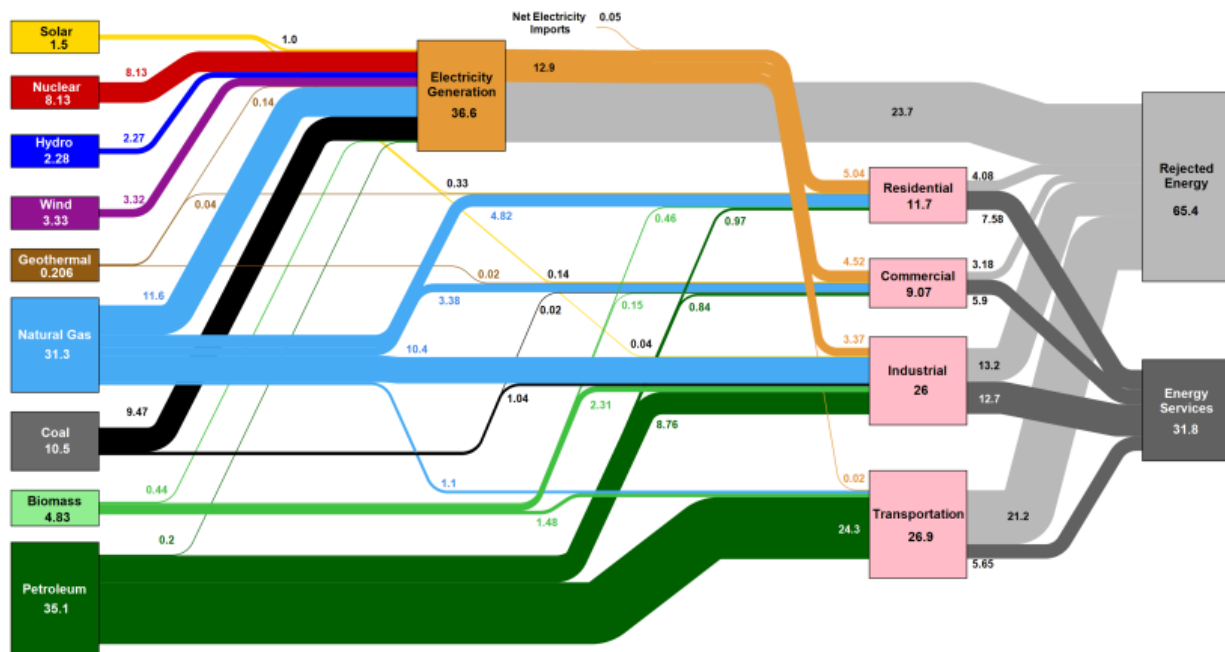


Figure 1. U.S. total energy Sankey Diagram (Lawrence Livermore National Laboratory and United States Department of Energy 2022).

The NE-IES program of the Department of Energy (DOE) is evaluating the opportunity for nuclear-generated energy to replace energy sourced from petroleum, coal, and natural gas in various areas of the economy. Nuclear reactors are heat generators that have traditionally almost exclusively made domestic electricity at relatively low rates of thermal-to-electric conversion efficiency. As seen above in Figure 1,

most of the energy is consumed as heat either directly at end use or in the production of goods. Direct thermal energy use from nuclear is so far an untapped market.

Thermally integrating nuclear reactors with industrial users is complex for a variety of reasons including engineering, social, legal, and regulatory (Szilard et al., 2017)(Horvathm 2016). The IES program generates decision frameworks, databases, models, and technoeconomic analyses that can provide structure and insight into the operation and deployment of systems with integrated nuclear energy.

Detailed process information is required to understand the opportunity for nuclear integration with particular industries. A compiled understanding of the magnitude and conditions of energy flows within industrial processes is needed to engineer nuclear generated heat integration. This resource needs to include internal material flows, specific thermal requirements of independently operated stages of industrial processes, and electrical requirements. To be specific, the differences must be characterized between internal and external loads, and process flow documentation must be developed that differentiates how heat is transported and consumed through a prototypical industrial plant. Figure 2 shows how various nuclear energy pathways may interact within multiple industries.

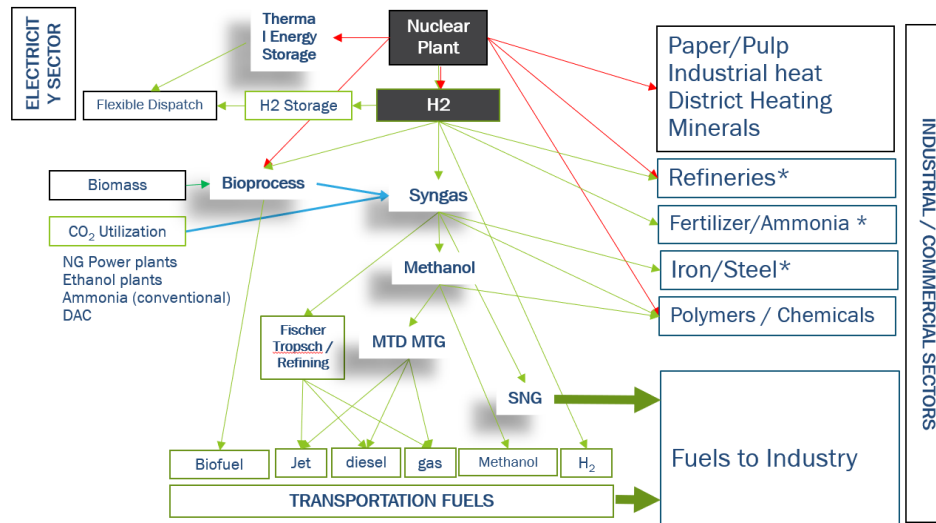


Figure 2. Advanced Nuclear Energy Pathways by Sector.

The NE-IES program has been reviewing industries that use large quantities of thermal and electrical energy. This process has so far been done primarily through open literature studies and through the distribution of an industrial survey sent to existing contacts of IES leadership. A narrowed down set of five candidate industries have been selected through prior work (Saeed et al., 2023). These industries: ammonia production, gasoline refinery, chlor-alkali production, methanol synthesis, and pulp and paper mills have been selected as initial technologies that are being analyzed down to the individual process level. This is a work in progress, wherein the current report shows an outlook and current preliminary analysis. Steel production from iron ore is one of the 5 largest industrial emitters, producing nearly 90 MMT/year of product and will be also analyzed in a follow up near-future work. The total energy demand for the entire energy sector was reviewed in previous work (Knighton, 2020). This work is also intended to leverage open-source information and publication where possible. By generating open-source materials, national laboratory resources can maximize the impact to the taxpayer. Future work can focus generalized results to specific industrial parks.

In this report, the industrial survey is reported. In addition, an overview of advanced reactors is included. Five industries have process documentation included in this report.

2. INDUSTRIAL SURVEY

To develop an effective decarbonization plan that integrates nuclear reactors integration with industrial processes, we conducted a survey that was shared with partners in various industrial companies. The survey was carefully crafted and shared with relevant industrial points of contact. The goal of the survey was to gather information on current process flow streams and energy consumption patterns, and to identify opportunities for integrating nuclear reactors into industrial processes.

2.1 Industrial Survey Questions and Results

The survey questions aimed to gather information about a wide range of industrial processes that included manufacturing, chemical, energy production and distribution, agriculture, transportation, and other related industries. Although the IES team has received some responses, we are still actively collecting data to improve the comprehensiveness of our analysis. The survey link is currently active, at least until the publication date of this report. The survey can be accessed using the following URL: [\[https://inlhrfedramp.gov1.qualtrics.com/jfe/form/SV_02sXEonBQBJVYma\]](https://inlhrfedramp.gov1.qualtrics.com/jfe/form/SV_02sXEonBQBJVYma). A list of these questions is included in Appendix A. There are presently six responses to the survey from the oil and gas industry, glass manufacturing, chemicals production, and thorium production and use. The responses identifying process priorities, capability research needs, and integration method are presented in Figure 3–Figure 5. Note that the analysis presented herein is based on a limited number of responses received at the present time and may not fully encompass a complete scoping of the entire industrial sector. For instance, none of the current responders were minerals producers, and hence the emphasis may change as additional responses received. While the survey is an on-going and progressive work, the initial responses serve as an indication of which specific industries have a strong interest in nuclear as a source of energy to their plants. The discussion and presentation of results in this section will follow the order of questions in the survey.

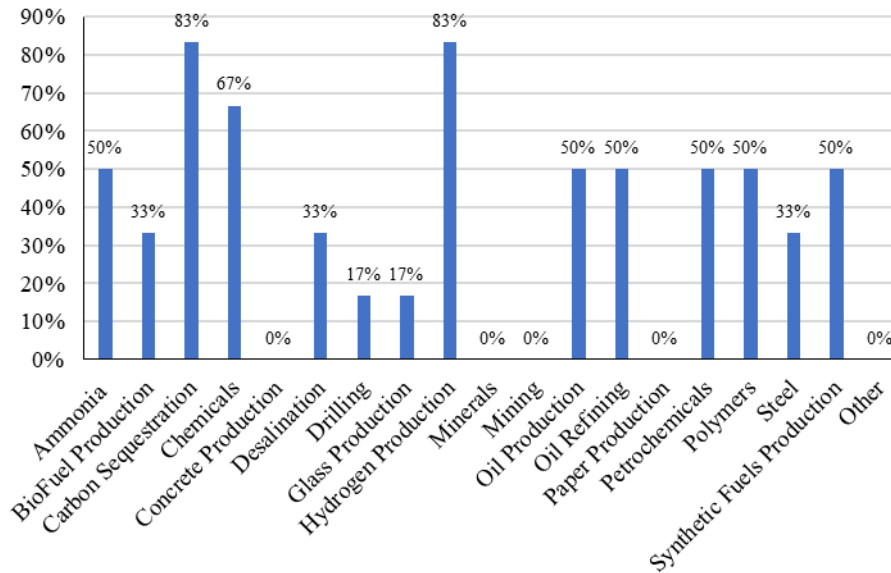


Figure 3. Areas of interest for industrial survey responders as of August 2023. Highest possible score is 100%.

The specific reported loads required to meet company needs range from 300–1,000MWe and 600–1,300MWth. These large loads show that there may be deployment cases that can handle the power output of entire advanced reactors—especially small modular reactors. The requested project timeline is noted by

multiple responders to be effectively as soon as possible, but pushed to 6–10 years to better align with the advent of advanced reactor deployments.

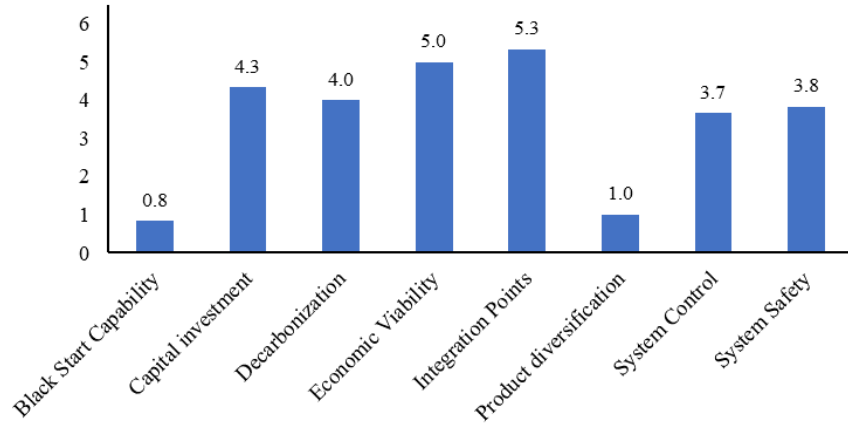


Figure 4. Average weighted score of identified research area priorities. Responders were asked to rank tasks 1–7, scores were averaged using the inverse of ranking so that in this figure, high scores are the most pressing research needs. Highest possible score would be 7.0.

The objective of this question is to collect insights into the challenges that have to be addressed. Respondents reported they require steam conditions from respondents ranged in pressure from 5 bar (75 psi) to as high as 170 bar (2,500 psi). Temperatures up to 700°C are of interest. These conditions requested of nuclear generators do not meet the highest temperature processes reported by respondents, which can reach 900°C for chemicals and 1,500°C for glass furnaces.

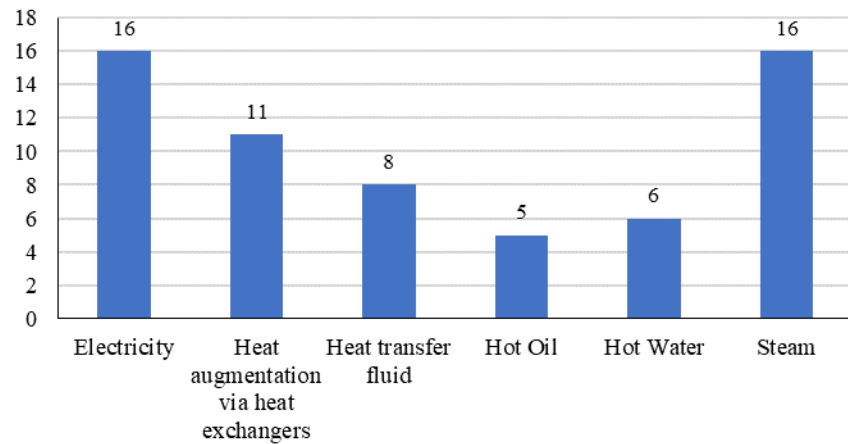


Figure 5. Energy integration method priorities. “High priority” was recorded as a score of 3, “medium priority” was recorded as a score of 2, “low priority” was recorded as a score of 1, and “no priority” was recorded as 0. Total possible score is 18.

From the comments, reliability is of particular importance to the respondents. The demand schedule reported is continuous across the year and even between years except for during unplanned downtime. One comment noted that missed demand on the order of seconds is unacceptable for their processes. This level of reliability must be well-understood for the proposed integration into an industrial system and must be a primary design basis for interfacing.

As future responses are submitted, the survey results should be updated in future reports.

3. OVERVIEW OF ADVANCED REACTORS

Demand for industrial heat is significant and currently largely met by fossil fuel sources resulting in a considerable environmental impact due to greenhouse gas emissions. To address this issue, the use of advanced nuclear reactors for industrial heat production is gaining attention as a promising alternative. Coupling advanced nuclear reactors with industrial heat users offers a range of benefits, including a source of reliable, clean, and cost-effective energy for industries that require high-temperature heat, such as hydrogen, ammonia, mining, steel, district heating, and several other energy products discussed in this study.

Unlike traditional nuclear reactors, advanced reactors are designed to use non-traditional types of fuel and coolant fluids that allow them to operate at higher temperatures, which makes them particularly well-suited for coupling with industrial heat users. To continue and expand the environmental benefits of existing nuclear power plants operating globally, new advanced reactors need to be designed and developed to replace older plants as they retire. The Generation IV International Forum (GIF) is an international forum forming a technology roadmap for examining and developing these new nuclear systems with a focus on the nuclear reactor and its energy conversion systems, as well as facilities related to the fuel cycle, extraction, and waste disposal, which are crucial for overall performance and capability (Abram 2002).

Private industries are currently developing numerous advanced nuclear reactors, often with the help of federal research laboratories. These advanced reactors are primarily categorized based on the type of coolant they use as follows:

- Liquid metal fast reactors (LMFR)
 - Sodium-cooled fast reactors (SFR)
 - Lead-cooled fast reactors (LFR)
- Water-cooled reactors
 - Advanced light-water reactors (ALWRs), including pressurized water reactors (APWR) and boiling water reactors (ABWR)
 - Advanced heavy water reactors (AHWR)
- Gas-cooled reactors (GCR)
 - Gas-cooled fast reactors (GCFR)
 - High-temperature gas-cooled reactors (HTGR) or very high-temperature reactors (VHTR)
- Molten-salt reactors (MSR)
 - Molten salt cooled reactors
 - Molten salt fueled reactors.

For coupling nuclear systems with industrial applications, the four main types of nuclear reactors selected and identified as potential options for industrial decarbonization are: HTGRs, LMFRs, MSRs, and ALWRs. One reasonable option is to categorize advanced reactor systems based on their thermal output and operating temperature range. Table 1 shows three operating temperature ranges identified: low (<350°C) for ALWR and heavy-water reactors, medium (350–650°C) for MSRs, SFRs, and LFRs, and high (>650°C) for GCRs and HTGRs or VHTRs. Each of these categories was further divided into three subcategories: micro/small (<25 MWth) for microreactors, small to medium (25–750 MWth) for small modular reactors (SMRs), and large NPPs (>750 MWth).

Table 1. Classification of advanced NPPs, based on their operating temperature ranges and thermal outputs.

Low Temperature ~(<350°C)			Medium Temperature ~(350–650°C)			High Temperature ~(>650°C)		
<25 MWth Microreactors	20–700 MWth SMRs/medium	>700 MWth Larger NPPs	<25 MWth Microreactors	20–700 MWth SMRs/medium	>700 MWth Larger NPPs	<25 MWth Microreactors	20–700 MWth SMRs/medium	>700 MWth Larger NPPs
—	APWR	AHWR	Heatpipes	MSR	GCFR	Heatpipes	HTGR	HTGR
—	ALWR	ABWR	HTGR	LFR	SFR	HTGR	GCFR	—
—	—	APWR	—	SFR	MSR	—	MSR	—

The temperature requirements for heat applications can vary widely depending on the specific use. Figure 6 presents a visual representation of this variation and how it corresponds to several nuclear reactor types, including the temperature requirements range from just above room temperature for applications such as hot water and steam for agriculture (agro) industry, district heating, and sea water desalination, to as high as 1,000°C for applications such as process steam and heat for the chemical industry, high-pressure injection steam for enhanced oil recovery, oil shale and oil sand processing, oil refinery processes, olefine production, and coal and lignite refinement. Water splitting for hydrogen production requires even higher temperatures as well as low temperatures. The use of nuclear energy for supplying process heat is limited to an upper temperature limit of 1,000°C based on the current design of advanced nuclear systems. Some industrial processes, such as steel production, require temperatures above 900-1,000°C, and in such cases, nuclear energy may still be utilized through secondary energy carriers such as electricity, hydrogen, and synthesis gas as described further in the relevant subsequent sections in this report.

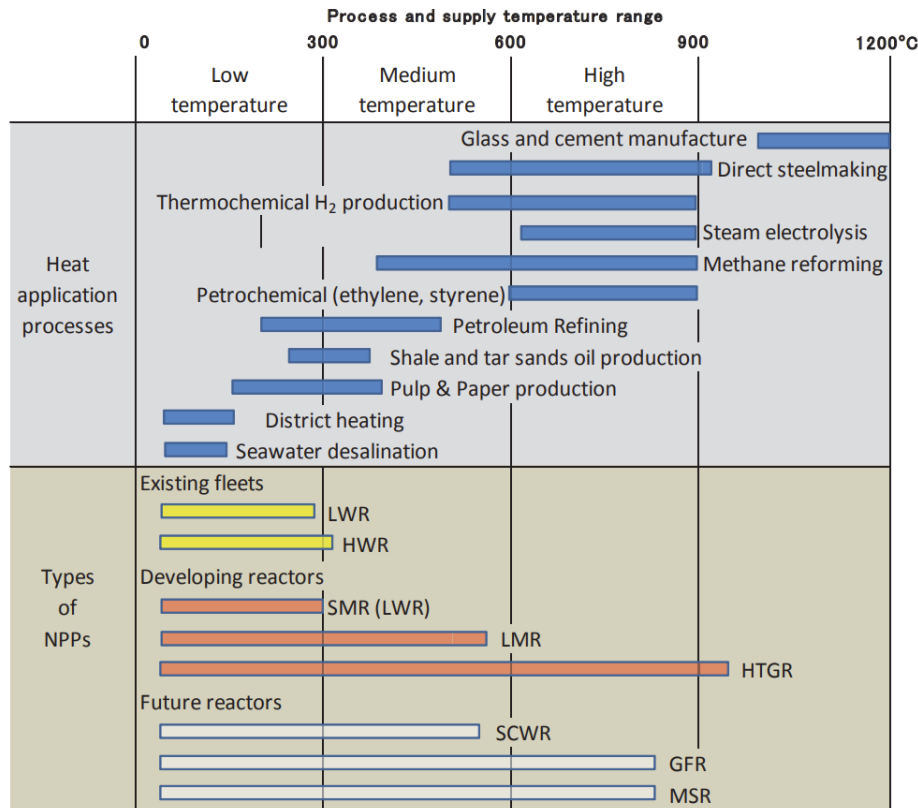


Figure 6. Visual representation of a few industrial applications and how they correspond to several nuclear reactor types (IAEA, 2017).

3.1 High-Temperature Gas Reactors

HTGRs are a promising technology for decarbonizing industrial applications due to their ability to provide relatively higher temperature heat for a range of industrial processes. HTGRs utilize helium gas as a coolant and graphite as a moderator, enabling them to operate at higher temperatures than conventional nuclear reactors, up to 950-1,000°C for some of the VHTRs designs, as illustrated in Figure 7, showing their nominal outlet temperature versus their maximum potential temperatures. Note that even higher maximum VHTR temperature exceeding 1,000°C were often reported for VHTRs, but that refers to optimistic long-term target temperature, which will not be realized until later generations. The 950-1000°C high but realistic temperature operation range makes VHTRs well-suited for supplying heat to industrial processes that require temperatures of up to 1,000°C, such as chemical manufacturing, hydrogen, steel production, and cement production.

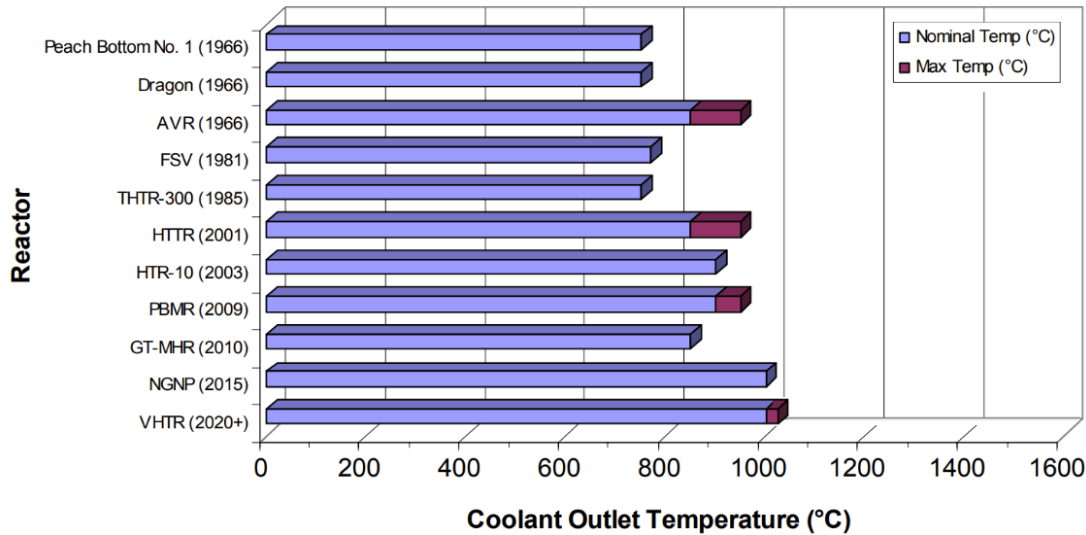


Figure 7. Coolant outlet temperatures for some of the HTGR and VHTR designs (Chapin 2004).

One key advantage of advanced HTGRs for industrial applications is their high efficiency. Because they operate at high temperatures, they can achieve higher conversion efficiencies than conventional NPPs. HTGRs can also be designed for cogeneration, in which both electricity and heat are produced, further improving their efficiency, and reducing the overall cost of energy production.

Another advantage of HTGRs for industrial decarbonization is their inherent safety features. The use of helium gas as a coolant eliminates the possibility of a coolant ingress, and the graphite moderator has a high melting point and low coefficient of thermal expansion, reducing the risk of structural failure (Reitsma, Silady, and Kunitomi 2014). HTGRs are also compatible with Brayton power cycles, allowing for even higher operating temperatures on the power cycle side and optimized operation by minimizing water usage and cooling requirements.

Figure 8 shows a schematic of a graphite-moderated and helium-cooled VHTR system that can be utilized for both electricity and hydrogen cogeneration. The reactor core is typically either a prismatic block or a pebble bed design, with an initial target temperature of 1,000°C for hydrogen production. The first VHTR, the pebble bed modular reactor (PBMR), was planned for construction in South Africa, with temperatures of 950°C, but it lost government funding in 2010 (Buckthorpe 2017). In 2012, China began constructing a 200-MW high-temperature pebble bed reactor, with design outlet temperatures of 750°C. Many national programs are considering the deployment of HTGR within Generation IV, and some are planning to construct a prototype that uses gas outlet temperatures ranging from 750–950°C.

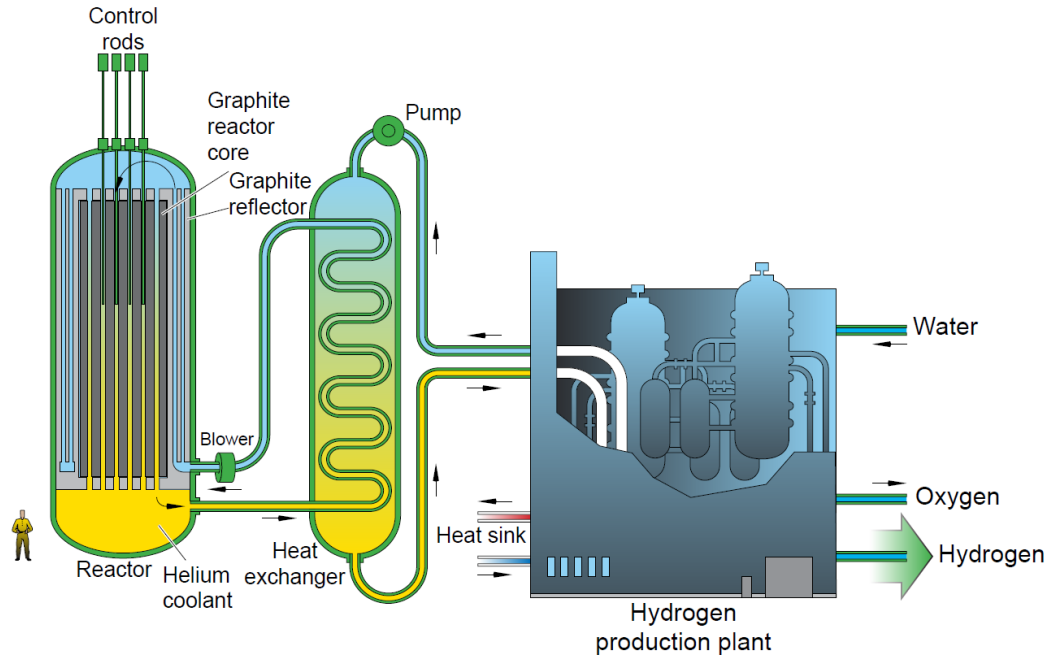


Figure 8. Schematic diagram of a VHTR (Buckthorpe 2017).

3.2 Liquid Metal Fast Reactors

LMFRs are a type of nuclear reactor that utilizes liquid metal (usually sodium or lead) as both the coolant and the neutron moderator. LMFRs are capable of high-temperature operation and can achieve very high conversion efficiencies due to their fast-neutron spectrum, making them a promising technology for decarbonizing industrial applications.

The medium- to high-temperature operation of LMFRs allows them to co-supply heat to industrial processes that require temperatures up to 570°C, such as hydrogen production, metal smelting, and glass manufacturing (Peakman and Merk 2019). LMFRs can also be designed for cogeneration, in which both electricity and heat are produced, further improving their efficiency and reducing the overall cost of energy production.

LMFRs also have the potential to improve the sustainability of the nuclear fuel cycle. Because they operate on a fast-neutron spectrum, they can utilize fertile materials (i.e., depleted uranium and thorium) as fuel, in addition to traditional enriched uranium and plutonium fuels. This has the potential to reduce the amount of high-level nuclear waste generated by the nuclear fuel cycle, while also improving the sustainability and security of the fuel supply.

Figure 9 shows a diagram for a possible design of an SFR, a type of LMFR. The significant experience accumulated with LMFR designs (specifically in Europe for SFRs) means that this system can be deployed earlier than other advanced reactor prototypes, however, there are challenges to be addressed in the deployment of LMFRs for industrial decarbonization, including the relatively high capital costs associated with building and deploying the reactor relative to other traditional reactor types (Cochran 2015).

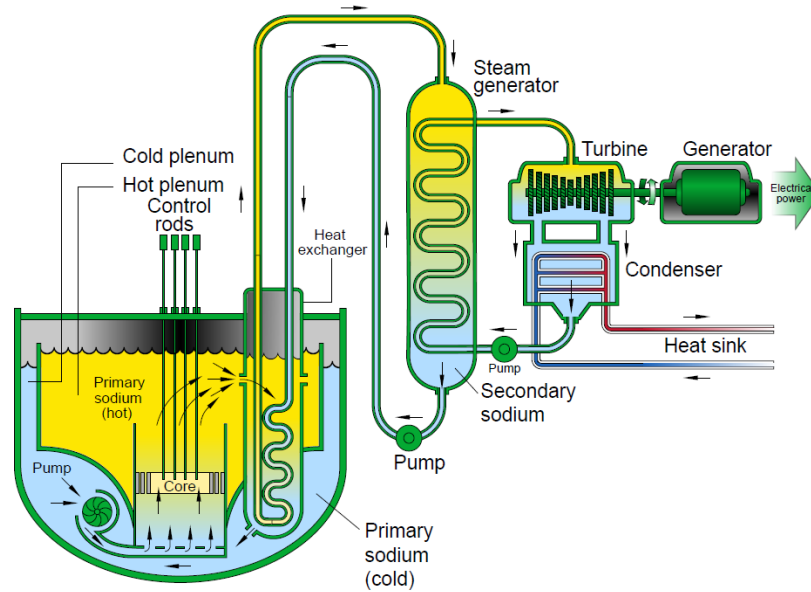


Figure 9. Schematic diagram of an SFR (Buckthorpe 2017).

3.3 Molten Salt Reactors

Molten salt fueled reactors are a type of nuclear reactor that uses a liquid mixture of salts as both the coolant and the fuel carrier. MSR's have several unique features that make them a promising technology for decarbonizing industrial applications. One key advantage of MSR's is their ability to operate at high temperatures, up to 750°C or higher, which makes them well-suited for supplying high-temperature process heat for a range of industrial processes (Serp et al. 2014).

MSR's can also utilize a variety of fuels, including thorium, uranium, and plutonium, as well as spent nuclear fuel, which could help reduce the amount of nuclear waste generated by the nuclear fuel cycle (Humphrey and Khandaker 2018). A typical salt-fueled MSR has at least two loops: a fuel loop and a coolant loop. The coolant salt loop is typically a fluoride mixture, although it can be a chloride mixture. The fuel loop has a similar mixture to the coolant loop except that it has the addition of a fuel, typically dissolved uranium. For moderation, the fuel salt circulates through channels in the core that are made of graphite. The fission products can be continually removed and the actinides fully recycled, while plutonium and other actinides can be introduced into the reactor, along with U238, without requiring fuel fabrication. This means that MSR's have the potential to operate on a continuous basis rather than requiring shutdowns for refueling. In addition, MSR's have a built-in safety feature, the fuel mixture expands as it heats up, which reduces the reactor's reactivity and prevents the possibility of a runaway chain reaction.

Figure 10 shows a diagram for a possible design of an MSR. Despite its potential, there are still technical and regulatory challenges to be addressed in the deployment of MSR's for industrial decarbonization. These include the need for advanced materials that can withstand the corrosive salt mixture, specifically for cogeneration and heat extraction via heat exchangers from the molten salt loop, and the need for regulatory frameworks that can accommodate the unique features of MSR's. Overall, MSR's have the potential to play an important role in decarbonizing industrial processes and reducing greenhouse gas emissions. Ongoing research and development efforts are focused on overcoming the challenges and realizing this potential.

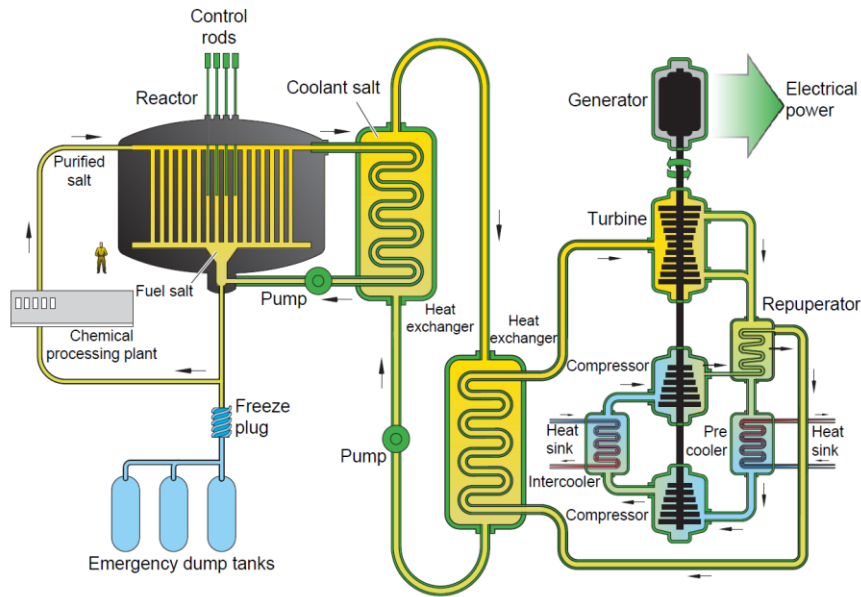


Figure 10. Schematic diagram of an MSR (Buckthorpe 2017).

3.4 Advanced Light-Water Reactors

ALWRs are a type of nuclear reactor that builds on the design of existing Light Water Reactors (LWRs) with advanced features and improvements. ALWRs are designed to have fewer active safety systems and are more efficient and more flexible than previous generations of LWRs. These features make them well-suited for decarbonizing industrial applications. ALWRs use light-water as both the coolant and the neutron moderator, and they typically operate at higher temperatures and pressures than earlier LWR designs. The typical fluid temperatures for ALWRs are generally higher than those of traditional LWRs. ALWRs typically operate at fluid temperatures up to 350°C and pressures between 10–15 MPa.

One promising ALWR design for industrial decarbonization is the Small Modular Reactor (SMNR¹). SMNRs are smaller and more compact than traditional nuclear reactors, which allows them to be manufactured and transported more easily. SMNRs can also be deployed in remote or off-grid locations, where they can provide reliable and low-carbon electricity and heat for industrial processes. As it relates to their potential for industrial decarbonization, ALWRs build upon a proven track record of safety and reliability, with decades of operational experience in nuclear power plants around the world. ALWRs are also designed with advanced safety features, such as passive cooling systems, which make them more resilient to accidents or other events.

Supercritical water-cooled reactors (SCWRs) are also promising for industrial decarbonization, though they are still under development with conceptual designs. Figure 11 shows a diagram of a supercritical ALWR represented within the GIF forum, which is a SCWR design. The design employs water above the thermodynamic critical point (374°C, 22 MPa), which results in higher thermal efficiency compared to current light-water reactors. The supercritical water drives the turbine directly, without the need for a secondary steam system. Such design allows the plant to operate at higher pressures and temperatures, offering a significant increase in thermal efficiency (~44% or more, offering up to 33% efficient improvement over current LWR designs) (Schulenberg and Leung 2023, Rahman et al. 2020). The SCWR employs uranium oxide fuel, which is dissolved in the supercritical water, and is enriched in

¹ Note that SMR is the traditional acronym both for small modular reactor within the nuclear industry and steam methane reforming in processes producing hydrogen. For this report, SMNR will address small modular [nuclear] reactors.

the case of the open fuel cycle option. The reactor operates in a direct, once-through cycle, similar to the Pressurized Water Reactor (PWR), and employs a thermal-neutron or fast-neutron spectrum with light- or heavy-water moderation.

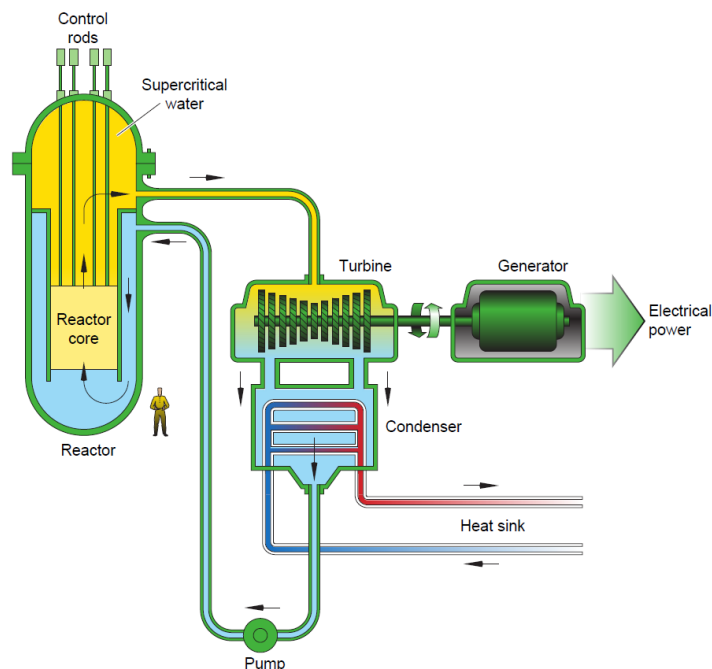


Figure 11. Schematic diagram of a supercritical ALWR, more specifically a SCWR (Buckthorpe 2017).

However, because supercritical water has different chemical properties from liquid water, and because it requires a higher operating temperature, materials used in traditional reactors may not be suitable for an SCWR (Prchal et al. 2009). Materials used in fuel cladding and pressure tube designs will require much longer expected lifetimes, and there is ongoing work to characterize the mechanical properties of candidate alloys. Additionally, the SCWR presents challenges in high-temperature creep and strength, irradiation, stress corrosion cracking, corrosion, and water chemistry stability, all of which impact safety. At this point in time, no reactors have been built using supercritical water as the coolant. Typical ALWRs and SMNRs remain a more realistic target for ALWR integration with industrial process, at least in the short term.

4. INDUSTRIAL NUCLEAR INTEGRATION POTENTIAL

4.1 Oil Refining

The United States refines approximately 12 million bbls/d of crude oil in petroleum refineries to usable products such as transportation and heating fuels, chemicals, chemical feedstocks, petroleum coke, and asphalt. The refineries are located throughout the U.S. as shown in Figure 12 below. A typical upgrading refinery block diagram with the refining unit operating conditions is shown in Figure 13 with an associated a process flow diagram (PFD) shown in Figure 14. This figure includes unit reference numbers to relate the reader between Figure 13 and the ongoing discussion in this report section and in the appendices. The unit mass balances and energy inputs for each unit are provided in the appendices.

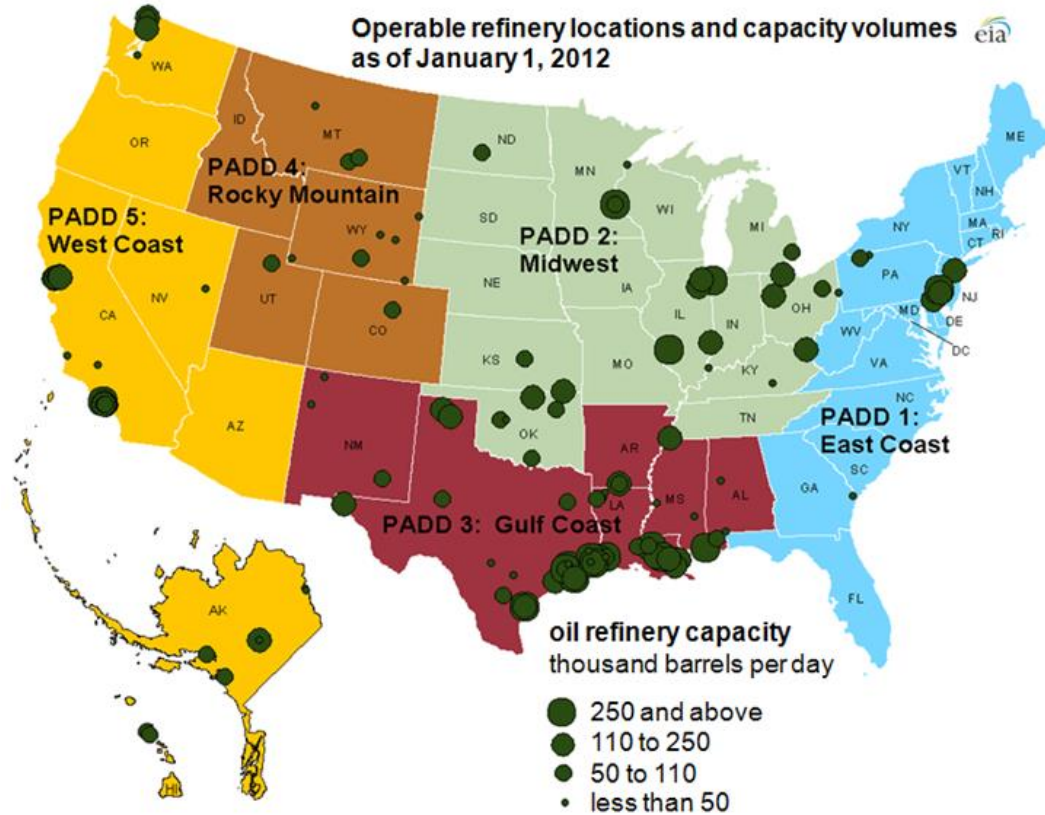


Figure 12. Locations and sizes of oil refineries in the United States.

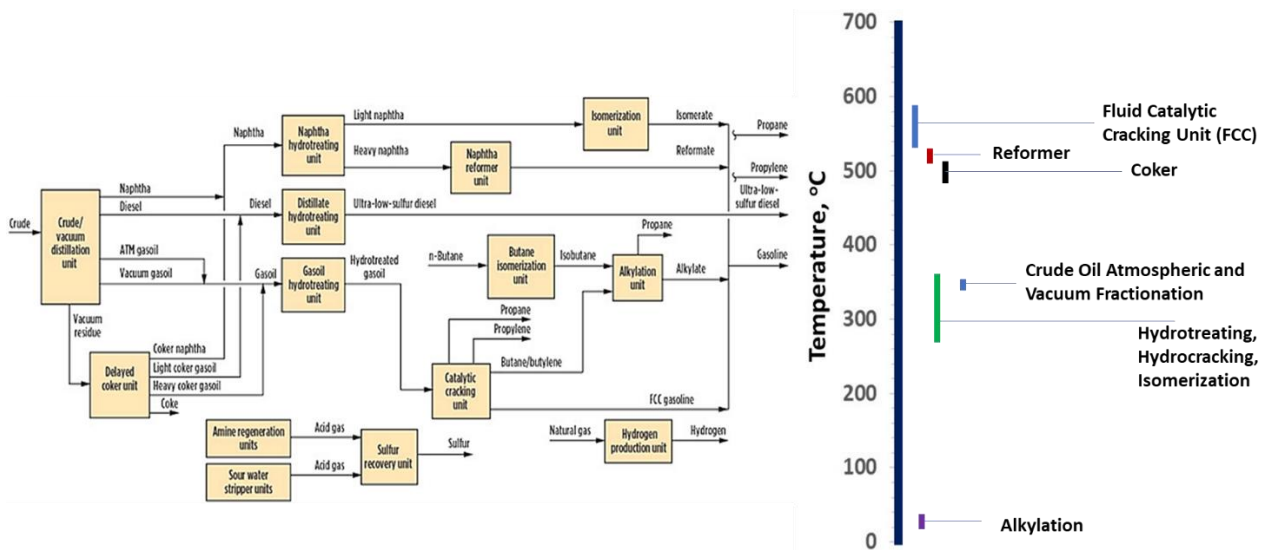


Figure 13. Refinery block flow diagram.

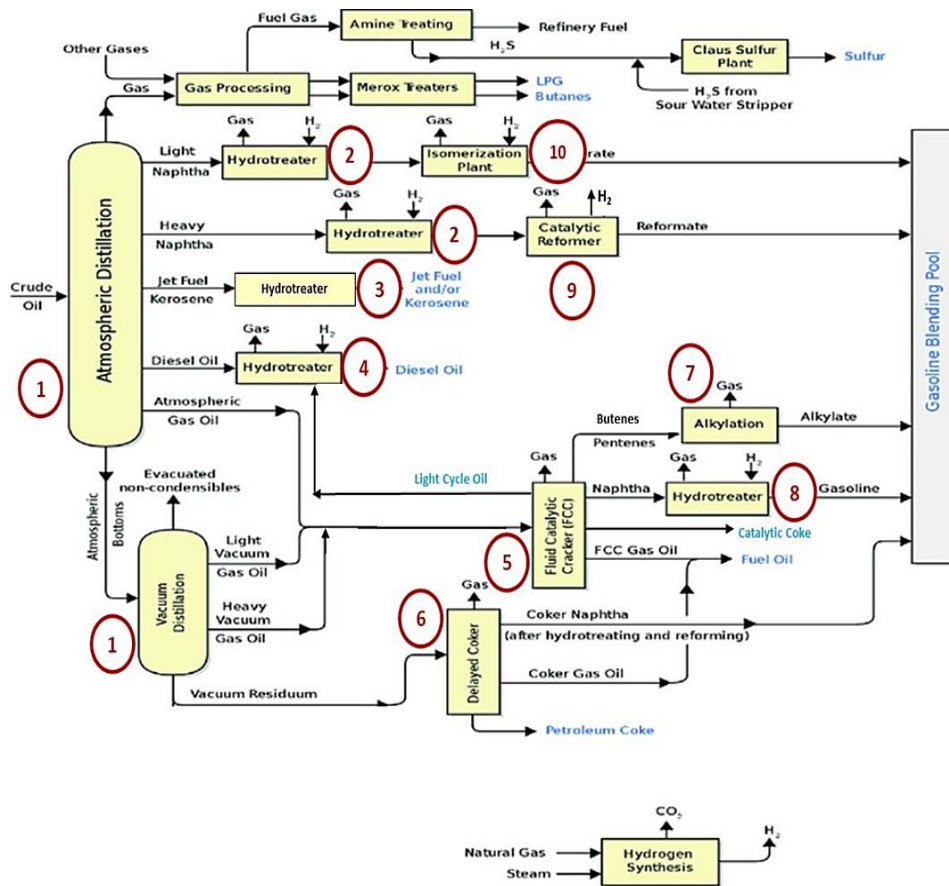


Figure 14. Typical refinery PFD showing various process operations.

An overall mass and energy balance for the refinery PFD is presented in Figure 15. The detailed mass and energy balances for each refining unit is shown in Appendix B.

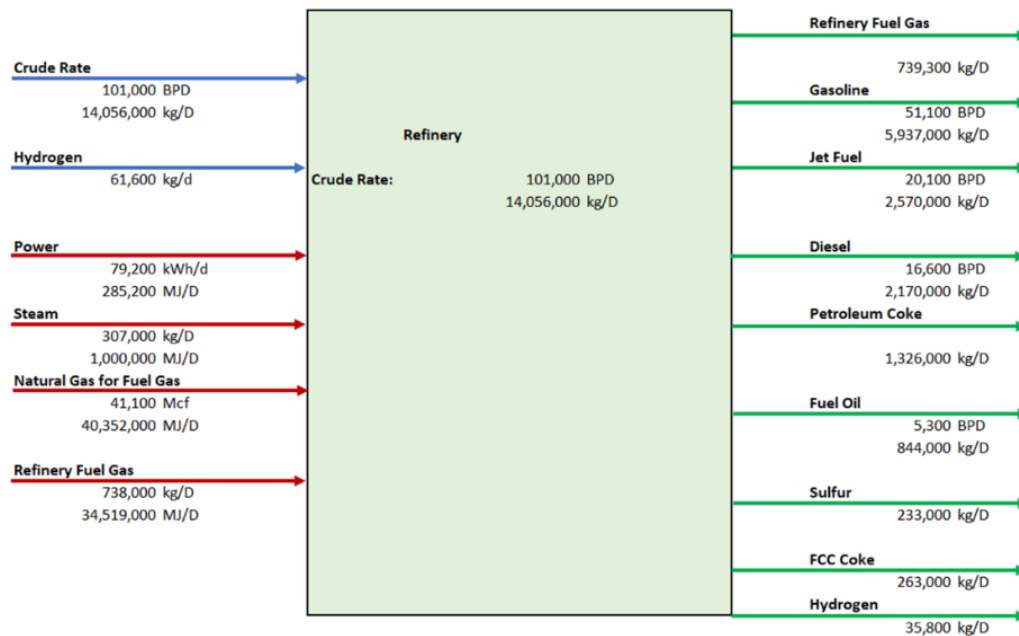


Figure 15. Refinery Mass and Energy Balance

4.1.1 Refinery Energy System

The refining systems require energy input as shown in Figure 16 is supplied by heat from the combustion of natural gas, refinery gas and produced steam. Refinery gas is composed of light hydrocarbons such as methane, ethane, ethylene, propane and propylene which are produced in the refinery cracking operations. The energy from combustion is used to produce power, separation of hydrocarbon streams by fractionation and steam production.

The steam supplied to refinery is produced from auxiliary boilers, heat exchange with refinery streams and combined heat and power units. A typical refinery steam system typically is composed of three levels: high pressure (400 to 600 psig with 100o to 200o degress of superheat), medium pressure (140 to 175 psig and low pressure (15 – 40 psig). These various steam levels are employed for the following services:

- High pressure steam: power turbines for compressors and blowers, reboiling distillation columns and high temperature applications.
- Medium pressure steam: power turbines, reboil heat for distillation columns and other heat exchange applications.
- Low pressure steam: reboil heat for distillation columns, boiler water conditioning and low level heat for auxiliary applications.

A typical refinery steam system is exhibited in Figure 16. The refining and upgrading of crude oil to finished products of gasoline, jet fuel and diesel fuel are discussed below.

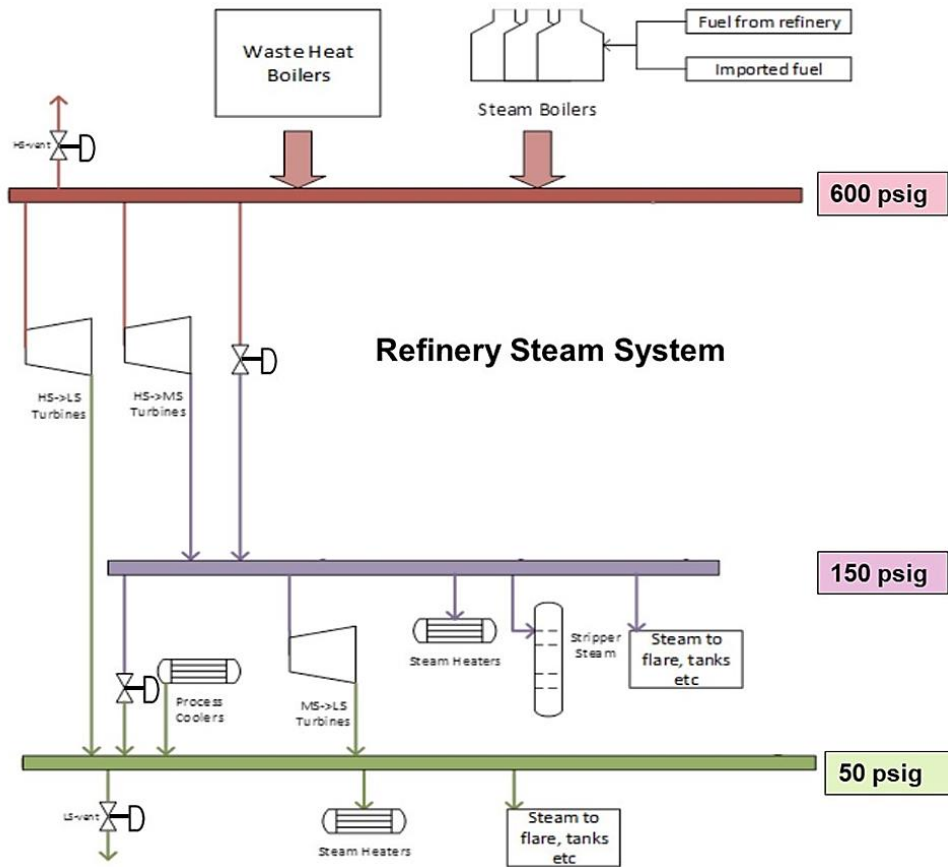


Figure 16. Typical refinery steam system.

4.1.2 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, with reference number 1 in Figure 14, 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.

4.1.3 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. Also, some cracking processes use hydrogen to catalytically reduce the heavy hydrocarbon streams. Complex refineries can use fluid catalytic cracking with reference number 5 in Figure 14, coking with reference number 6 in Figure 14 and hydrocracking/hydrocracker units for the cracking process (United States Energy Information Administration 2013c). The heat energy generated in these cracking units is recovered with preheat heat exchange systems and steam-generating. A cracking unit consists of one or more reactors and a network of furnaces, heat exchangers, and other vessels.

Petroleum refineries vary in complexity but include these basic steps to produce these products. In general, refining is an energy-intensive process. Intermediate oil streams require conversion and upgrading steps which are endothermic and exothermic. A table of refining operations and their respective operating conditions are provided in Table 2.

Table 2. Operating conditions for selected refinery unit operations. The numbers correspond to the reference numbers seen in Figure 14.

Process	Temperature	Pressure	Reaction Type
1- Crude Oil Atmospheric Fractionation	340–355°C	1.5–1.9 bar	NA
1 - Crude Oil Vacuum Fractionation	340–355°C	28–30 mmHg absolute	NA
7-Alkylation	10–15°C	—	Exothermic
9-Reforming	510–526°C	9–10 bar	Endothermic
2,3,4,8-Hydrotreating	300–350°C	40–100 bar	Exothermic
Hydrocracking	300–350/500°C	80–204 bar	Exothermic
5-Fluid Catalytic Cracking	527–593°C	1.7–2.0 bar	Endothermic
6-Coking	485–505°C	0.7–2.0 bar	Endothermic
10-Isomerization	250–300°C	35–41 bar	Endothermic

Note: Hydrocracking was not included in this refinery upgrading scheme.

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 with reference number 7 in Figure 14, 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

(United States Energy Information Administration 2013a). 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 (United States Energy Information Administration 2013a).

A key cracking/upgrading unit in the refinery is the fluid catalytic cracking (FCC) unit. The FCC breaks long chain hydrocarbons such as heavy gas oil into shorter chains such as naphtha. The endothermic cracking reactions occur at temperatures from 480 to 540°C and are fueled by the heat produced during catalyst-regeneration. About 5% of the feed ends up as coke; therefore, air is used in the regenerator to burn the coke off. The exit temperatures of the regenerator are between 925 to 815°C. A fractionator column is used downstream of FCC to separate and recover the hydrocarbon vapors.

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 (United States Energy Information Administration 2013b).

4.1.4 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 ultimately be blended into the products. Hydrotreating and hydroprocessing processes with reference numbers 2, 3, 4 and 8 in Figure 14 are employed for this purpose, using 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 or integrated with other refining units to conserve energy.

4.1.5 Stream Quality Improvement and Blending

Several extraneous refinery streams possess characteristics that prevent the streams from being blended into fuels. In particular, straight chain alkane hydrocarbons such as pentanes and hexanes have a low octane value (~60 octane). An isomerization process unit with reference number 10 in Figure 14 is used to upgrade the octane value of these streams. The octane value is improved through the utilization of high temperature, moderate pressure and catalysis to an adequate octane blending value of (75–92).

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

4.1.6 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 200–800°C (400–1,500°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 lbm/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. This power generation method requires 20–30 lbm/hr/kW of power generation.

4.1.7 Refining CO₂ Emissions

As mentioned, refineries require a large quantity of heat and energy to accomplish the separation and low-valued intermediate oil stream upgrading. This energy is supplied from the combustion of natural gas. Also, the conversion processes consume hydrogen which is commonly produced through the steam reforming of natural gas. As a result, the refineries produce approximately 0.45 kg of CO₂ per kg of crude oil charged to a refinery. Based on the crude oil refined in the U.S., the CO₂ emissions from petroleum refining in 2022 was approximately 238 million tonnes.

4.2 Methanol

4.2.1 A Brief Overview

The potential to leverage methanol for large-scale industrial production of gasoline can provide a major thrust for transportation sector decarbonization (Idaho National Laboratory 2010). It must be noted that within the U.S., gasoline accounts for 54% of the combustible fuel in transportation sector (Wendt et. Al. 2022). In addition, methanol is a crucial feedstock for the chemical industry. As illustrated in Figure ES1, methanol serves as a feedstock in chemical industries (Perez Sanchez et al. 2022), as a stand-alone fuel, and as a fuel blend in gasoline to boost its octane number (Verhelst et al. 2019). Figure 17 illustrates a significant growth in methanol production in the U.S. since the year 2010.

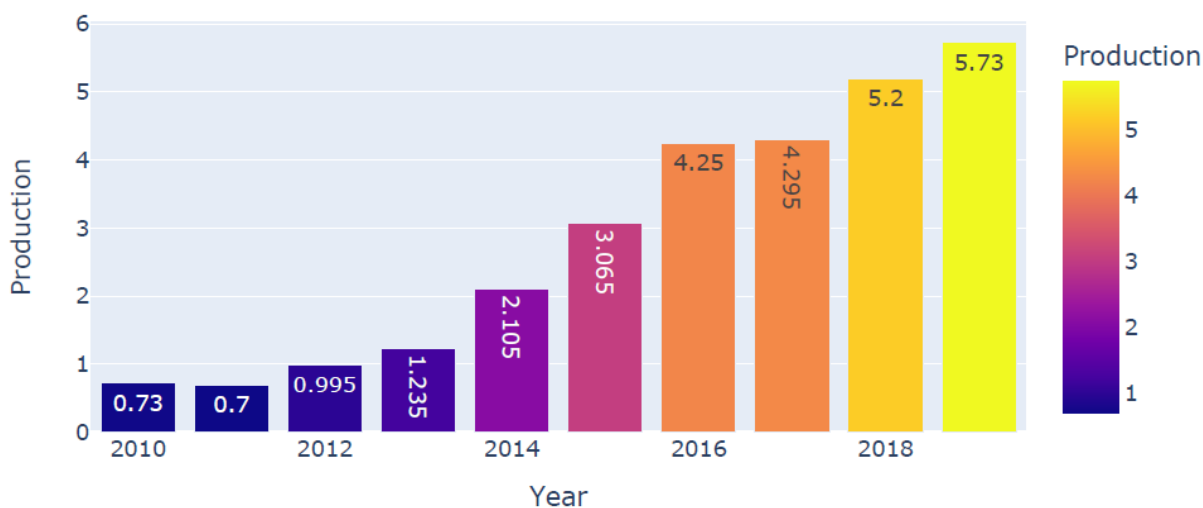


Figure 17. Methanol production in units of million metric tons in the U.S. during 2010–2019 (American Chemistry Council, 2020).

4.2.2 Methanol: Applications

To broadly summarize, the two primary end uses of methanol are in chemical production and fuels production. In chemical and petrochemical processes, methanol serves as a feedstock for production of formaldehyde (Brown and Parkyns 1991; Malik, Abatzoglou, and Achouri 2021), olefins—especially ethylene and propylene—used as intermediates for other chemical products (Tian et al. 2015; Idaho National Laboratory 2012), and for generation of synthetic gasoline (Idaho National Laboratory 2010). Methanol’s role as a fuel blend or additive, or for direct combustion, generates high-volume demand in the transportation sector. As a fuel additive, methanol’s higher octane rating compared to gasoline enhances efficiency of internal combustion engines (Verhelst et al. 2019). Additionally, methanol powered portable appliances are quite popular in China and Africa, and methanol as a substitute to fuel oil for heating in chemical processes is also gaining significant traction (see Applications in [Methanol Institute n.d.]).

For the year 2021, a net global production of 107 million metric tons (MMT) of methanol was estimated by Methanol Market Services Asia of the Methanol Institute (Methanol Institute n.d.). Figure 18 illustrates breakdown of global methanol demand by application. The applications corresponding to methanol-to-olefins (34 MMT) processes, formaldehyde production (25 MMT), and combustion and gasoline blending (12 MMT) lead the chart. The global methanol end-use categorization in MMT is shown in Figure 19.

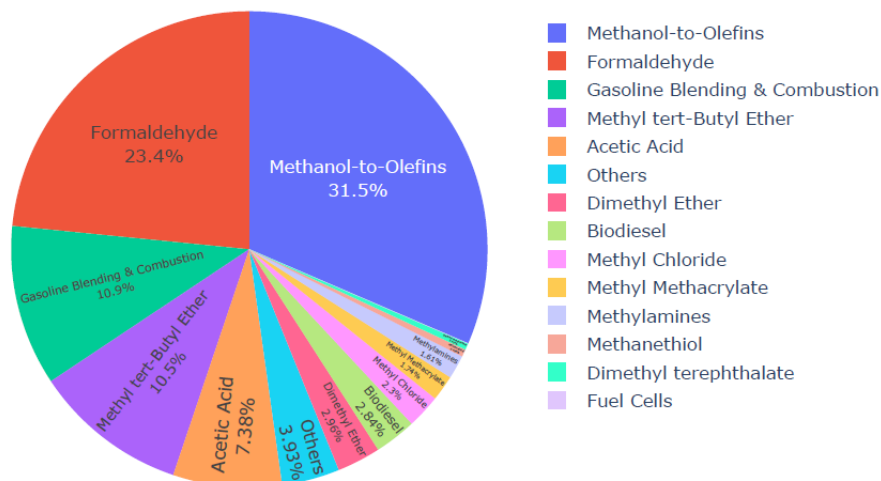


Figure 18. Global methanol demand by application for the year 2021 (Methanol Institute n.d.).

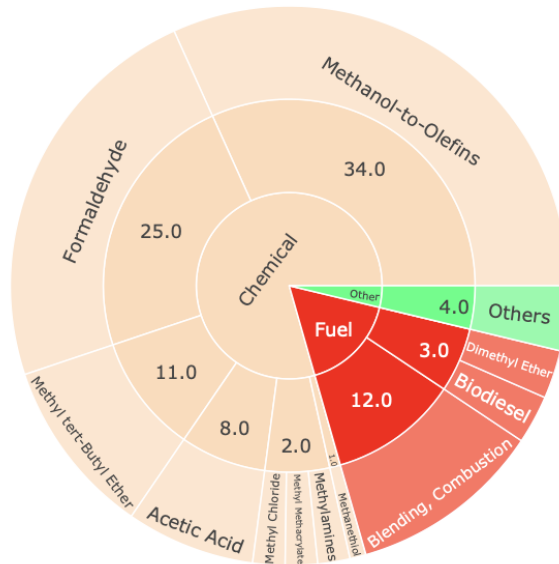


Figure 19. Global methanol end-use categorization (in MMT, Methanol Institute n.d.).

4.2.3 Top Five Target Markets for Methanol

This section highlights the target sectors with a potential for bulk or high-volume methanol demand as a feedstock. The data was collected over the years from 2017 to 2021. Figure 20 illustrates the top five sectors with highest demands for methanol as an input or a chemical precursor. There are two core observations.

1. A significant global growth of methanol-to-olefins (MTO) production is noted, which has increased by around 62% since the year 2017.
2. High-volume methanol demands from the rest of the four sectors are near constant and numerically significant.

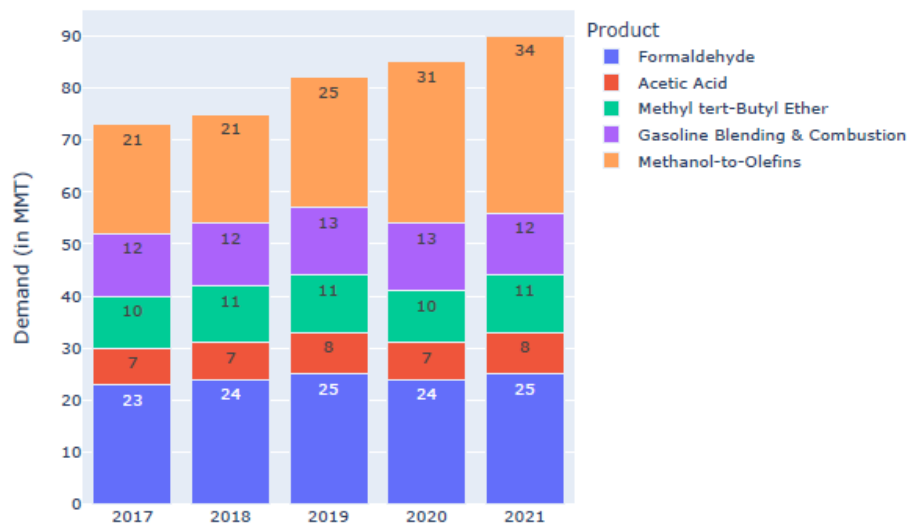


Figure 20. Target markets for methanol based on end use (in MMT, Methanol Institute n.d.).

Most importantly, as shown in Figure 21, light olefins are projected to be fastest-growing segment within the U.S. Light olefins, ethylene and propylene, are unique due to their ubiquitous end use in various industries including the textile industry and in manufacturing of plastics, detergents, antifreeze, synthetic fibers, and coatings and paints. Furthermore, the U.S.'s annual market size of methanol is projected to increase to 8.4 MMT by the year 2027, as highlighted in Figure 22. This is expected as global prices for methanol have shown a significant growth in the post-pandemic years, as observed in Figure 23, with an uptick in manufacturing activity. China, the largest methanol consumer, accounts for roughly 20% of the total global volume. This is about twice the methanol consumption within the U.S. (Methanol Institute and Methanol Market Services Asia 2023).

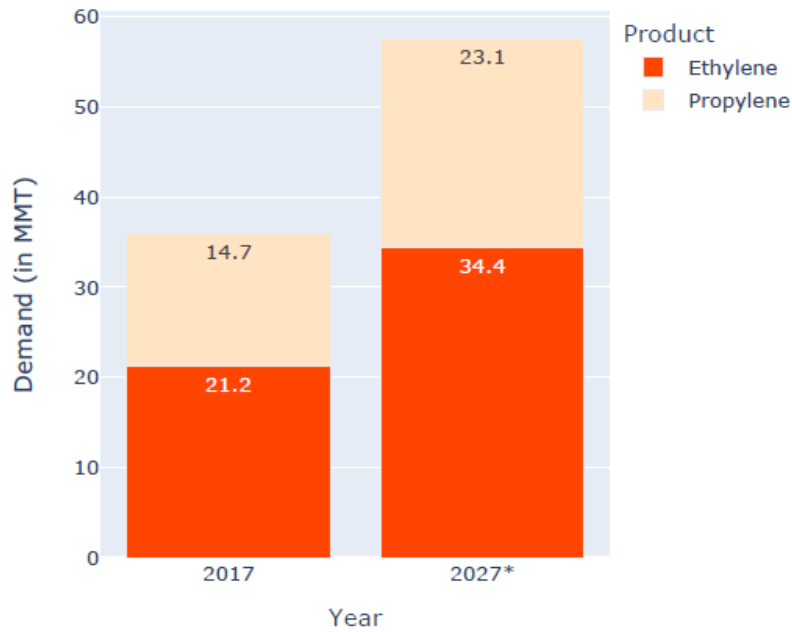


Figure 21. Demand forecasts for light olefins in the U.S. (in MMT, Statista 2020b).

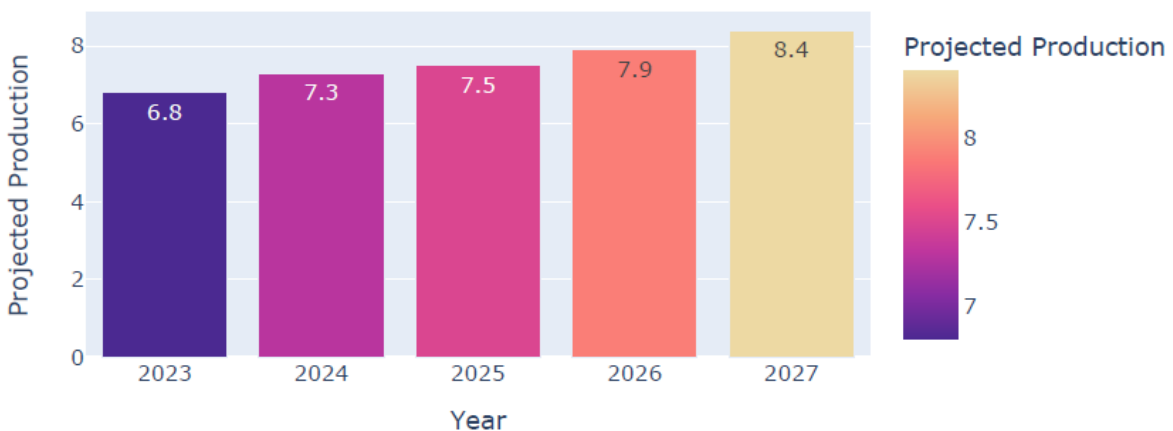


Figure 22. Projected methanol market volume (MMT) in the U.S. by the year 2027 (Statista 2020a).

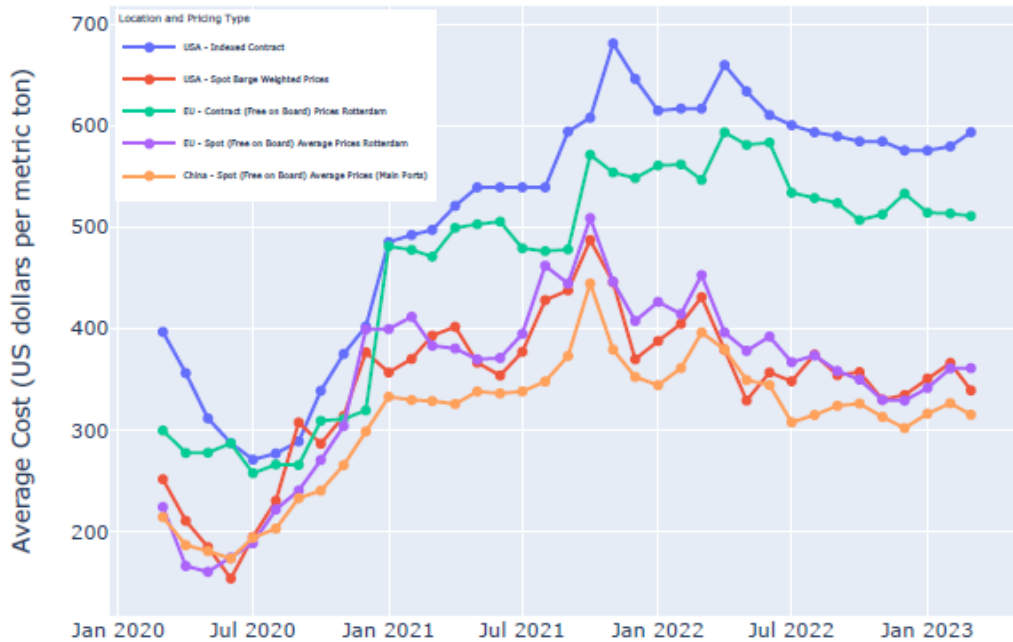


Figure 23. Global monthly methanol prices (U.S. dollar per metric ton) by location and type (Methanol Institute, 2023).

4.2.4 Methanol Production

Synthetic gas, or syngas, which is composed of hydrogen, carbon monoxide, and carbon dioxide, serves as the primary precursor for methanol production. Consequently, there are multiple feedstocks and pathways commercially available for methanol production.

4.2.4.1 Feedstocks and Pathways

Around 55-65 % of global methanol producers use natural gas as a feedstock for syngas generation. Next, lignite or brown coal provides syngas for 30-35% of global methanol generation. The rest of the methanol production is enabled by biomass in the form of coking gas. In summary, there are three main feedstocks: natural gas, coal, and biomass (IndexBox 2023; Harris et al. 2021).

Another feedstock is methane, which is directly converted into methanol using a catalyst, but its industrial-scale adoption is yet to be realized (Ravi, Ranocchiari, and van Bokhoven 2017). Carbon dioxide reduction using hydrogen is also an alternative being explored possibly sourcing byproduct high-purity carbon dioxide from ammonia or ethanol production (Zang et al. 2021). Such pathways create a potential for integrated industrial processes with chemical co-productions.

The above-mentioned feedstock breakdown, however, corresponds to global methanol production. In effect, these average numbers are heavily skewed by coal-driven methanol production in mainland China, with a record methanol production of 69 MMT observed in the year 2019 (Methanol Institute n.d.). Referring to Figure 17, there is a meteoric eight-fold growth in methanol production within the U.S. from 2010 to 2019. This growth is concomitant with availability of competitively priced natural gas, which, since the year 2010, had an average (yearly) closing price under \$7 per million British thermal units. Therefore, the percentage of methanol produced using natural gas in the U.S. can be safely assumed to be at least 80%. To construct an accurate Sankey diagram of the feedstock breakdown in the U.S. and their corresponding pathways, future work involves a deeper dive into finer details.

4.2.4.2 Process Flow: A Macro View

The process flow for methanol production can be broadly described under three macros, as illustrated in Figure 24. A brief overview of each macro process is listed next.

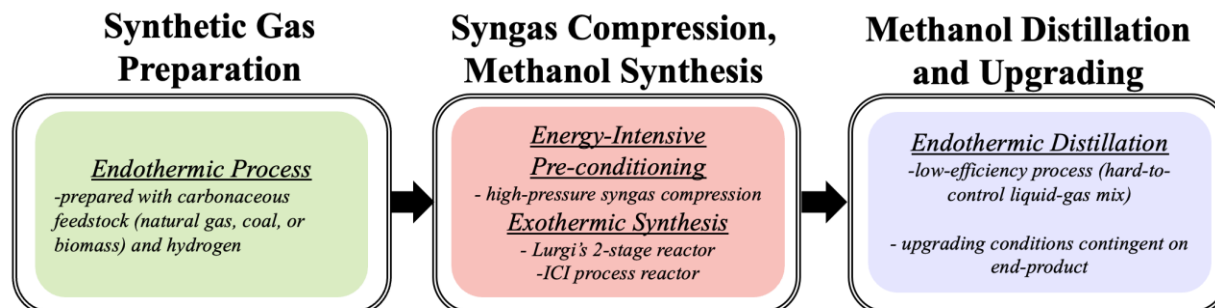


Figure 24. A high-level architecture of process flow for methanol production .

1. *Syngas Preparation:* First, the feedstock is cleaned, dried and/or pulverized. Subsequently, it is treated with steam and oxygen at high temperatures. Next, the syngas is cleaned to preclude corrosion within the *reactor* downstream. The syngas fed in the methanol reactor downstream is conditioned to a typical 2:1 molar ratio of hydrogen and carbon monoxide and is brought to appropriate temperature and pressure requirements . Syngas preparation is a highly endothermic process. The process conditions vary with feedstock: coal gasification (Idaho National Laboratory 2012), natural gas processing via steam methane reforming , auto thermal reforming, or a mix of both, (Idaho National Laboratory 2010), and biomass gasification (IndexBox 2023). Consequently, the temperature and pressure conditions for a syngas processor (reformer or gasifier) are also contingent on feedstock. For instance, based on moisture content and bed type, a gasifier’s exit temperature ranges between 350–1700°C (Idaho National Laboratory 2012; Steynberg 2004; Shao et al. 2023) with steam input pressure ranging over 50–80 bar. In contrast, natural gas reforming, a dominant method for hydrogen generation within the U.S., occurs at conditions of 700–1,000°C and 3–25 (Basu 2018). The pressure ranges can, however, move up and beyond. For example, an Exxon-patented process to convert natural gas to methanol and then gasoline requires pressure at 40 bar (Idaho National Laboratory 2010). To conclude, regardless of syngas’s exit temperature and pressure, it must be conditioned and cooled prior to its synthesis to methanol in downstream methanol reactors (where requirements vary between 200–300°C). The information for this macro process is summarized in Figure 25.

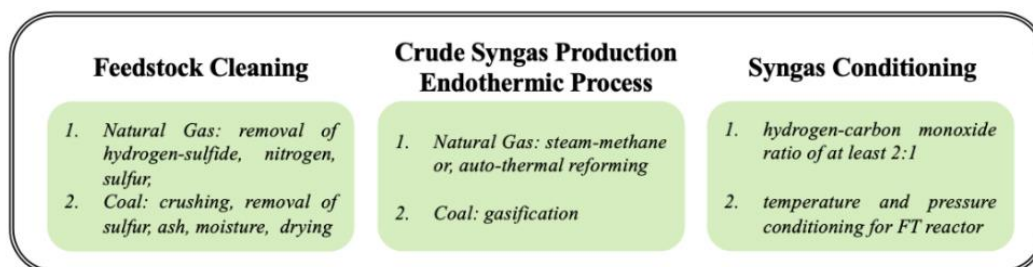


Figure 25. A zoomed-in architecture of the process corresponding to syngas preparation.

2. *Methanol Synthesis Process*: In the next macro process, a classical methanol reactor converts the syngas into crude methanol. The steam methane reforming is followed by a methanol reactor-based synthesis, resulting in a two-step methanol production (Idaho National Laboratory 2010). Prior to methanol synthesis, syngas requires preconditioning in the form of compression and cooling. Besides, methanol synthesis as a stand-alone sub-process is highly exothermic in nature. Consequently, heat is recovered from the syngas cooling and methanol synthesis. The heat recuperation can support feedstock preconditioning and steam generation, or to power compressors and distillation towers (Zang et al. 2021; United States Department of Energy n.d.). Lastly, one-step methanol production pathways are being investigated and explored, wherein the carbon dioxide and hydrogen sourcing are direct, and reverse water gas shift reaction is leveraged to adjust the composition of carbon monoxide. Figure 26 concisely summarizes the methanol synthesis, and classical methanol reactors.

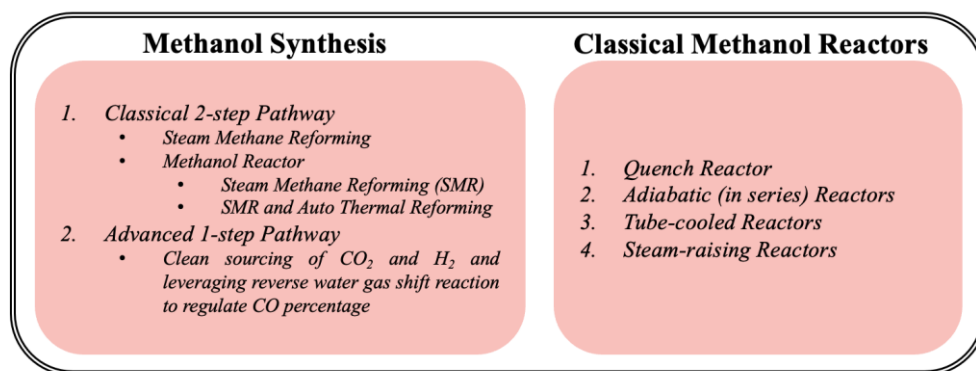


Figure 26. Methanol synthesis pathways and characterization of classical reactors.

3. *Product Upgrading*: Any additional downstream processing involves product upgrading. The first step mainly involves methanol de-watering (separation from water). Then, based on the desired end products, the number of subprocesses and their corresponding temperature and pressure conditions vary, as illustrated in Figure 27.

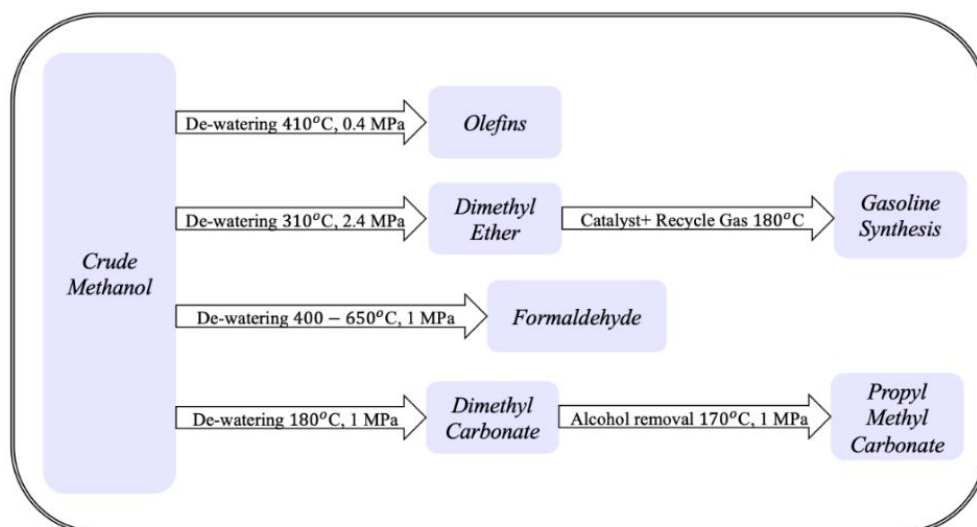


Figure 27. Upgrading conditions contingent on end-product (Idaho National Laboratory, 2012, 2010; Zang et al. 2022; Matsukata et al. 2011; Maldonado et al. 2010)

4.2.5 Industrial Processes, Reformers, Exothermic Synthesis, Process Control and Optimization

4.2.5.1 Industrial Processes

The manufacturing of synthetic methanol has evolved over the past few decades. Some of the major processes are briefly summarized below with timeline and operating conditions.

BASF was the first to come up with synthetic methanol production, based on a zinc-chromium oxide catalyst. The catalyst necessitated operating conditions with a pressure range of 25–35 MPa, and temperature between 320–450°C. A major bottleneck involved energy-intensive compressors to achieve high-pressure conditions. Then, Imperial Chemical Industries (ICI) overcame the high-pressure operating condition by developing the copper-zinc-alumina catalyst, which, till date, is the most preferred catalyst for methanol synthesis. It drastically reduced the pressure range to 5–10 MPa, and the temperature to 210–270°C. Using a similar catalyst, Lurgi subsequently developed steam-raising reactors for low-pressure methanol manufacturing, which in turn reduced the cost associated with syngas compression. The ICI-developed process and Lurgi's process are widely used to produce synthetic methanol the world over, with ICI's low-pressure methanol process being utilized at majority of the methanol production sites.

4.2.5.2 Reformers

In general, a typical process flow diagram for methanol manufacturing involves combined two-step reforming of natural gas, as seen in Figure 28.

- A) *Primary Reformer*: A classical and the most dominant one-step reforming process used in conventional low-capacity production facilities. Designed for operations at high pressure and low temperature.
- B) *Secondary Reformer*: Operating temperature of the secondary reformer is higher with oxygen fed as an oxidant (for further reduction in residual methane). As an example, in modern large-scale methanol production plants, an auto thermal reformer serves as a stand-alone secondary reformer, typically deployed for production at scales greater than 5000 tonne/day.

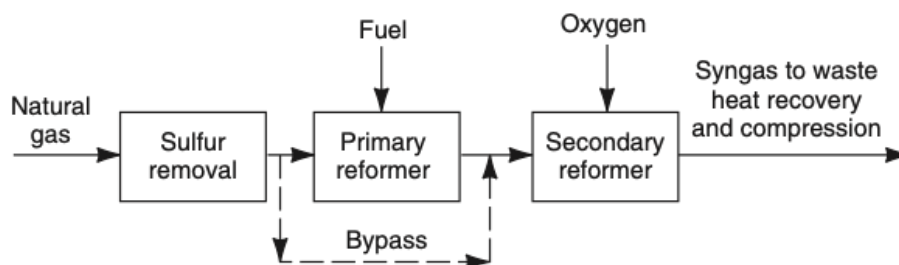


Figure 28. Combined reforming process for syngas production.

A gas-heated reformer (GHR) is also used as an extension of combined reforming. In the case of GHR, heat is recuperated from the secondary reformer effluent. This effectively fulfills the heat requirement for the primary reforming reaction. The ICI low-pressure industrial process, incorporated with GHR, is depicted in Figure 29. In addition, the macro-view of the process flow for methanol production using coal or fuel oil is depicted below in Figure 30.

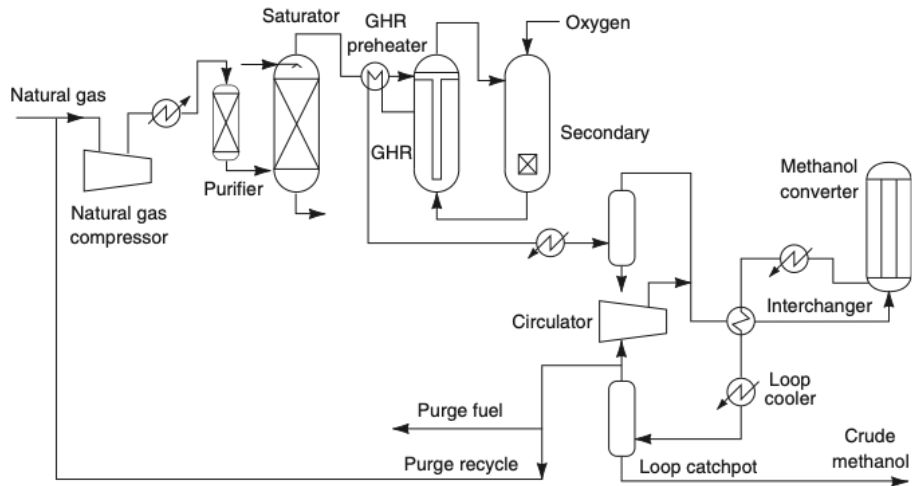


Figure 29. ICI process incorporating a GHR in conjunction with oxygen-blown secondary reformer.

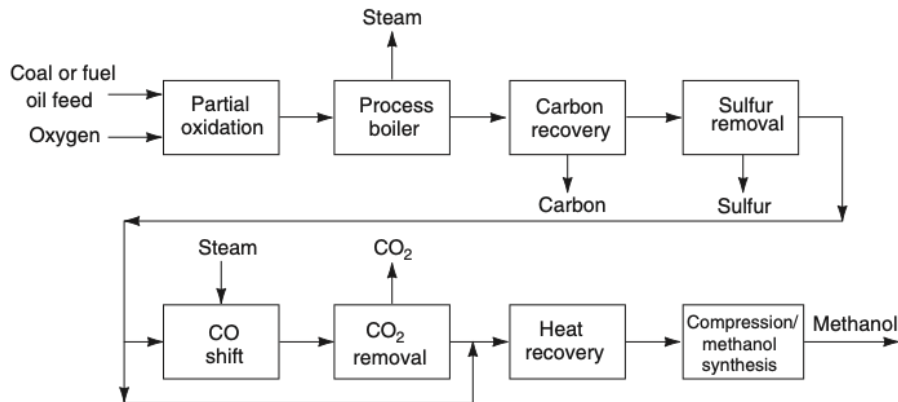


Figure 30. Process-flow sequence for methanol production from coal or fuel oil.

The combined reforming and GHR sub-processes are an opportunity for High-Temperature Steam Electrolysis (HTSE) supported by nuclear powered steam generator. This can potentially feed both hydrogen and oxygen streams for syngas production, resulting in lower natural gas usage.

4.2.5.3 Exothermic Synthesis

The stand-alone process involving methanol synthesis is exothermic in nature. Furthermore, there are two core sources of heat recovery within the step associated with methanol synthesis (see red-highlighted macro process in Figure 24):

1. **Heat Released within Methanol Reactor:** catalyst-enabled conversion of synthetic gas to methanol inside methanol reactor is an exothermic reaction.
2. **Cooling of Crude Methanol:** cooling of crude methanol prior to its distillation is also a potential avenue of heat recovery.

In addition, the synthesis process is favored at high pressure and lower temperatures, as illustrated in Figure 31.

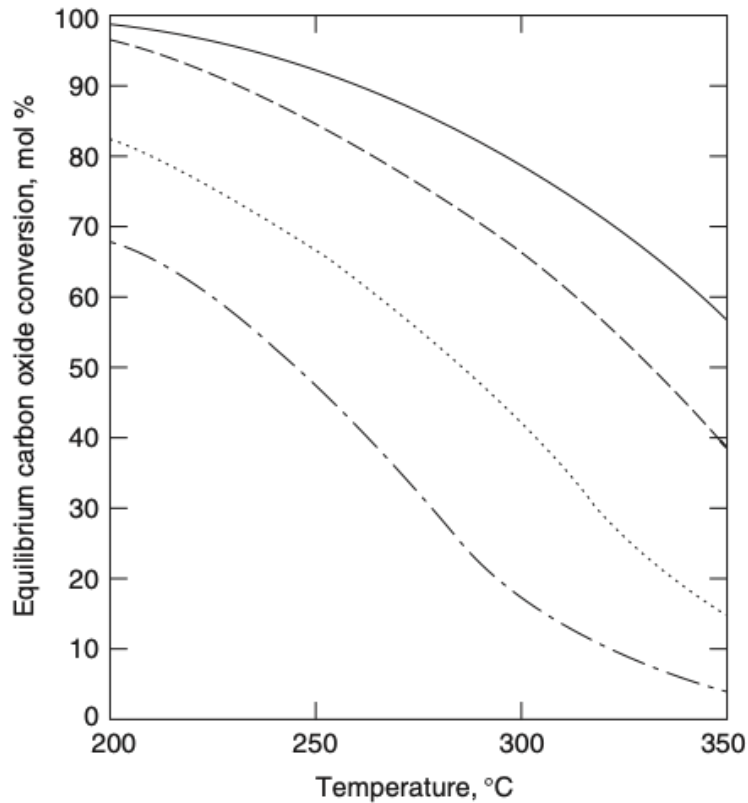
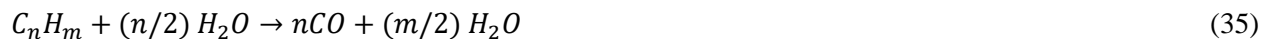


Figure 31. Carbon oxides's equilibrium conversion to methanol based on (reformed) natural gas with a composition of 73% hydrogen, 15% carbon monoxide, 9% carbon dioxide, 3% methane.

The equilibrium conversions of the carbon oxides to methanol synthesis reactions are summarized as following:



Notice that water-gas shift reaction can be obtained by subtracting the above equations. The composition or the ratio of the carbon oxides and hydrogen is primarily driven by syngas sourcing. It is contingent on the type and the quality of the hydrocarbon being converted to syngas, and the process deployed for syngas generation. The stoichiometric relations with steam (reforming) and oxygen (gasification) are summarized as following:



The R value for syngas is computed for stoichiometry characterization as:

$$R = (H_2 - CO_2)/(CO_2 + CO) \quad (36)$$

Where R must have a value of at least 2 (i.e., prior to syngas injection into methanol synthesis reactor). Within the methanol synthesis reactor, a copper-zinc-alumina catalyst is commonly used for adsorption where copper is partially covered by adhered or adsorbed oxygen (if carbon dioxide is added to the reacting mixture):



In contrast, if no carbon dioxide is added, carbon monoxide is adsorbed on copper where it is later hydrogenated to methanol. The zinc-oxide fraction in the catalyst helps maintain the catalyst activity by ensuring the surface area of the copper sites. Any reduction in potency of the catalyst is often attributed to loss of surface area available with copper; for instance, blockage by larger-sized by-product molecules including halogen- and sulfur-induced poisoning (producing copper salts irreversibly). Temperature control can be critical as selectivity of the catalyst is temperature driven.

4.2.5.4 Process Control and Optimization

A typical methanol production involves a synthesis loop as depicted in Figure 32. An improved net conversion and higher efficiency are enabled by methanol-water condensation, feeding recycled gas to syngas, recuperating heat from converter effluent to heat boiler feedwater and potentially using the steam to power compressors. The crude methanol is fed to distillation column.

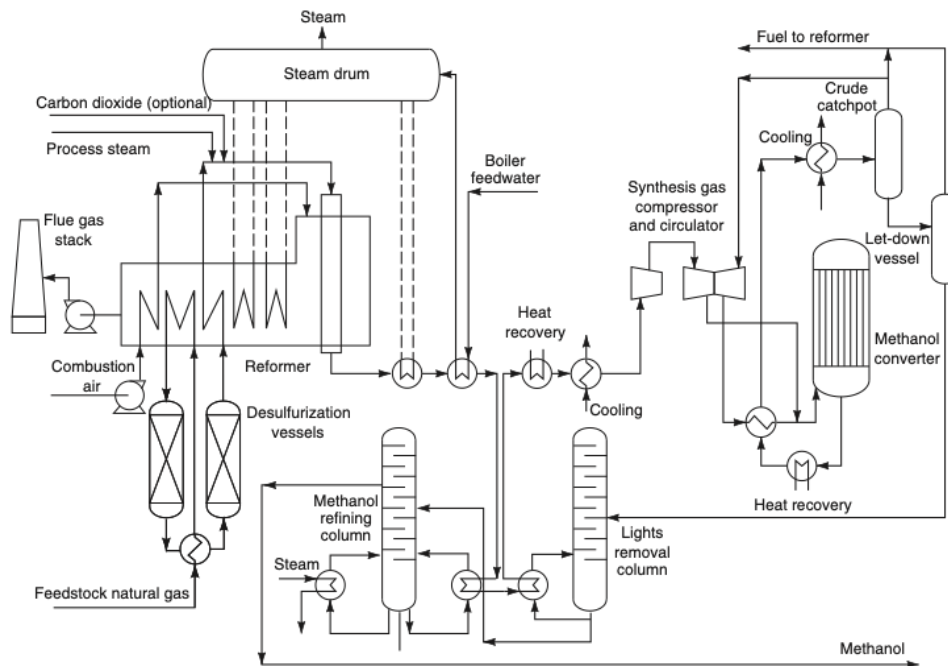


Figure 32. Process flowsheet for methanol synthesis.

The most distinguishable feature in a methanol production plant is the reactor or the converter, wherein the methanol is generated. Further details on some of the commonly used commercial methanol reactors are provided in APPENDIX C. Finally, the most complex aspect of optimizing the synthesis rate in the methanol reactor is the temperature control. In effect, the process optimization for a nuclear-integrated methanol production will entail a larger set of decision variables. Specifically, the time-varying optimal bifurcation of thermo-electric energy streams from advanced nuclear plants will significantly impact the process control and dynamic operations at the methanol production site.

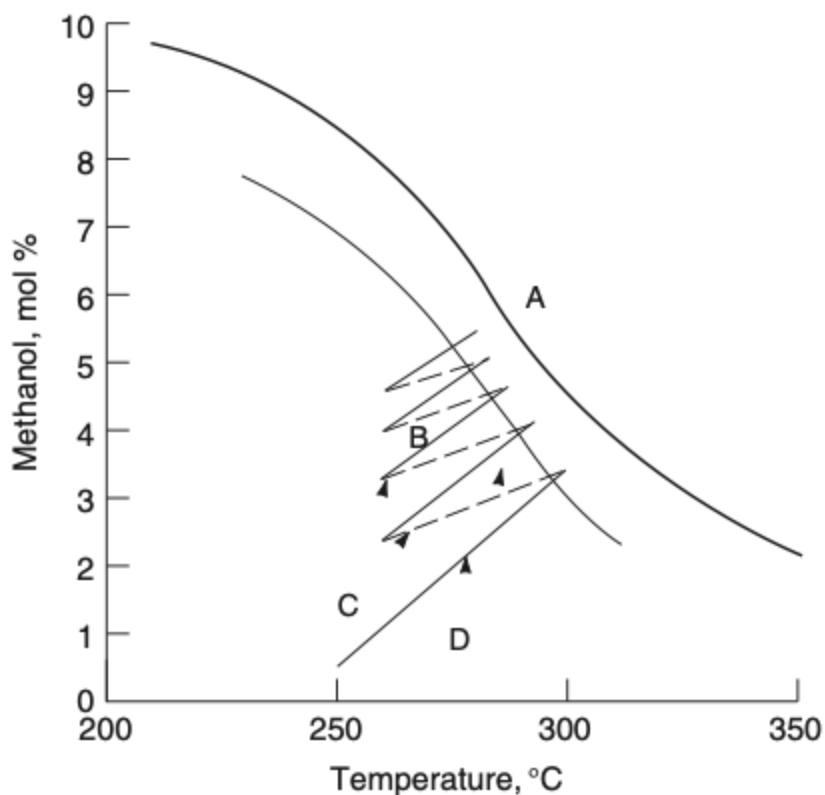


Figure 33. Sawtooth temperature profile within a Quench reactor: A – equilibrium line, B – maximum rate line, C – quench line, and D – intra-bed line.

Lastly, cascading towers are utilized for distillation, with the number of towers largely driven by the impurities in crude methanol. The goal is removal of water, higher alcohols, and other inorganic and organic impurities.

4.2.6 Downstream Products

4.2.6.1 Energy Needs

As detailed in the preceding subsections, methanol is used to derive multiple end-products. The chemical reactions for some of the downstream products are summarized in Table 3.

Table 3. Summary of chemical reactions for downstream product upgrading with methanol.

Product	Process	Catalyst	Reaction
Formaldehyde	Oxidative dehydrogenation	Silver Oxides or Molybdenum Oxides	$2\text{CH}_3\text{OH} + \text{O}_2 \rightleftharpoons 2\text{HCHO} + 2\text{H}_2\text{O}$
MTBE	With Isobutylene in liquid phase	Acidic catalyst	$\text{CH}_3\text{OH} + \text{CH}_2\text{C}(\text{CH}_3)_2 \rightleftharpoons \text{CH}_3\text{OC}(\text{CH}_3)_3$
DME	Dehydration	Acidic catalyst	$2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$
Acetic Acid	Direct carbonylation	Rhodium (homogenous) or Cobalt-based Catalyst	$\text{CH}_3\text{OH} + \text{CO} \rightleftharpoons \text{CH}_3\text{COOH}$

29–31 GJ of energy is required to produce 1 tonne of methanol. In addition, the case material balance diagram for methanol is shown in Figure 34.

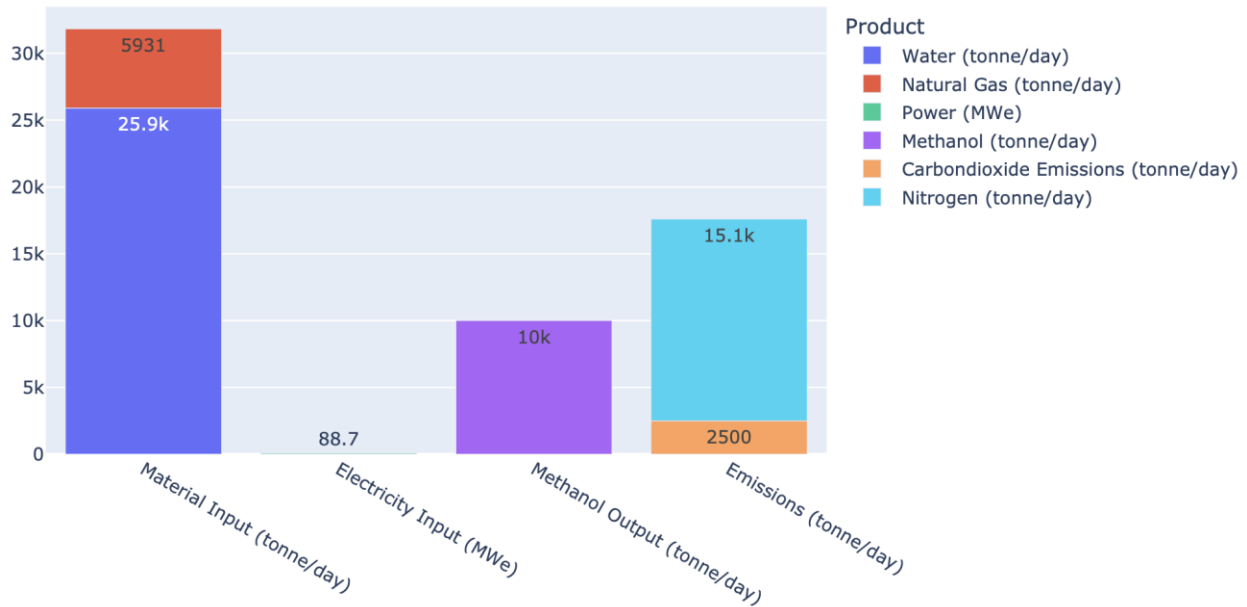


Figure 34. Average case material balance summary for methanol production (based off natural gas as a feedstock) (McMillan 2016).

4.2.6.2 Decarbonization Potential for Methanol-to-Gasoline, Methanol-to-Olefins Pathways

From the perspective of synthetic fuels, methanol serves as a potential precursor. Most importantly, one study performed at INL shows potential net decarbonization of gasoline through the use of a large-capacity high temperature steam electrolyzer, thermally and electrically powered by an HTGR, in a methanol-to-gasoline (MTG) pathway (based on patented ExxonMobil process). For this decarbonized MTG pathway, the material and energy requirements are contrasted in Figure 35 for a coal-based synthetic fuel production. It can be noticed that nuclear-generated heat can significantly offset use of coal as fuel-based feedstock. Similarly, natural-gas based gasoline production can be partially offset by 30 million standard cubic feet per day (see APPENDIX C for a detailed mass and energy balance diagram).

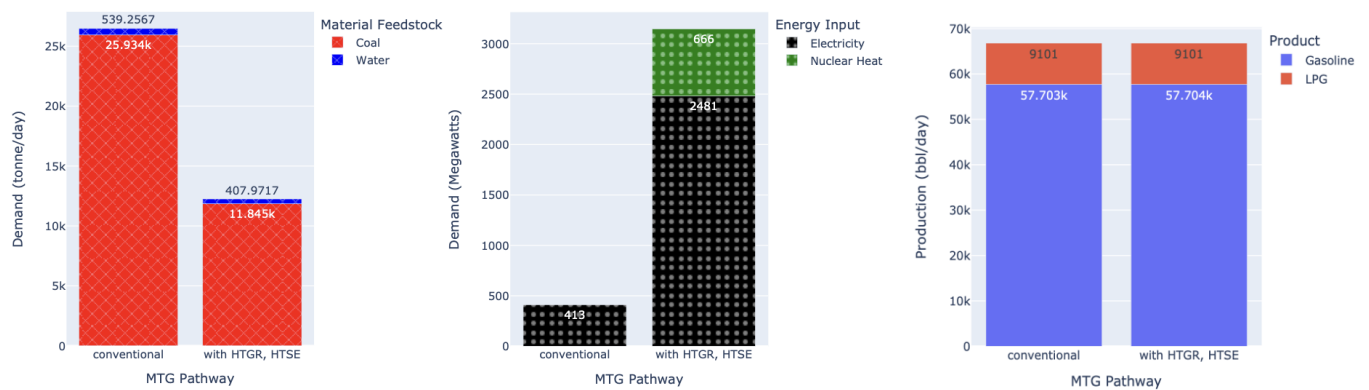


Figure 35. Comparative figure contrasting material feedstock and energy requirements for coal-driven MTG pathway using conventional approach and with HTSE and HTGR. Comparison performed for similar daily production profiles of gasoline and liquefied petroleum gas (LPG).

In addition, lighter olefins, especially ethylene and propylene, serve as precursors to many chemical industries. Methanol is a potential feedstock to their manufacture. At INL, the case study on integrated HTSE and HTGR for decarbonizing methanol-to-olefins (MTO) pathway was also investigated, with the case material balance summary illustrated in Figure 36. Both pathways investigated direct methanol conversion with a FT reactor. It can be noticed again that coal requirement has a feedstock is reduced by half with the utilization of nuclear-generated heat.

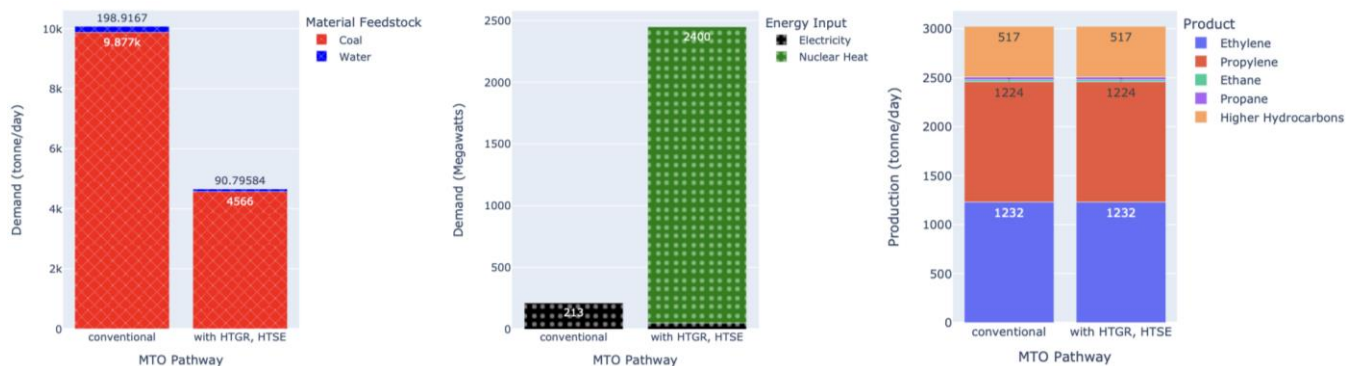


Figure 36. Average material and energy balance summary for MTO pathway using conventional approach and with HTSE and HTGR, with similar output profile of olefins being produced.

4.2.7 Major North American Methanol Producers and Port Storage Capacities

In North America, the major methanol producers are ExxonMobil Chemical Company (U.S.), Methanex Corporation (Canada), and Celanese Corporation (U.S.). Based on publicly available data from the Methanol Institute, a storage capacity of 1.9 million metric tons can be confirmed at 10 of the 17 ports in the U.S. (Methanol Institute and Methanol Market Services Asia 2023). California ports in Long Beach and Los Angeles have a combined bulk liquid methanol storage capacity of 344,565 metric tons. The largest domestic capacity of 600,000 metric tons is on the gulf coast at St. Rose, Louisiana. The nested pie-chart in Figure 37 summarizes data for methanol storage capacities at North American ports.

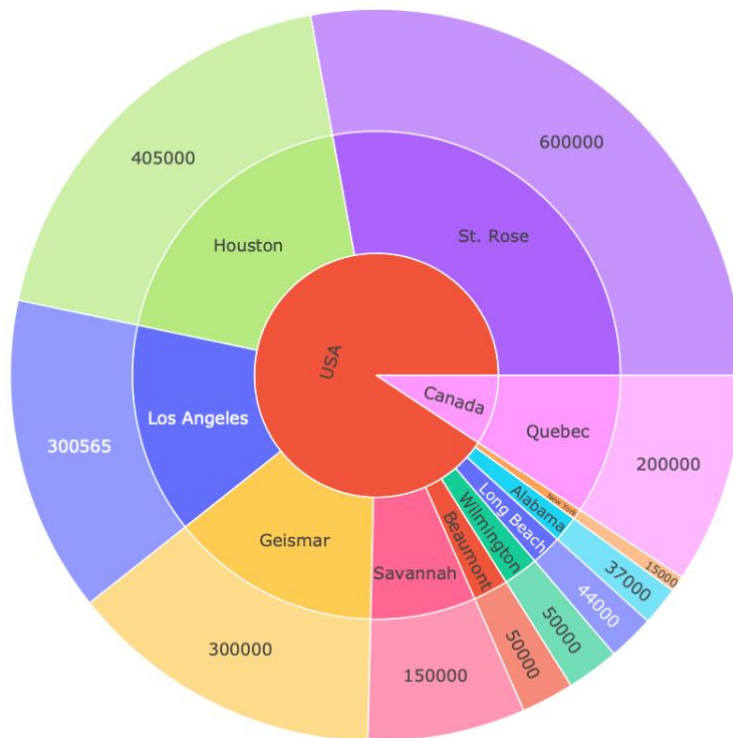


Figure 37. North American ports with confirmed methanol storage capacities (in metric tons).

4.2.8 Nuclear-Integrated Methanol Production

In the case of nuclear-driven methanol synthesis, nuclear-generated heat would be most relevant during syngas production. Syngas generation is a highly endothermic process and requires additional heat typically sourced by burning feedstock such as natural gas or coal. The process heat for syngas production is also sourced by combusting the tail gas (as a refinement of the sour gas obtained as a byproduct from gasifier) or by burning light fuel gas (Idaho National Laboratory 2012, 2010).

Moreover, the efficiency of syngas generation is driven by hydrogen content in the feedstock. In the case of coal as a feedstock, hydrogen and oxygen can be sourced from HTSE operation driven by nuclear heat. Technical evaluations, with detailed Aspen models, were performed for integration of an HTGR-HTSE hybrid with coal-based MTO conversion (Idaho National Laboratory 2012) and with coal-based MTG conversion (Idaho National Laboratory 2010). For natural gas as a feedstock, nuclear-generated steam can be directly fed into the steam methane reformer (Idaho National Laboratory 2010).

The FT reactor must be designed to recuperate heat from the syngas preparation. As a result, the first two macro processes in Figure 24 involve significant thermal exchanges. Additional technical evaluation studies on nuclear-integrated methanol production must also be initiated for other end products with high-volume demands. The remaining four sectors include formaldehyde, acetic acid, methyl tert-butyl ether, and fuel-based utilizations, as seen in Figure 20.

A deeper dive is needed to assess economic viability, specifically in terms of variable or fluctuating natural gas prices. The nuclear-sourced direct or indirect heat for methanol production can potentially reduce methanol-price susceptibility to natural gas cost. Other factors include carbon pricing, methanol storage and transportation costs, local environmental protection laws, and most importantly, finding leverages with the recently introduced Inflation Reduction Act. Nonetheless, the cost of natural gas as a feedstock is of paramount importance. BASF, one of the world's largest chemical companies, announced

closure of its toluene di-isocyanate plant in Ludwigshafen, Germany due to higher gas prices in Europe contributed to the Russia-Ukraine conflict.

The section on nuclear-driven methanol production concludes with the following key takeaways:

- A large-scale syngas generation process requires heat sourcing above 800°C;
- Syngas generator and FT reactor must be co-designed to maximize overall process efficiency via heat recuperation from syngas conditioning;
- A nuclear-HTSE hybrid is most appropriate for augmenting hydrogen and oxygen content in gasifiers;
- Use of natural gas, with methane as its core component, is most conducive toward efficient catalysis, but increases susceptibility of methanol prices to gas markets;
- Use of biomass as a feedstock requires heat sourcing at diverse temperature and pressure ranges based on biomass composition and moisture content.

4.3 Pulp and Paper

The kraft process accounts for approximately 85% of pulp production in the United States. This process, invented in 1879, has remained so dominant because its chemical recovery process can recover approximately 95% of the pulping chemicals while producing steam. The kraft process can also handle a wide variety of wood species, and the pulp strength is considered superior to other pulping processes. The other three processes principally used in chemical pulping are sulfite, neutral sulfite semichemical, and soda (United States Environmental Protection Agency 1990). Chemical pulping processes use harsh chemicals and heat to separate plant cellulose fibers from lignin. The dissolved lignin is later burned as fuel, while the cellulose pulp is separated and washed to become paper.

An alternative to chemical pulping is mechanical pulping, which is a low-cost, high-yield process in comparison. However, the products are of lower quality because the grinding process damages the fibers, as opposed to chemical processes dissolving the lignin around the fibers. Mechanical processes also require an external energy source, while chemical processes generate their own energy when the lignin is burned in the recovery process.

The suitability of pulp and paper mills for nuclear integration hinges on the assertion that pulp and paper production is a stable, if not growing, industry. From a high-level perspective of the paper industry, one might expect that paper demand is decreasing due to the conversion to digital platform. However, while consumption of newsprint, graphic and printer paper has greatly decreased, the demand for packaging paper and paperboard is still increasing, as shown in Figure 38. Despite the conversion of many paper products to digital, it is reasonable to assume that paper products like cardboard, paperboard, and household tissue will remain stable or increase in the future.

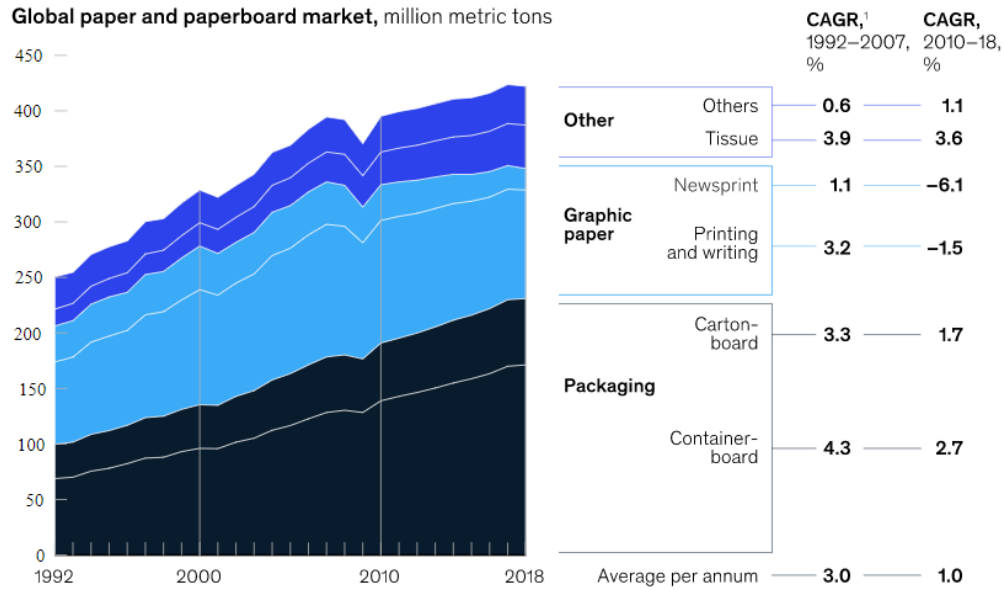


Figure 38. Global pulp and paper market evolution (Berg and Lingqvist 2019).

Because the kraft process is so dominant in the United States, it will be the main focus of integration efforts with the pulp and paper industry. Although not covered in this paper, it is expected that a mechanical pulping process could be integrated with an NPP similarly to other industries that require only electricity inputs, or potentially small amounts of heat. NPP integration with and decarbonization of the kraft process requires extensive consideration regarding the process byproducts, internal energy generation, steam temperature sensitivity, and the impacts of design changes. Fortunately, over 100 years of both process improvements and operating experience make the kraft process a good candidate for investment in decarbonization opportunities.

4.3.1 Process Description

A block diagram of a typical integrated pulp and paper mill is shown in Figure 39. From a material balance perspective, pulp and paper making is a highly efficient process. The chemical recovery process is designed to maximize the retrieval of high-quality cellulose fibers and dispose of remaining solids through energy generation. Lime materials in the causticizing step can be reused many times after being heated to high temperatures. Because the cellulose fibers adhere to each other with hydrogen bonds, used paper can be effectively converted back to fibers to be pressed and used in new products. Waste material consists largely of particulate emissions of sodium salts and calcium salts from the recovery boiler, lime kiln, and smelt dissolving tank. Gas emissions consist of sulfur dioxide, carbon monoxide, hydrogen sulfide, nitrogen oxides, and carbon dioxide from combustion processes and lime generation in the lime kiln.

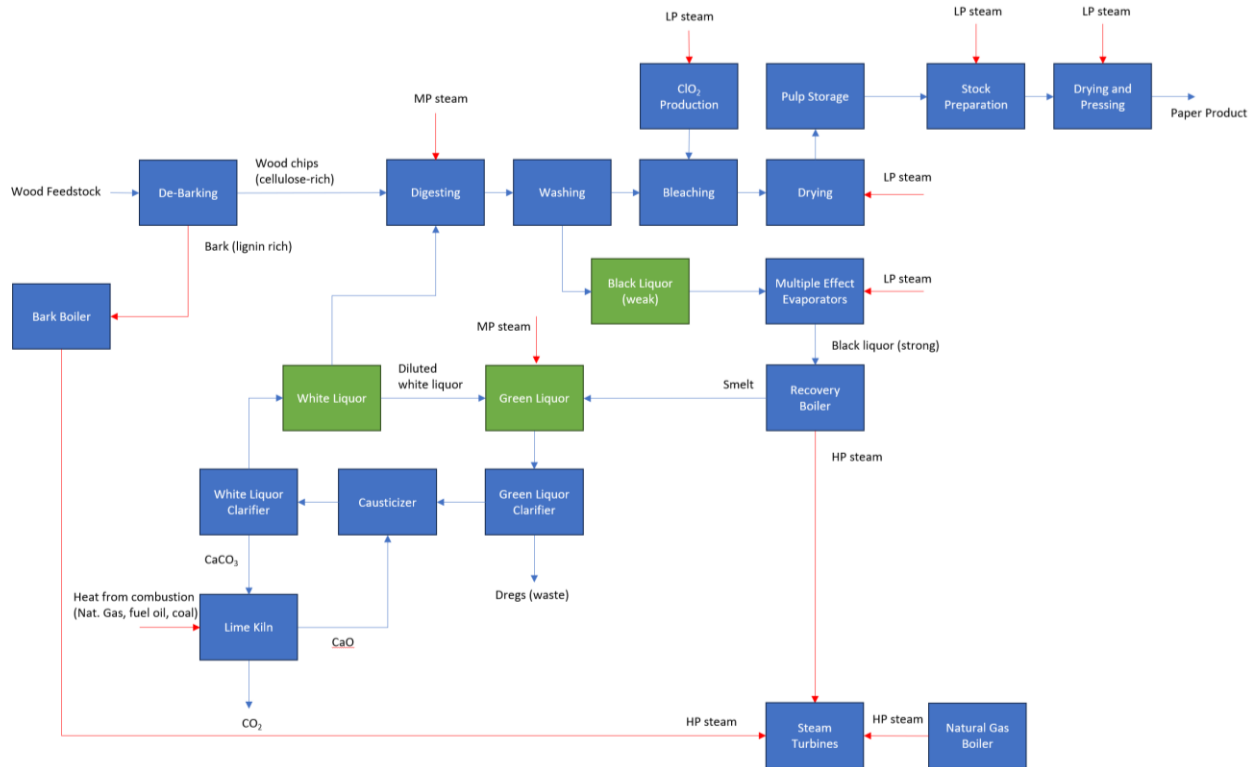


Figure 39. Pulp and paper mill block flow diagram.

4.3.1.1 Kraft Pulping Process

The specific design details of the kraft pulping process will vary based on each specific facility, which is why the feasibility studies for integration are so important. The description of the process here is developed through several generic and specific descriptions of kraft pulp mill designs (United States Environmental Protection Agency 1990; Eriksson and Hermansson 2010; Thompson Equipment Company n.d.). A high-level depiction of the kraft process is given in Figure 40.

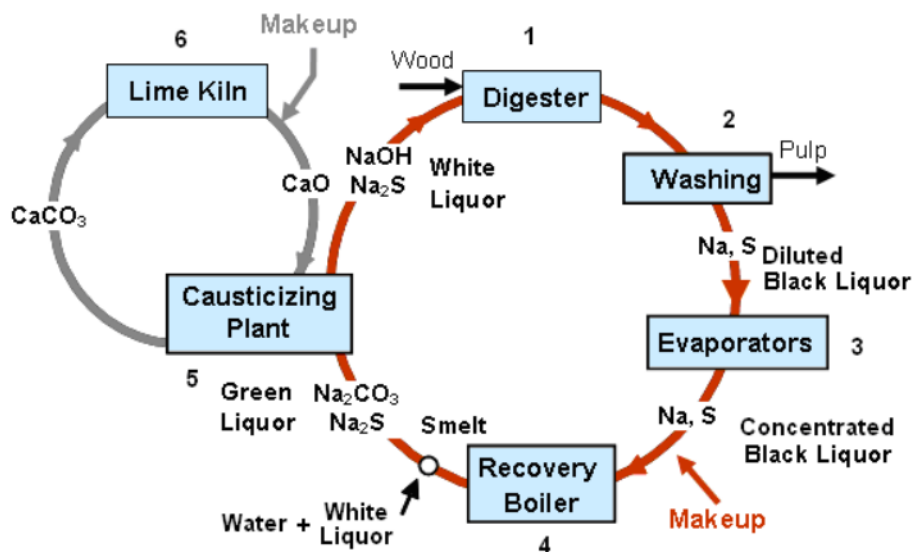


Figure 40. High-level overview of the stages of the kraft cycle (Tran and Vakkilainen 2012).

The process begins with wood logs. The logs may be washed to remove dirt, ice, and gravel. Bark is mechanically removed in the debarking process, separated, and dried as fuel in a bark boiler. The logs are then cut into chips and preheated in a drying process.

The wood chips are mixed with white liquor, a fresh batch of sodium hydroxide (NaOH) and sodium sulfite (Na₂S), for digesting, which can occur in continuous or batch processes. The digester is heated and cooked at a sustained temperature to facilitate delignification until the strong cooking liquor is displaced with a weaker liquor. When the cooking is finished, a cooling liquor displaces the weaker liquor. In the final digesting step, the pressure in the digester is lowered, which depolymerizes the fibers through rapid evaporation and a subsequent pressure increase. The various liquor stages are either cooled and stored, reused directly in the digesting cycle, or sent to the evaporation plant. The process of digesting is depicted in Figure 41.

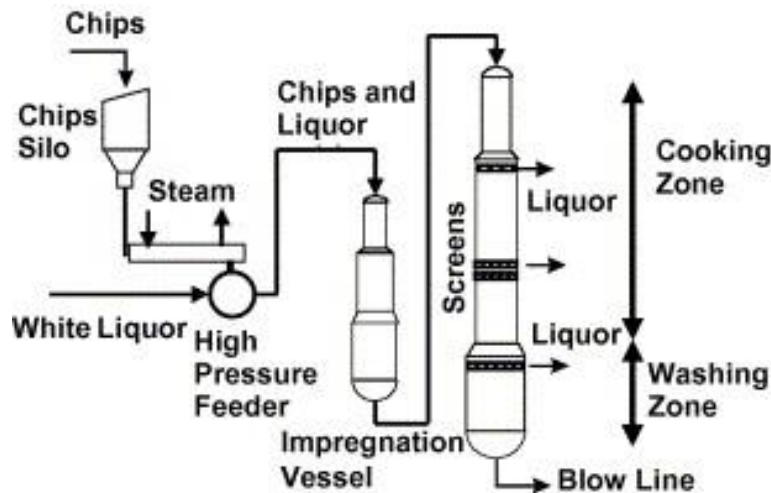


Figure 41. Depiction of a continuous digester (Pougatch, Salcudean, and Gartshore 2006).

The digested components consist of pulp and a mixture of lignin and cooking chemicals called black liquor. The weak black liquor contains about 12–15% solid lignin, oxidized inorganic compounds (Na₂SO₄ and Na₂CO₃), and white liquor (Na₂S and NaOH). The black liquor is removed in several washing steps, and the pulp is screened to remove knots and incompletely cooked fibers.

The last step of the pulping process is bleaching. Remaining lignin can be decreased by prebleaching the pulp with oxygen. This is followed with further bleaching with hydrogen peroxide, chlorine dioxide, and caustic soda. If the paper production process does not occur on-site, the pulp is dried and transported to the customer. If it is an integrated mill, the pulp will be pumped into storage.

The chemical recovery process follows the production of pulp. The weak black liquor is concentrated in a multi-effect evaporator, increased to about 50% solids, and then further concentrated in a direct-contact evaporator to 65% solids. Water removed in the evaporator is stripped and drained. Sops can be extracted from the condensate and acidified into tall oil, which can be converted to beck oil to power the lime kiln. The highly concentrated black liquor is combusted in the recovery boiler to generate steam. The combustion itself is an important part of the recovery process, because it reduces sodium sulfate (Na₂SO₄) to sodium sulfide (Na₂S), a main component of white liquor. Unburned residuals from the black liquor form a smelt in the bottom of the recovery boiler, and the smelt is dissolved in weak white liquor creating a mixture called green liquor, a solution of carbonate salts (primarily Na₂S and Na₂CO₃) and insoluble, unburned carbon and inorganic impurities called “dregs.” The “dregs” are removed in the green liquor clarifier. This process is depicted in Figure 42.

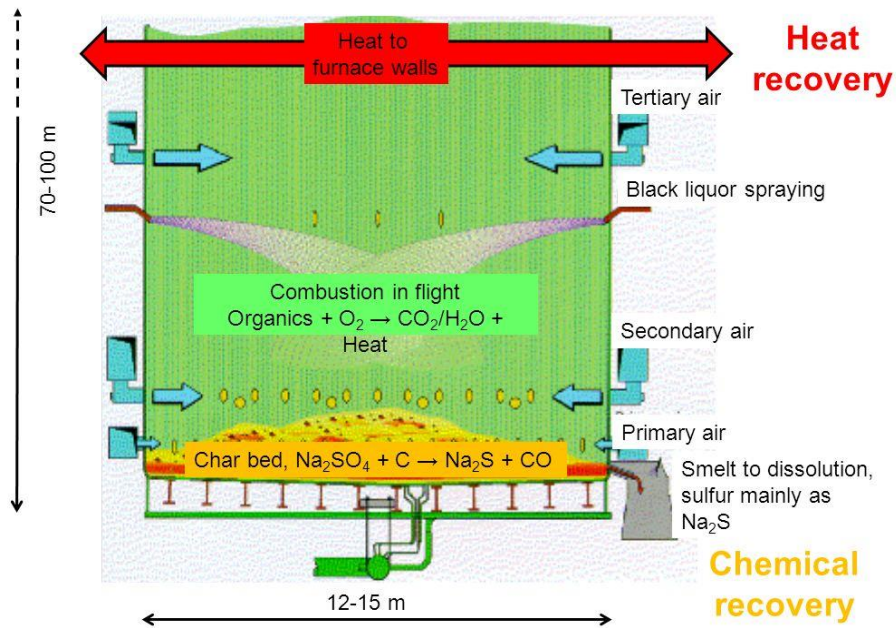


Figure 42. Chemical reactions in the black liquor recovery boiler (Jarvinen 2016).

The last step of the chemical recovery process is causticization. In the lime kiln, calcium carbonate (CaCO_3) is heated and split into calcium oxide (CaO), or quicklime, and CO_2 . Quicklime is added to the green liquor and reacts with water to form calcium hydroxide (Ca(OH)_2). In a series of agitated tanks called causticizers, Ca(OH)_2 reacts with Na_2CO_3 to form NaOH and CaCO_3 to complete the causticizing reaction. A white liquor clarifier removes the CaCO_3 precipitate, or "lime mud" and washes it along with the dregs to remove the last traces of sodium. The mud (mostly CaCO_3) can be dried and added back to the lime kiln to produce "reburned" lime. The mud washer filtrate can be used to dissolve smelt. After clarifying, the resulting mixture is white liquor, and is returned to the digesters to begin the process over again. Figure 43 shows a graphical depiction of the chemical reaction cycle of causticization.

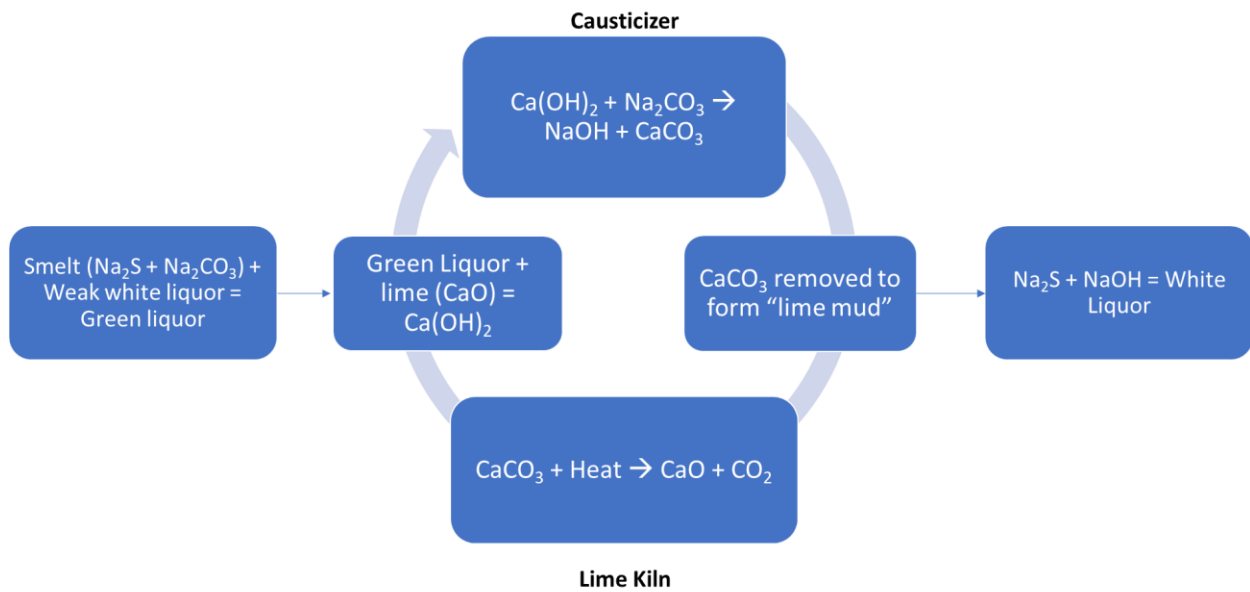


Figure 43. Chemical reactions occurring in the causticization cycle.

4.3.1.2 Paper Production Process

The paper machine consists of four sections: the wet end, press section, dry end, and calendar section. On the wet end, pulp is diluted with water and distributed onto a belt of wire mesh, which encourages all the fibers to go in one direction. Water drains from the pulp resulting in about 80% moisture content. In the press section, rollers remove the water and decrease moisture content to 50–65%. The belt in the press section is often made of felt or wool to absorb moisture. On the dry end, the pulp is run across felt-covered steam-heated cylinders used to dry the pulp and reduce moisture to 5–10%. The calendar section uses rollers mounted opposite each other to pressurize the paper for a smooth finish. This process is depicted in Figure 44. As water drains from the pulp, the fibers are forced together to form hydrogen bonds. The dry paper gets spooled into rolls to be converted to various paper products. Different types of paper or paperboard can be produced by altering the drying or calendaring process, and using different kinds of wood pulp (Eriksson and Hermansson 2010; Casey 2017).

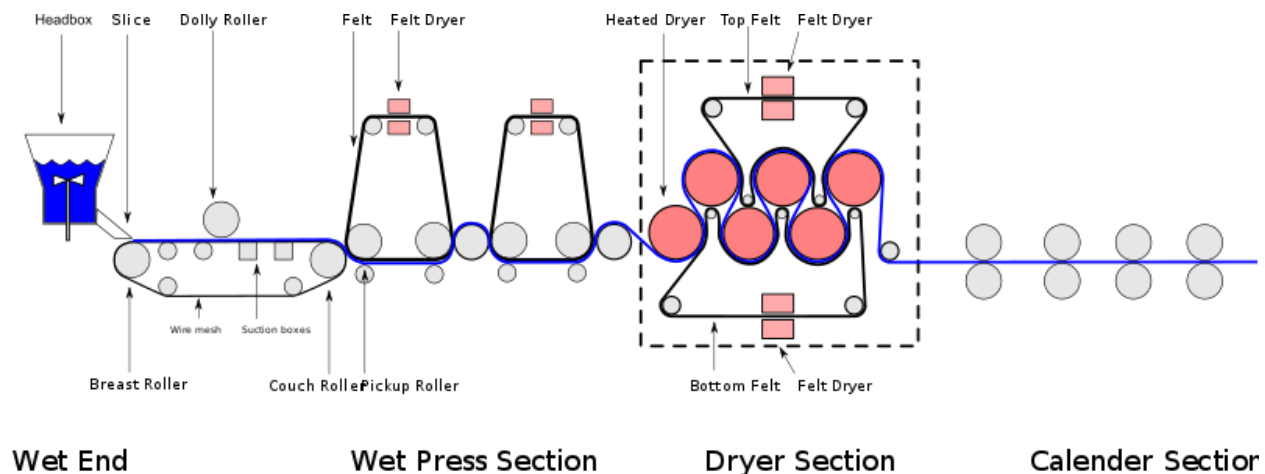


Figure 44. Depiction of a paper machine (Egmason 2010).

4.3.1.3 Recycling Fibers

The ability to recycle and downcycle cellulose fibers completes the almost entirely circular nature of pulp and paper making. According to the American Forest and Paper Association, 80% of U.S. paper mills use some recycled paper to make new products. Nearly half of all recycled paper is used to manufacture containerboard, and the rest is used for newsprint, tissue and boxboard, and about a third of the material is exported. The recycled pulping process uses mechanical shredding, water, and chemicals such as hydrogen peroxide, sodium hydroxide, and sodium silicate to break down the paper back into separated fibers. The recycling process has such a high utilization rate because contaminants like plastic, tape, and staples can be screened out in the pulping process, and ink can be removed in flotation (Greentumble 2018). It is also efficient because the paper can be returned directly to the cellulose fiber state because lignin has already been removed. The mechanical shredding processes mean that the fibers can only be recycled five to seven times before they become too short to be usable (United States Environmental Protection Agency 2016). For this reason, some virgin pulp is often combined with recycled pulp to increase strength.

4.3.2 Plant Load Data

There are several publicly available data sources for paper mill heat and steam loads. This information is described here for use in future case studies.

4.3.2.1 Plant 1: Medium Integrated Mill

Plant 1 is a medium-sized integrated pulp and paper mill in the southeastern U.S. (Worsham 2020). A depiction of the steam systems of the plant is shown in Figure 45. Steam is generated from two black liquor recovery boilers, one bark boiler, and a natural gas boiler. The outputs of the recovery and bark boilers depend on the output of the plant and the chemical recovery process. The natural gas boiler can make up steam if there is a deficit in the other processes. The boiler characteristics are listed in Table 4.

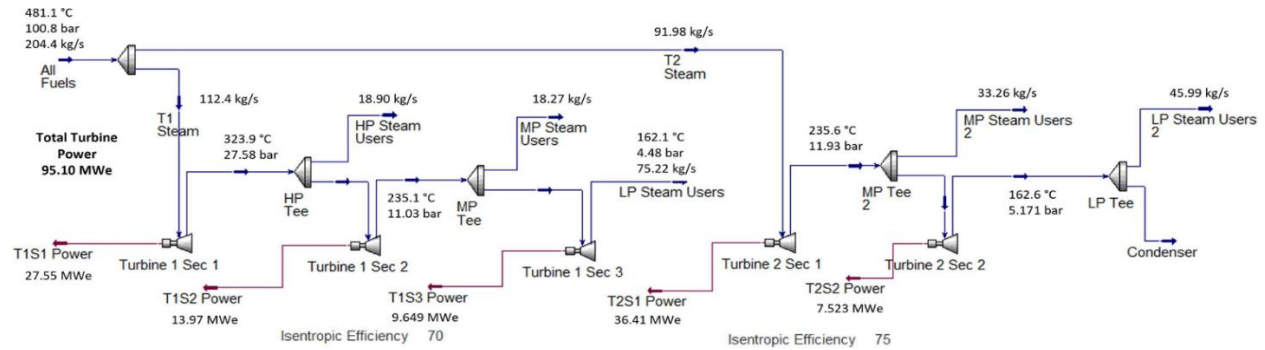


Figure 45. Model of a pulp and paper mill steam system (Worsham 2020).

Table 4. Plant steam sources (Worsham 2020).

Steam Source	Fuel	Mass Flow (kg/s)	Pressure (bar)	Temperature (°C)	Percent of Total
Recovery Boiler 1	Lignin (from black liquor)	34	101	481	17%
Recovery Boiler 2	Lignin (from black liquor)	108	101	481	53%
Bark Boiler	Bark and wood residuals	32	101	481	15%
Natural Gas Boiler	Natural Gas	30	101	481	15%

The plant produces high-temperature steam which is sent through turbines to both bring the steam to the appropriate condition for use and generate electricity. The turbine characteristics are listed in Table 5.

Table 5. Turbine Electricity Generation (Worsham 2020).

Turbine Name	Electricity Generated (MW)	Mass Flow Rate (kg/s)
Turbine 1 Stage 1	27.6	112
Turbine 1 Stage 2	14.0	93
Turbine 1 Stage 3	9.6	75
Turbine 1	51.2	280
Turbine 2 Stage 1	36.4	92
Turbine 2 Stage 2	7.5	59
Turbine 2	43.9	151
Total	95.1	431

The plant utilizes high pressure (HP), medium pressure (MP) and low pressure (LP) steam to supply various processes. The characteristics of steam sent to plant processes is listed in Table 6.

Table 6. Plant steam demands (in terms of mass and energy) (Worsham 2020).

	Use	Pressure (bar)	Temperature (°C)	Mass flow rate (kg/s)	Total Enthalpy of superheated steam (MJ/s)	Percent of total thermal demand
HP Steam	Small secondary operations	27.6	324	19	58.1	10.7%
MP Steam	Digesting, drying, smelt recovery	11.0	235	18	52.3	9.7%
		12.0	236	33	95.8	17.7%
			Total	51	148.1	27.3%
LP Steam	Evaporator, deaerator, drying, digesting, chlorine dioxide production	4.5	162	75	208.2	38.4%
		5.2	163	46	127.5	23.5%
			Total	121	347.9	61.9%

The plant also uses natural gas to fire the lime kilns. This heat does not come from the boiler sources. The lime kiln heat demands and fuel consumption rates are listed in Table 7.

Table 7. Non-steam producing heat sources (Worsham 2020).

	Type of Fuel	Lime Load (mtons/day)	Heat Demand (MJ/ton)	Average Fuel Consumption (Nm ³ /day)
Lime Kiln 1	Natural Gas	200	7,385	40,776
Lime Kiln 2	Natural Gas	325	6,330	57,086

4.3.3 Decarbonization Opportunities

Pulp and paper mills are not typically a priority for decarbonization because a large portion of the steam comes from burning biomass. The important balance of the chemical recovery process also limits some opportunities for replacing the biomass fuel. Based on data from the Environmental Protection Agency (EPA), the burning of spent fuel accounts for about 71% of total plant CO₂ emissions. The national total and plant average CO₂ emissions for the pulp and paper industry are listed in Table 8. The various decarbonization opportunities are described in this section.

Table 8. Emissions from the pulp and paper industry.

Energy Medium	Fuel	National CO ₂ emissions from P&P	Average Plant Emissions ²	Percentage of Total CO ₂ Emissions
Steam	Spent Liquor	73.5	0.71	61%
	Wood and Other Biomass	26	0.22	19%
	Natural Gas (or alternative fossil fuel)	24.2	0.1	9%
Combustion Gases ¹ (or alternative fossil fuel)	0.1		12%	

¹ Combustion of fossil fuels also contributes 0.4 MMT each of CH₄ and N₂O emissions, which are tracked by the EPA (United States Environmental Protection Agency 2023).

² Based on 103 pulp and paper reporters to the EPA in 2021 (United States Environmental Protection Agency 2023).

³ Includes the CO₂ released chemically from the calcination of lime. Fossil CO₂ emissions are based on the non-biogenic emissions tracked by the EPA. The percentage of total plant CO₂ emissions allocated to the lime kiln is 12% (Yang, Meerman, and Faaij 2021). The rest of the fossil emissions are allocated to the fuel boiler for steam production.

4.3.3.1 Lime Kiln

The lime kiln releases CO₂ through the combustion of fossil fuels and by the chemical reduction of CaCO₃ into CaO and CO₂. The outgoing CO₂ stream is relatively pure because it is mixed only with combustion gases. This makes it ideal for capture and sale to other industries like carbonated beverage production. However, the lime kiln could also be modified to reduce total CO₂ output or produce an even more pure stream of CO₂ for sale.

Because lime kiln temperatures are 1,000°C or higher, nuclear heat cannot be used as a fuel source without significant heat topping. Even in a decarbonization scenario, combustion is still the preferred method for heat production because it will require minimal design changes to the plant. Oxy-fuel combustion is one simple solution; although it would not decrease CO₂ emissions, it would result in a purer stream for carbon capture. To eliminate CO₂ emissions from fuel burning, hydrogen fuel could be generated by a nuclear-powered electrolysis unit and burned in the lime kiln. Alternatively, the combustion-based lime kiln could be replaced with an electric kiln, which could use nuclear electricity to achieve the high temperatures required for calcination.

Another option for combustion fuel is processing biogenic fuels such as spent liquor or bark waste into suitable fuel for the lime kiln. This would decrease fossil fuel use but would not necessarily decrease overall CO₂ emissions of the plant—it is possible that replacing these biogenic fuels with nuclear heat elsewhere in the process could result in lower total CO₂ emissions. Using these biogenic fuels for the lime kiln can damage the kiln, negatively affect the quality of lime and contaminate the outgoing CO₂ stream (Kuparinen and Vakkilainen 2017).

Regardless of the fuel used for combustion, capturing carbon from the lime kiln is essential for total plant decarbonization because it will reduce approximately 12% of total CO₂ emissions (Yang, Meerman, and Faaij 2021). Captured CO₂ could be utilized for chemical production, sequestered, or sold to other markets; the best option will depend on the location of the plant and the distance to market opportunities.

4.3.3.2 Black Liquor Boiler

Alternatives to the black liquor boiler are contentious in the pulp and paper community. The kraft cycle relies on the combustion of black liquor to reduce sulfur in Na_2SO_4 to Na_2S and complete the chemical recycling process. Black liquor gasification (BLG), an alternative to combustion, causes a “sulfur-sodium split” in the chemical recovery process. Sulfur leaves the gasifier in the gas phase instead of with the sodium in the solid phase. The sulfur then must be captured from the flue gas and reintroduced into the remaining smelt before causticization. Reducing the amount of sulfur in the solid phase also increases the causticizing load, potentially resulting in greater CO_2 emissions.

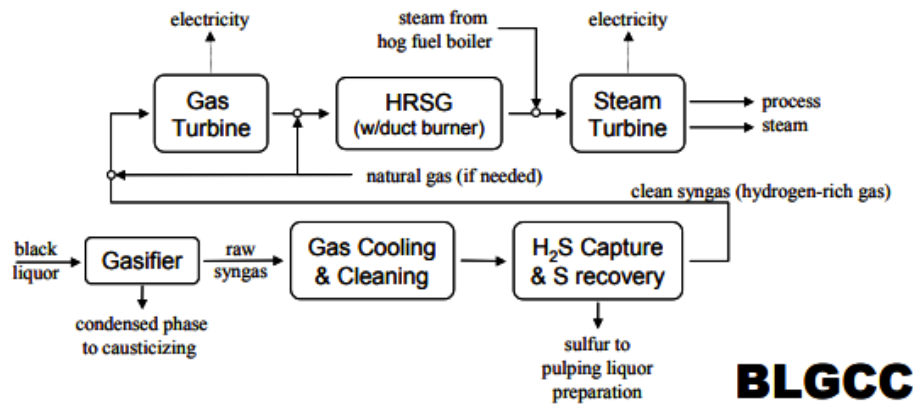


Figure 46. Black Liquor Gasification Combined Cycle (BLGCC) process diagram with sulfur recovery (Larson, Consonni, and Katofsky 2003)

The energy-rich component of black liquor is lignin. BLG is generally presented as the alternative to black liquor boilers because the lignin is converted into a gaseous fuel that can be used in other parts of the plant. The resulting syngas also contains fewer contaminants and is therefore easier to clean than the combustion flue gases. Syngas produced from lignin could be used in the lime kiln or in a separate boiler to produce steam. Chemrec commercialized a BLG process in 1989 and successfully operated pilot-scale processes in several pulp mills until industry interest and funding reduced around 2012 (Chemrec 2017).

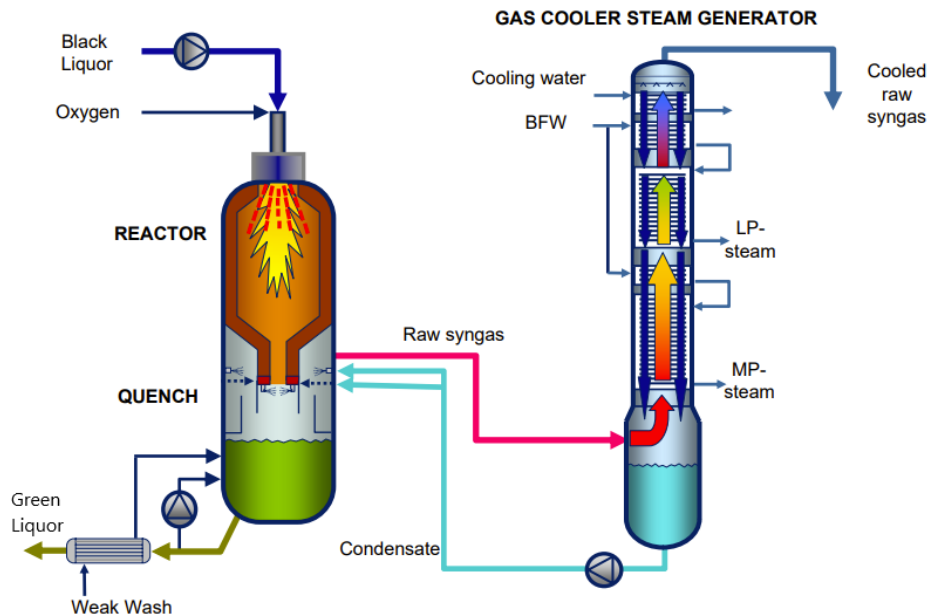


Figure 47. Chemrec process diagram (Chemrec 2011).

An alternative to converting the lignin to fuel is separating it from the black liquor and using it as a carbon-rich feedstock to produce other products. While black liquor gasification was heavily researched and developed in the 1980s and 1990s, lignin separation development appears to have started in the early 2000s. There are two commercialized options available for this separation process: LignoBoost and LignoForce. These processes acidify the liquor to precipitate out lignin. Removing lignin from black liquor can increase pulp production in the mill if the recovery boiler capacity is limited; recovery boilers have a limited heat transfer capacity, removing the lignin and burning it in a separate boiler increases the amount of heat that can be produced in the mill, and therefore can increase the raw material processing capacity of the plant (Vakkilainen 2009) Lignin could also potentially be used as a natural gas replacement for the lime kiln.

The recovery boiler produces most of the steam for an integrated pulp and paper mill, providing electricity and low-pressure steam for downstream processes. However, an NPP could directly replace the boiler to provide steam and electricity. Because of this, it is recommended that the recovery boiler be removed in a nuclear-integrated decarbonization scenario. Aside from decarbonization potential, the main reason to remove the recovery boiler is to increase safety and reliability of the mill. Because of the corrosive materials and harsh operating conditions, the recovery boiler has unique operational and safety problems compared to conventional boilers (The Black Liquor Recovery Boiler Advisory Committee 2017). Because the recovery boiler produces a majority of the steam for the plant, its outage inhibits production and therefore revenue throughout the entire plant. The recovery boiler also presents a major safety risk for mill workers. Two types of explosions can happen at the recovery boiler and the connected smelt dissolving tank: smelt-water and combustible gas explosions. Smelt-water explosions account for nearly 75% of explosions in the black liquor recovery boiler as of 2008 (Grace n.d.). These explosions are caused by rapid steam generation when molten salt in the smelt is exposed to water. These explosions can occur on a small scale and cause injury by spattering high temperature smelt. On a large scale, they can cause massive damage to the plant. A total of 574 recovery boiler incidents were reported to the Black Liquor Recovery Boiler AC between 2009 and 2019, and the median downtime for an incident was 46 hours. Seven of these incidents were dissolving tank explosions and four were smelt water furnace explosions (Haraga 2019). The safety and reliability of NPPs far exceeds that of the recovery boiler, and thus removal could improve overall operations and safety at the plant.

4.3.3.3 Conversion of Wood Waste to Biomaterials

Pulp and paper mills typically utilize all the wood content they process: cellulose fibers are used to make paper, lignin is burned in the recovery boiler, and bark and other feedstock contaminants are burned in the hog boiler. Nuclear steam could replace these sources, and instead, lignin and wood waste could be converted to other forms or fuel, chemicals, or materials. If lignin is to be reprocessed, the recovery boiler will need to be removed or modified to support lignin extraction.

Lignin is the compound in wood that gives it strength and rigidity, which makes it unideal for using in paper. High percentages of lignin also cause paper to yellow. Lignin's strong carbon bonds also make it difficult to break down and convert it to other products; it is categorized as a biopolymer. There are several depolymerization techniques that can turn lignin into aromatics like vanillin. Alternatively, lignin can be valorized to produce thermoplastics, foams, adhesives and more.

Lignin is typically considered a low-value product at a pulp mill, because it can be difficult and expensive to separate and reprocess. This is why the lignin is burned as a fuel in the recovery boiler. A pulp mill may process many species of wood in a single batch, and the lignin can be partially depolymerized and repolymerized during the digesting process. The lack of consistent structure makes it difficult to process into high-performance products with consistent qualities (Ganewatta, Lokupitiya, and Tang 2019).

Alternatively, extracted lignin could be converted to fuels that can be used elsewhere in the mill or sold to a local market. Gasification and pyrolysis of lignin are both options to produce a portion of

syngas. Pyrolysis will also result in a substantial portion of solid residue, or biochar. Returning char to soil is a form of sequestering carbon, and helps soil retain moisture and nutrients. It is possible that in the future, tax credits will be offered for this form of carbon sequestration, which would produce a new source of revenue for the plant.

4.3.3.4 Recycle Material at its Source

The paper recycling process is generally done using mechanical methods; there is no steam produced by the process and the plant relies entirely on energy from external sources. Mechanical mills, however, eliminate the safety and emissions issues from the kraft process, and can therefore be sited in densely populated areas. The first material recovery center in the U.S. was built in New York in 1897 to recycle paper, fabric, and metals (Bradley 2016).

New nuclear reactors are also suitable for siting in populated areas, due to increased safety and a decreased emergency planning zone. These plants could power mechanical recycling closer to the source of the waste, cutting down on costs and greenhouse gas emissions to transport recyclable materials to a handling facility. Paper is one of the most recycled materials in the U.S., but exports of recovered paper are decreasing year over year, with India reducing its imports by nearly 27%, Taiwan decreasing by 16%, and exports to Canada decreasing by 14.2% (McNees 2023). Planning more paper recycling facilities in the U.S. means that it can continue recovering and recycling paper economically in the future.

4.4 Ammonia

Ammonia, comprised of hydrogen and nitrogen atoms (NH_3), is the second-largest chemical product produced in the world. Ammonia is a primary feedstock of fertilizer used in food production supporting half of the global population. The ammonia process requires significant energy consumption, accounting for about 1.8% of global energy use on its own. In addition, more than half of the world's hydrogen use is associated with ammonia production, and it also results in significant CO_2 emissions. Five hundred million tonnes of carbon dioxide are produced as a byproduct during the process (The Royal Society 2020). Due to the significant carbon dioxide emissions associated with the ammonia process, coupling the process with an integrated energy system that incorporates nuclear energy is an appealing option.

4.4.1 Statistics: Production, Usage, Price, Location

The first commercial ammonia plant using the Haber-Bosch process was built by Badische Anilin und Soda Fabrik (BASF) at Oppau, Germany in 1913; it had a production capacity of 30 tonne/day (Venkat Pattabathula 2016). Since then, the ammonia production capacity has perpetually increased. Ammonia production was estimated at 130 and 183 Mt worldwide in 2000 and 2020, respectively, and it is expected to increase to 223 Mt by 2030 and 333 Mt by 2050 (International Renewable Energy Agency and Ammonia Energy Association 2022). Eighty-five percent of ammonia is used as a raw material for fertilizer production while the remaining percentage is used for other products including textiles, refrigeration, and explosives. Demand for ammonia as fertilizer accounted for 156 Mt in 2020 and is expected to increase to 267 Mt by 2050 (International Renewable Energy Agency and Ammonia Energy Association 2022). In addition to existing ammonia demand, there is emerging new demand for ammonia. Liquid ammonia is one of the emerging candidates for alternative maritime fuel for large ships as part of net-zero carbon economy (Fahnestock and Bingham 2021, Sveistrup Jacobsen et al. 2022). Another emerging demand for ammonia is an energy carrier as the means of transporting hydrogen (Aziz, Wijayanta, and Nandiyanto 2020). All considered, global ammonia demand may reach up to 688 Mt in 2050 (International Renewable Energy Agency and Ammonia Energy Association 2022).

According to Mineral Commodity Summaries by the United States Geological survey (United States Geological Survey 2021, 2022), 17 Mt of ammonia was produced in 2020 by 17 companies at 37 plants across 18 states of the United States (U.S.). Figure 48 shows the location of ammonia production facilities in the U.S. along with their annual capacities in kilotons. The U.S. ranks third in ammonia production, behind China (51.14 Mt) and Russia (19.6 Mt). Production capacities in Louisiana, Oklahoma, and Texas account for 60% of the total production capacity in the U.S. CF Industries Inc. has the largest production capacity in the U.S., accounting for approximately 40% of total capacity. U.S. producers operated at about 84% of rated capacity. The ammonia produced is distributed through the ammonia pipeline, barges on the Mississippi river, and by railroad train. The amount of ammonia consumed in the U.S. 2020 is about 19.1 Mt, which is approximately 2 Mt more than the U.S. produces. This difference is mainly made up for through imports from Trinidad and Tobago (55.8%) and Canada (43.4%) (United States Geological Survey 2021).



Figure 48. Ammonia production facilities in the U.S. and their capacity in metric kilotons per year (United States Geological Survey 2021).

Anhydrous ammonia refers to ammonia in its pure form that contains no water, as opposed to an ammonia-water solution, which is the most traded form of ammonia. The price of anhydrous ammonia in Illinois, U.S. are seen in Figure 49, representing that the average price from September 2008 to September 2021 was \$653 per short ton while the average price between October 2021 and October 2022 was \$1,421 per short ton. The price increase is attributed to the Ukrainian-Russia war and the accompanying high natural gas price (Schnitkey et al. 2022, Schnitkey et al. 2023).

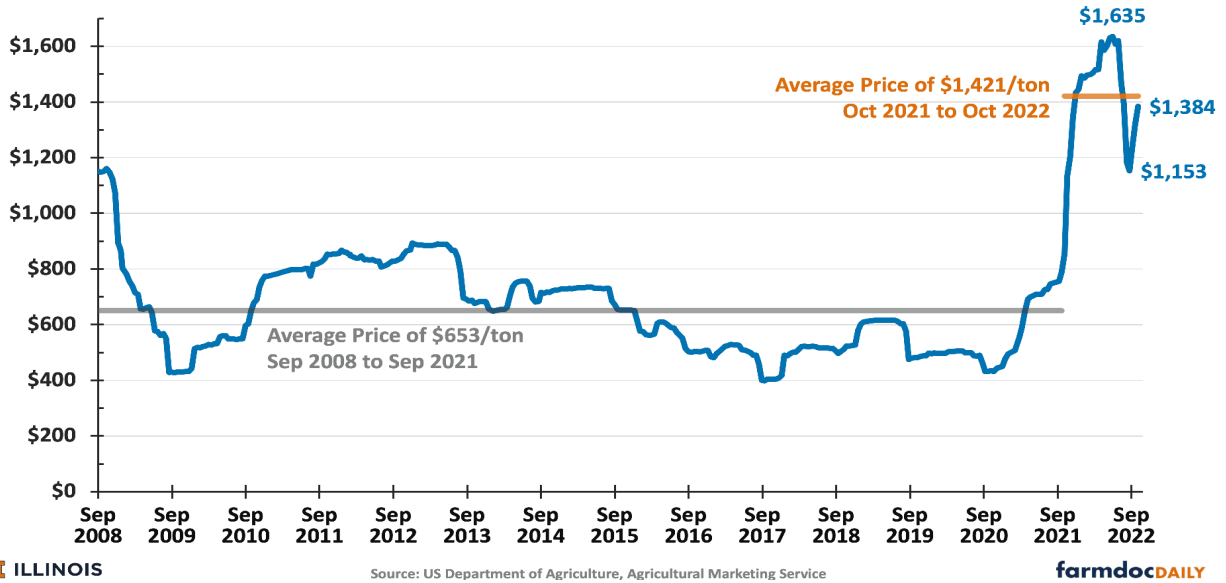


Figure 49. Anhydrous ammonia price in Illinois (Schnitkey et al. 2022).

The price of ammonia is affected by that of natural gas which is ordinary raw material of ammonia as seen in Figure 50. The more expensive natural gas is, the more expensive ammonia is. The interesting point is that the price of ammonia at U.S. Gulf coast has sharply risen, with a close relationship to the natural gas price of international (Western Europe and East Asia) natural gas, not that of U.S. Gulf coast. Prices for ammonia in the U.S. have risen consistent with international natural gas prices (\$6/MMBtu to \$35/MMBtu), rather than rising similarly to domestic (\$2.6/MMBtu to \$5.00/MMBtu) natural gas prices. (Tejasvi Raghuvver et al. 2022, Raghuvver and Wilczewski 2022).

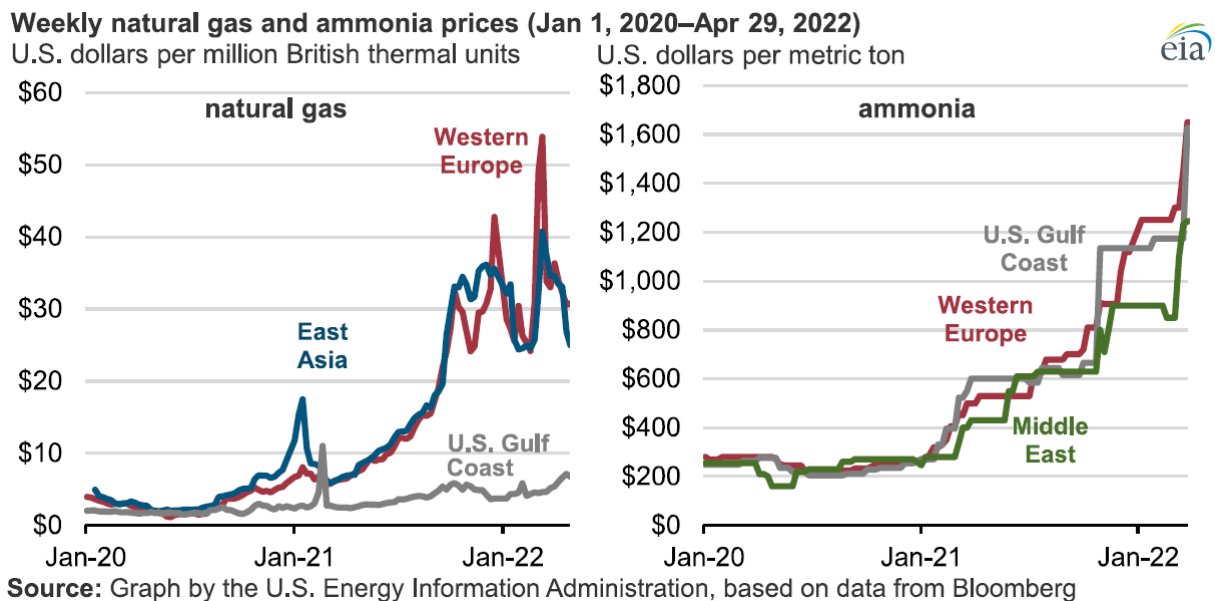


Figure 50. National gas and ammonia prices in last 2 years (Raghuvver and Wilczewski 2022).

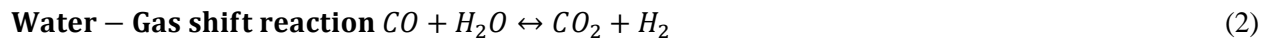
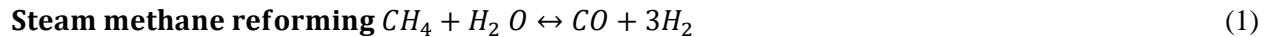
4.4.2 Preparation of Feed Material for Ammonia Synthesis

This chapter covers different methods and sources to prepare hydrogen and nitrogen which are used as feed materials of ammonia.

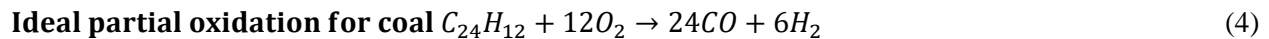
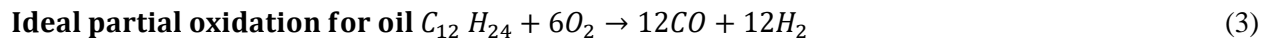
4.4.2.1 Hydrogen Preparation

In hydrogen manufacturing, a variety of raw materials and corresponding methods have been suggested, which tabulated in Table 10 with their production cost estimate. Please note that each study was done, but that the costs are whole dependent on the cost of electricity and natural gas, as well as the purity of hydrogen that is needed. Please do not use the value in the table for cost comparison before cost adjustments to reference year.

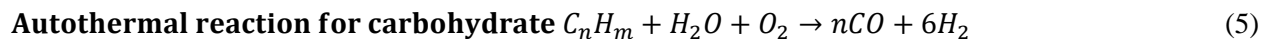
Steam methane reforming (SMR) using natural gas is the most popular and economical method for commercial hydrogen production for ammonia synthesis in the U.S. In SMRs, methane from natural gas reacts with steam and is converted into hydrogen and carbon monoxide with the aid of a catalyst. Water-gas shift (WGS) reaction accompanies SMR to produce additional hydrogen. SMR is an endothermic reaction, and some of the natural gas is burned as a fuel to obtain the energy required to drive the reactions. Total energy consumption in an ammonia plant based on SMR is estimated as 28 GJ/tonne NH₃.



Partial oxidation is the process to produce CO and H₂ by supplying a limited amount of oxygen. This exothermic process does not require additional energy. This process is usually employed when either heavy oil or biomass is selected as the raw material. It is also employed as an ancillary hydrogen conversion method used for the Haber-Bosch process. Partial oxidation is divided into two methods based on catalyst use. Thermal partial oxidation (TPOX) requires a high temperature of 1,200°C without a catalyst, whereas catalytic partial oxidation (CPOX) requires relatively low temperature of 800–900°C with the aid of a catalyst. However, the catalysts used in this method can be easily poisoned by sulfur contents. Thus, the CPOX method cannot be used for materials containing high amounts of sulfur.



Coal autothermal gasification is the second most popular method to produce hydrogen in the world, mostly employed in China. Raw material (usually coal) reacts with both water and oxygen introduced in a high temperature environment; the operating temperature can reach up to 1,500°C. This process is an integration of steam reforming and partial oxidation. Instead of burning extra fuel, the energy required for an endothermic steam reforming reaction is replenished by the exothermic partial oxidation reaction, which is the reason that the process is called autothermal.



Hydrothermal gasification is the process in which raw materials react within a pressurized high-temperature water solution. Water participates not only as a solvent but also as a reactant. As supercritical water is usually employed for gasification purposes, it is also referred to as supercritical water gasification (SCWG). Supercritical water has high diffusivity and low polarity, in which most organic compounds can become soluble. In addition, organic salts that were soluble in the ambient water are no longer soluble and deposited in supercritical water. Alkali salt (NaOH, KOH, Na₂CO₃, K₂CO₃ etc.) can be employed as a homogenous catalyst. This process targets sewage sludge and wet biomass as the raw material.

Electrolysis is defined as a chemical decomposition technique using direct electric current. Based on the electrolyte used and corresponding ions transport, the electrolysis type is distinguished into Alkaline, Proton Exchange Membrane electrolysis (PEM), and Solid Oxide Electrolyzer Cell (SOEC); details are outlined in Table 9. SOEC has the best efficiency compared with other methods but requires a high reaction temperature of 500–850°C. There are studies to utilize waste heat from nuclear reactors to supply heat for SOEC operation. INL studies reference hydrogen production process using light water reactor and high temperature steam electrolysis and performed techno-economic assessment. (Wendt et al. 2022)

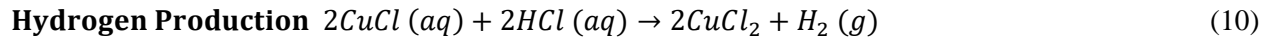
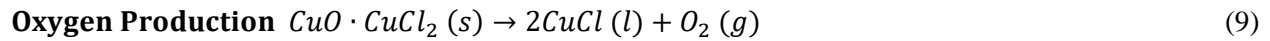
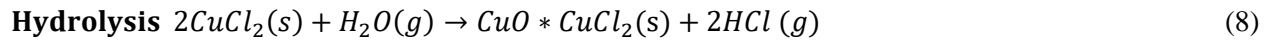


Table 9 Electrolysis type: electrolyte, ion transport and reactions.

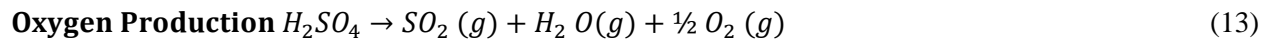
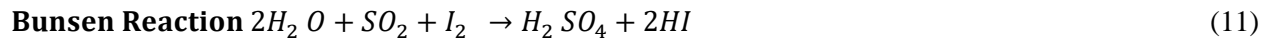
Electrolysis process	Electrolyte	Ions transport	Anode reaction	Cathode reaction
Alkaline	NaOH, or KOH solution	Hydroxyl OH ⁻	$4OH^-(aq) \rightarrow O_{2(g)} + 2H_2O(l)$	$2H_2O(l) + 2e^- \rightarrow H_{2(g)} + 2OH^-(aq)$
PEM	Polymer	Protons H ⁺	$2H_2O(l) \rightarrow 4H^+(aq) + 4e^- + O_{2(g)}$	$4H^+ + 4e^- \rightarrow 2H_{2(g)}$
SOEC	Solid Oxide or Ceramic	oxygen ion O ²⁻	$O^{2-} \rightarrow \frac{1}{2} O_{2(g)} + 2e^-$	$H_2O(l) + 2e^- \rightarrow H_{2(g)} + O^{2-}$

Instead of using electric grid, Photoelectrochemical (PEC) and Photovoltaic (PV) electrolysis directly harness solar energy to proceed electrolysis. The difference is that the PEC device contains an electrolyte phase, whereas PV is purely a solid-state device.

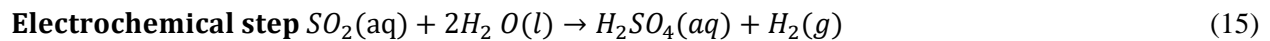
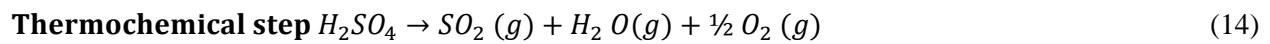
There are many methods to produce hydrogen by thermochemical water splitting. The Cu-Cl cycle is a four-step thermochemical cycle for hydrogen production that avoids direct water electrolysis. The benefit of this process is that the maximum temperature required is about 530°C (Dincer 2012). The series of reactions for this process is seen as below.



The sulfur-iodine cycle is one the best-known thermochemical cycles to produce hydrogen, also referred to as ISPRA Mark 16 cycle or general atomic cycle. The series of reactions for this process is seen as below. Reaction temperature for each reaction are 120, 830, and 840°C, respectively.



The hybrid sulfur cycle (HyS) is a two-step water splitting process intended to be used for hydrogen production based on sulfur oxidation and reduction. It is classified as a hybrid thermochemical cycle because it uses an electrochemical reaction for one of the two steps. The remaining thermochemical step is shared with the sulfur-iodine cycle. Electrochemical step performs at temperature range of 80-120 °C while thermochemical step does at temperature above 800 °C.



Methane pyrolysis is one alternative method to produce hydrogen. Instead of adding another reactant to decompose feedstock into hydrogen, feedstock is directly decomposed into hydrogen gas and carbonaceous particles through pyrolysis. This process does not produce carbon dioxide. The enthalpy of reaction of methane pyrolysis is smaller than that of either SMR or water electrolysis. Nickel-based (500–700°C), iron-based (700–900°C), and carbon-based catalysts (800–1,000°C) are candidates for methane pyrolysis. A non-catalytic process requires high temperatures of 1,000–1,200°C. It is possible to produce other hydrocarbon materials like methylene, ethylene, propylene or benzene as coproducts (Sánchez-Bastardo, Schlögl, and Ruland 2020). Two commercial-scale facilities have been constructed or are planned by Monolith. Their first commercial-scale facility built in Nebraska produces 5 kilotonnes of hydrogen and 15 kilotonnes of carbon black annually. The other facility is planned to produce 60 kilotonnes of hydrogen annually which will be used for ammonia synthesis (275 kilotonnes of ammonia annually) (Hanson 2021; IDTechEx 2023).



Table 10. Hydrogen production cost associated with different sources and processes.

Energy source	Process	Cost [\$/kg H ₂]	Reference
Natural Gas	SMR	1.06	(Lewis 2022)
Natural Gas	SMR	1.08	NR(Penev 2022d; National Renewable Energy Laboratory 2018)
Natural Gas	SMR	2.08	(United States Department of Energy 2020)
Natural Gas	SMR + CCS	1.64	(Lewis 2022)
Natural Gas	SMR + CCS	2.27	(United States Department of Energy 2020)
Natural Gas	SMR + CCS	1.86	(Penev 2022a)
Natural Gas	ATR + CCS	1.59	(Lewis 2022)
Natural Gas	ATR + CCS	1.48	(United States Department of Energy 2020)
Natural Gas	ATR + CCS	1.74	(Penev 2022c)
Natural Gas	Pyrolysis	2	(Pacific Northwest National Laboratory 2021)
Coal	Gasification	2.92	(Penev 2022b)
Coal	Gasification	1.34	(United States Department of Energy 2020)
Coal	Gasification (Shell)	2.58	(Lewis 2022)
Coal	Gasification + CCS	1.63	(United States Department of Energy 2020)
Coal	Gasification (Shell) + CCS	3.09	(Lewis 2022)
Coal + Biomass	Gasification (Shell) + CCS	3.64	(Lewis 2022)
Grid	Electrolysis, PME	5.5	(Shaner et al. 2016)
Grid	Electrolysis, PME	4.83	(DeSantis 2019a)
Grid	Electrolysis, SOEC	4.66	(DeSantis 2019b)
Nuclear	Electrolysis, SOEC	1.86	(Wendt and Knighton 2022)
Nuclear	Electrolysis	5.58	(United States Department of Energy 2020)
Nuclear	Electrolysis	2.41	(Dincer 2012)
Nuclear	Cu–Cl cycle	2–3.49	(Naterer et al. 2008)
Nuclear	S–I cycle	4–5.5	(Khamis 2011)

Energy source	Process	Cost [\$/kg H ₂]	Reference
Nuclear	Thermolysis	2.4	(United States Department of Energy 2020)
Solar	Electrolysis, PEC (Type 2)	3.88	(James 2018b)
Solar	Electrolysis, PEC (Type 3)	11.4	(Shaner et al. 2016)
Solar	Electrolysis, PEC (Type 4)	9.2	(Shaner et al. 2016)
Solar	Electrolysis, PEC (Type 4)	4.27	(James 2018a)
Solar	Electrolysis, PEC	10.14	(de Jong 2018)
Solar	Electrolysis, PV	7.75	Jong 2018
Solar	Electrolysis, PV	6.1-12.1	Shaner et al. 2016
Solar	Thermochemical, NiFe ₂ O ₄	2.49	NREL, H ₂ A, 2022
Solar	Cu-Cl cycle	6.33	Sayyaadi et al. 2017
Solar + NG	S-I cycle	7.53	Giaconia et al. 2007
Biomass	Gasification	1.91	DOE, 2020
Biomass	Gasification	2.41	NREL, H ₂ A, 2020

4.4.2.2 Nitrogen Preparation

There are three technically mature commercial processes (with Technology Readiness Level of 8–9) to produce purified nitrogen from air: air cryogenic distillation, pressure swing adsorption (PSA), and membrane permeation. (1) The cryogenic distillation method can separate the nitrogen from the air using the different boiling point of each of the gaseous components in the air, requiring extremely low temperatures. This process is adequate for large-scale capacity facilities (250–25,000 Nm³h⁻¹). Direct current (DC) electrical energy required is 0.396 GJ per tonne of N₂ produced. (2) The PSA method is a process that employs selective adsorbent materials. Zeolite, a selectively adsorbent material, attracts and adsorbs nitrogen more strongly than oxygen, allowing for only nitrogen to be captured within the separation vessel. The vessel is pressurized to enhance adsorption performance and adsorbed nitrogen is eventually released by decreasing the pressure. This process fits well for a small-scale capacity facility (25–800 Nm³h⁻¹). Nitrogen purity up to 99.8 weight percent (wt%) can be obtained and DC energy required is 0.792–1.116 GJ/tonne N₂. (3) The membrane permeation method employs selective permeability of a membrane to nitrogen. Nitrogen cannot permeate a membrane while other components of air such as oxygen, carbon dioxide and vapor can permeate the membrane. Thus, only nitrogen remains in the vessel and is purified. The drawback of this process is that the N₂ product is of relatively low purity at 95 wt%. The capacity of facilities using the membrane permeation method ranged from 3 to 3,000 Nm³h⁻¹. The DC energy consumed is 0.792–2.268 GJ per tonne of N₂ produced. Besides these matured major processes, there has been recent development looking at nitrogen preparation such that nitrogen gas can be obtained by depleting oxygen from the air by burning hydrogen and condensing water produced from the combustion, which can be a potential option for mini-ammonia plant.

4.4.3 Ammonia Synthesis: Haber-Bosch Process

The conventional Haber-Bosch process, the current dominant ammonia manufacturing method in the U.S., uses natural gas to produce hydrogen for ammonia synthesis. As natural gas passes desulfurization, steam methane reforming, WGS reaction, CO₂ capture, and methanation process, the feed material—a hydrogen and nitrogen gas mixture—is prepared for ammonia synthesis. Then, feed material is pressurized and introduced to the reactor, forming ammonia. After the separation process, pure ammonia is obtained. Today, major companies that have proprietary commercial processes for ammonia synthesis include thyssenkrupp (Uhde), KBR (Kellogg Brown & Root) and Haldor Topsøe. Figure 51 shows block diagram of the conventional ammonia production process using the Haber-Bosch process by Uhde and each unit's operating temperature (Asiri, Inamuddin, and Boddula 2020, Rouwenhorst et al. 2019). Figure 52 illustrates the industrial commercial-scale plant design suggested by KBR (top) and Haldor Topsøe (bottom). Note that the Haber-Bosch process can refer to two different range of processes: either only the reactor unit is needed to synthesize ammonia under high-pressure conditions with an iron catalyst in narrow scope or the entire process to manufacture ammonia including hydrogen generation in wide scope. This section will cover the entire conventional Haber-Bosch process categorized into two parts: (1) hydrogen production method (ranging from desulfurization to methanation) and (2) the ammonia synthesis including pressurization, ammonia synthesis, and ammonia separation and storage.

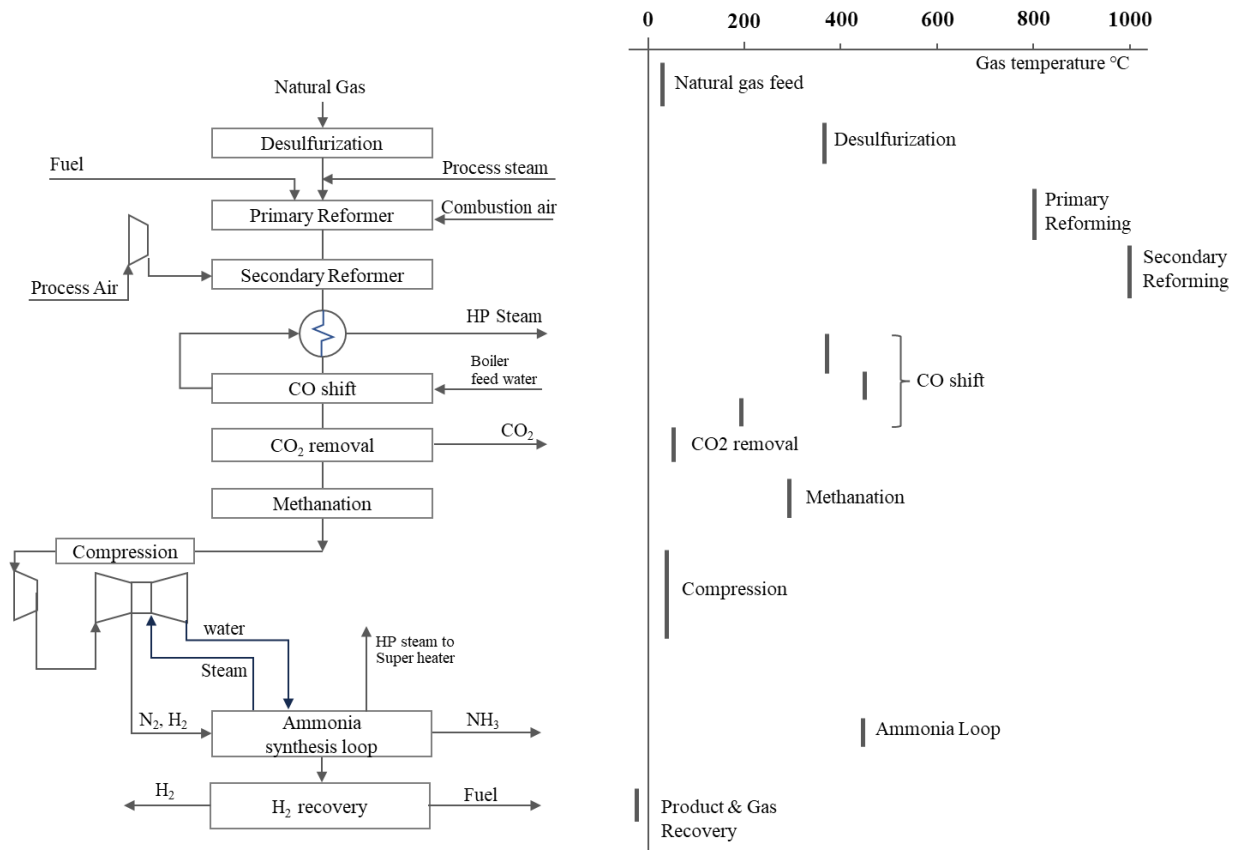
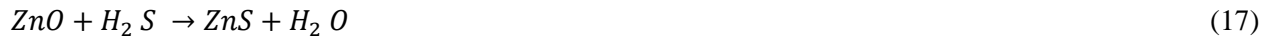


Figure 51. Conventional ammonia production process by thyssenkrupp (Uhde) and operating conditions (Asiri, Inamuddin, and Boddula 2020).

4.4.3.1 Hydrogen and Nitrogen Preparation

This section will explain the conventional preparation of hydrogen and nitrogen used for ammonia synthesis sourced from natural gas. The desulfurization process, the first step to produce hydrogen from the natural gas, removes inherent sulfur in the natural gas that might harm the catalyst of downstream processes. Zinc oxide reacts and with hydrogen sulfide to capture sulfur contained in the preheated natural gas (reaction at 350–400°C).



Commercial processes are usually configured in two-stage methane reforming. The primary reformer employs SMR, and most methane is converted into hydrogen and carbon monoxide. Since SMR is an endothermic reaction, some natural gas is burned to supply the energy. The secondary reformer performs partial oxidation reactions. The main purpose of this step is to introduce nitrogen without using an air separation unit. As air is introduced, oxygen reacts with methane and burns off, leaving only nitrogen that can be used for ammonia synthesis. Methane conversion to hydrogen comes incidentally. The secondary reformer is usually designed to operate as an adiabatic reactor. Typical operating conditions in the primary reformer are 750–820°C while the secondary reformer temperatures are raised to 950–1,025°C. Nickel catalysts are widely employed in this process, resulting in methane of 8–12 volume percent (vol.%) and 0.3–1.0 vol.% remaining after the primary and secondary reformer. The operating pressure is typically 25–30 bar. Note that although a low operating pressure is preferred, if only the thermodynamic yields are considered, a high-pressure ammonia unit is more practical when considering all used materials (Nielsen 1995).

A WGS is performed to increase the hydrogen yields and remove CO. Carbon dioxide is produced as a byproduct. The industrial practice uses two-stage treatment. The first stage operates at 350°C with a Fe-Cr oxide catalyst while the second-stage operates at 200–250°C with a Cu-based catalyst. High-temperature WGS can take advantage of rapid kinetics with a cheap catalyst while low-temperature WGS have a thermodynamic improvement on CO conversion. CO of 12–15% (dry gas base) from the secondary reformer is reduced to 0.2–0.4 % at the end of the process (European Commission 2007).

After the WGS reaction, the synthetic gas (syngas) might contain up to 20 vol.% CO₂. Carbon dioxide capture is required before the ammonia synthesis not only because it is considered to be a greenhouse gas, but also because it can react with ammonia to form carbamates which can clog pipelines. Organic sulfur material is also removed in this step. Options include chemical absorption using alkanolamine or potassium carbonate while physical absorption may occur using the Sulfinol (sulfolane + diisopropanol), Rectisol, (methanol), or Selexol (polyethylene glycol) process. Captured CO₂ can be used to synthesize other chemical materials including urea (as a product of ammonia and CO₂). The Rectisol process can treat CO₂ less than 10 ppm (European Commission 2007) .

Methanization is the process of removing trace amounts of CO and CO₂ entirely after the CO₂ capture before ammonia synthesis because even small amounts of CO and CO₂ can poison the catalyst for ammonia synthesis and reduce its performance. It is reported that 3 days of exposure to 500 ppm CO gas can reduce ammonia conversion from 26.4–8.2 % (Nielsen 1968). Methane is not involved in ammonia synthesis, but produced water supposed to be removed before the ammonia synthesis. CO₂ after the methanization can be less than 10ppmv (European Commission 2007). A Ru-based and Rh-based catalyst is preferred for the methanization process at operating conditions of 300–400°C.



4.4.3.2 Ammonia synthesis, narrow scope of Haber-Bosch process

The Haber-Bosch process employs a very simple exothermic reaction where nitrogen gas reacts with hydrogen gas to form ammonia in the net reaction.



However, it was an impractical reaction due to extremely low yield of ammonia under atmospheric pressure as seen in Figure 53. The key to Haber's idea was to run it at very high-pressure operating conditions to obtain thermodynamic preference and enhance yields of ammonia. The best operating conditions for the Haber-Bosch process are found to be 350–525°C and 100–300 bar, which is why this process becomes energy intensive.

The composition of species at chemical equilibrium can be theoretically calculated, showing possible maximum yields obtained without reflux under specific conditions. Figure 53 presents the mole fraction of NH₃ at chemical equilibrium, calculated by Aspen Plus V11 with the Gibbs reactor model and RKS-BM EOS model, where the inlet mole ratio of hydrogen to nitrogen is 3:1. The correlation for the chemical equilibrium constant of the ammonia formation reaction mentioned above is reported by Gillespie and Beattie as a function of temperature in Kelvin (Gillespie and Beattie 1930).

$$\text{Log}_{10} K_{eq} = -2.691122 \log_{10} T - 5.519265 \times 10^{-5} T + 1.848863 \times 10^{-7} T^2 + \frac{2001.6}{T} + 2.6899 \quad (21)$$

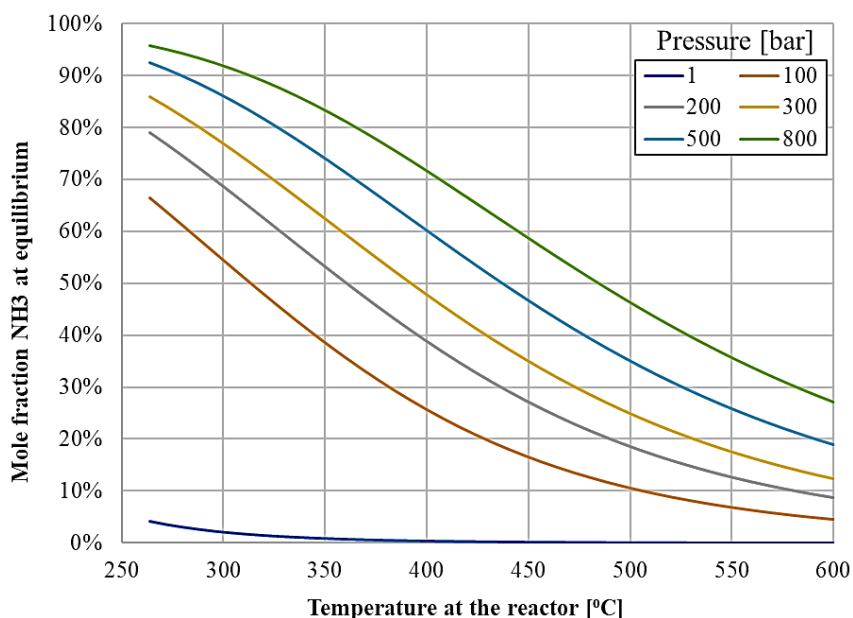
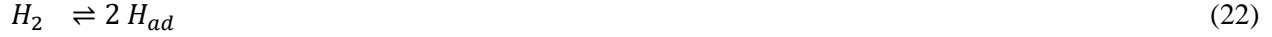


Figure 53. Mole fraction of NH₃ at equilibrium where inlet mole ratio of N₂:H₂ = 1:3 calculated from Aspen plus model

The mechanism of the catalytic reaction in the Haber-Bosch process is quite complicated. One of the achievements of Ertl, the winner of Nobel Prize in 2007, was to scrutinize and validate the mechanism of ammonia synthesis on an iron catalyst (Wennerström 2007). The reaction mechanism is written as Eq 22–28. In accordance with the Langmuir-Hinshelwood scheme, both hydrogen and nitrogen molecules are adsorbed on the iron surface. Dissociative adsorption of hydrogen molecules occurs on the iron surface and molecular adsorption of nitrogen molecules also occurs on the iron surface. Then, adsorbed nitrogen molecules are dissociated into nitrogen atom. Adsorbed nitrogen and adsorbed hydrogen react, forming adsorbed NH. Similarly, adsorbed NH₂ and NH₃ are formed from NH and NH₂, reacting with an adsorbed H atom. In the end, formed NH₃ is desorbed from the surface, becoming a NH₃ molecule. Cleaving of the nitrogen molecules is the rate-limiting step in the process, determining the form of reaction rate.



The kinetic reaction rate model for ammonia synthesis on an iron catalyst is suggested by Nielsen (Nielsen 1964; Palys et al. 2018). Activity is employed instead of partial pressure to make up for non-ideality due to high pressure. Reaction rate is expressed as:

$$R = A_c \left[\frac{k_a \left(K_{eq}^2 a_{N_2} - \frac{a_{NH_3}^2}{a_{H_2}^3} \right)}{\left(1 + K_a \frac{a_{NH_3}}{(a_{H_2})^\omega} \right)^{2\alpha}} \right] \left[\frac{(kg) mol NH_3}{m^3 cat \cdot hr} \right] \quad (29)$$

where a_{N_2} , a_{H_2} , and a_{NH_3} are the activity of nitrogen, hydrogen and ammonia gas, respectively, ω is specified as 1.5, implying that the nitrogen atom is dominant on the surface, α is the coefficient to show uniformity of the surface of the catalyst of which uniform surface is unity while and totally non-uniform is zero, and determined as 0.64, A_c is the catalyst activity, k_a is the overall reaction coefficient, K_{eq} is the equilibrium constant of chemical reaction for ammonia synthesis, and K_a is the equilibrium constant of adsorption for ammonia on the catalyst's surface. k_a and K_a are expressed as Arrhenius form in Kelvin as below.

$$k_a = 3.945 \times 10^{10} \exp\left(-\frac{5622}{T}\right) \quad (30)$$

$$K_a = 2.94 \times 10^{-4} \exp\left(\frac{12104}{T}\right) \quad (31)$$

Bosch and his team in BASF investigated and found that an iron catalyst is the best candidate for ammonia synthesis process. Type of crystal planes affect for nitrogen forms iron-nitrogen structure. It is known that Fe(111) and Fe(211) surfaces have by far the highest activity. The nitrogen fixed on the iron structure reacts with adsorbed atomic hydrogen, forming ammonia molecule in the end. The existence of potassium on the iron catalyst affects this step, enhancing the rate (Qian et al. 2018; Fuller et al. 2020). The most mature technology for the final separation of ammonia from the reaction mixture is condensation. As temperature decreases to -20 to 30°C based on pressure, only ammonia is condensed and separated as liquid. Ammonia separation via absorption with metal halide and adsorption with zeolite are other candidate processes. To keep the process running continuously, two absorbers swing the absorption and desorption of ammonia alternatively, referred to as pressure swing absorption process. This process allows use of lower pressure conditions for ammonia synthesis. Figure 54 represents the schematic flow stream of condensation and adsorption used for ammonia separation. The remaining reactant after the separation is refluxed and reused for ammonia synthesis. Thus, the more ammonia that is separated; the better the ammonia yields that can be obtained. Separated ammonia is usually cooled down and stored in liquid phase.

ICI and Uhde (now Thyssenkrupp Industrial Solutions) formed a new design of dual pressure ammonia synthesis, as seen in Figure 55. A once-through ammonia reactor passes in feed gas at 110 bar of pressure which is then introduced to another reactor operated under pressure of 210 bar with reflux. This process enables 3,300 tonne/day of ammonia production (Brightling 2018).

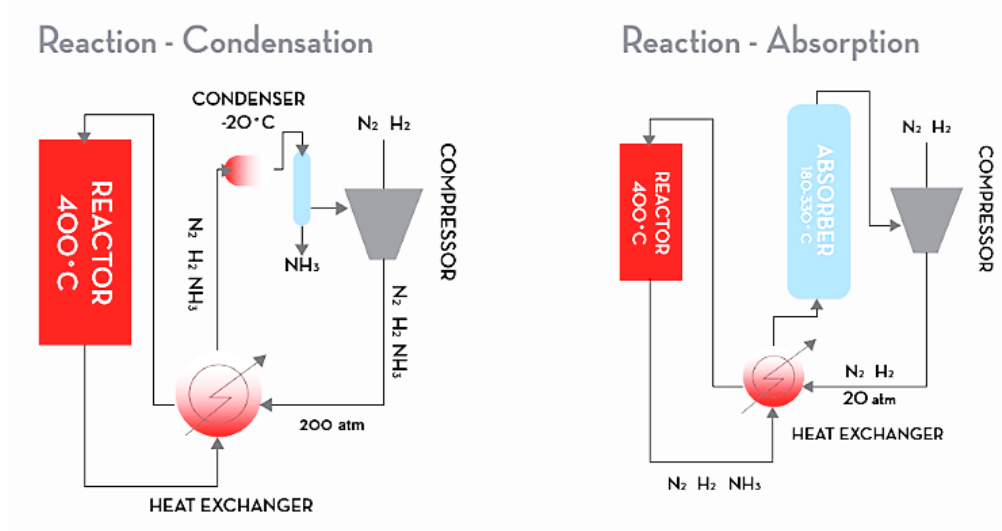


Figure 54. Ammonia separation (left) condensation, (right) adsorption.

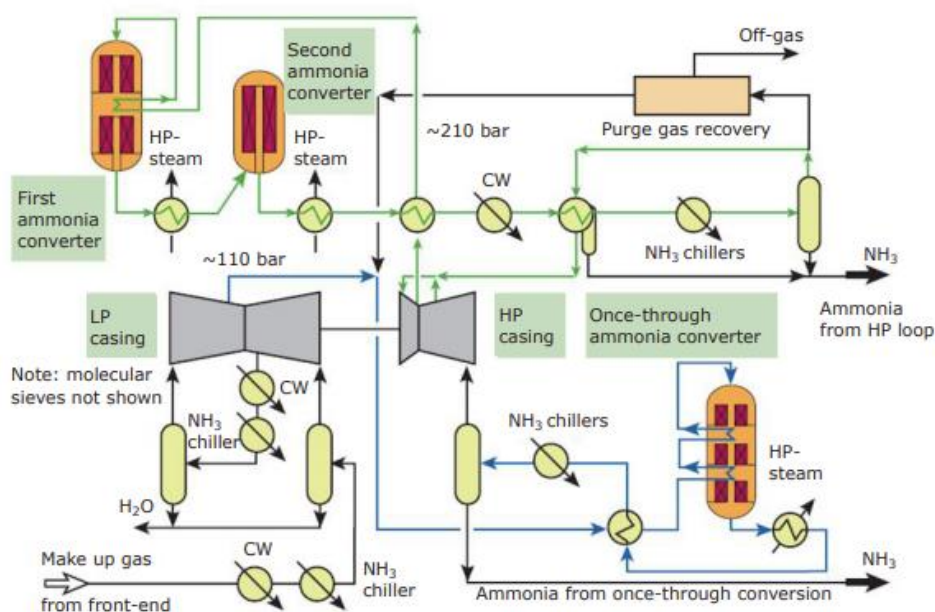


Figure 55. Schematic of the Ude process dual pressure ammonia synthesis (Brightling 2018).

4.4.4 Energy Consumption Analysis of the Process

This chapter will discuss the energy requirements for each process that synthesizes ammonia. There are some studies that investigate the energy requirement for each unit of the Haber-Bosch process. Dybkjaer (Dybkjaer 1995) performed energy analysis on the conventional methane-fed Haber-Bosch process with the following features: steam to carbon ratio of 2.5 at the reformer with combustion air preheat, two-stage with copper-based catalyst at the shift conversion, Selexol process at CO₂ capture, methanization at final purification, synthesis at 140 kg/cm²-g using a two-bed radial flow converter with indirect cooling, and centrifugal compressors driven by a steam turbine. The energy analysis result is summarized in Table 11. Heat losses are calculated by net summation of ingoing/outgoing stream and work within a unit, which energy rejection to either ambient surroundings or cooling water. Natural gas burning producing 29.33 GJ is required to produce a tonne of ammonia with 10.92 GJ of heat loss.

Similarly, Barton and Hunns (Barton 2001) investigates the energy flow in an ammonia plant that produces achieving 66% efficiency. The energy consumed by turbine compression has the largest energy loss, accounting for approximately 46% of total energy consumption of the best available technique Haber-Bosch process. Energy flow of ammonia synthesis and steam generation units are illustrated in Figure 56 (Soloveichik 2016, 2017). 1,350 tonne/day with fired primary reformer is investigated and tabulated in Table 12. Energy loss accounts for 28.1% of total energy flow of ammonia synthesis and compressors account for 53.1% of total loss. Smith et al. (Smith, Hill, and Torrente-Murciano 2020) scrutinize the energy consumption of different Haber-Bosch processes. The energy requirement for methane-fed Haber-Bosch processes and each of their units are tabulated in Table 13. As the process matures, the best available technique requires 28 GJ energy to produce a tonne of NH₃. The energy requirements mentioned here do not consider the emission of CO₂. It is estimated that the current methane-fed Haber Bosch process emits greenhouse gas of 1.5–1.6 tonne CO₂-eq to produce a tonne of NH₃ (Bicer et al. 2016). Though CO₂ capture is already included in the process, extra energy for CO₂ sequestration must be considered.

There is an example reference model for ammonia synthesis in Aspen Plus V11 (Aspen Technology, Inc. n.d.) for Haber-Bosch process as described in section 4.3.3. Figure 57 presents schematic material input, output and energy requirements for the ammonia synthesis process calculated from example model in Aspen Plus V11. A configuration wherein SMR and ATR are in series is selected for hydrogen production. Based on the developed model, the calculated energy requirement is 11.53 GJ/tonne ammonia. Note that this value does not include the energy contained in raw material. The amount of CO₂ produced from ammonia synthesis is approximately 1.85 kg CO₂ / kg NH₃. This process includes CO₂ capture using aqueous ammonia within the process but does not take into account the energy requirement for CO₂ capture in detail. CO₂ capture from the flue gas from the furnace is ignored, too. Total energy requirement can increase if the energy requirement for CO₂ capture is considered at the process and furnace.

Table 11. Energy consumed in Haber-Bosch process (Dybckjaer 1995).

Metric	HHV	LHV	Exergy
<i>Natural gas consumption (total)</i>	32.47	29.33	30.67
Reformer Feed	24.64	22.26	23.26
Fuel	7.49	6.78	7.07
Fuel, Aux. Boiler	0.33	0.29	0.33
<i>Energy in NH₃ production (total)</i>	20.96	17.11	20.13
<i>Heat losses (total)</i>	11.55	10.92	10.54
Reforming	0.38	0.38	4.94
Steam generation	0.33	0.33	2.38
Shift, CO ₂ removal, and methanation	1.30	1.30	0.67
Synthesis	1.72	1.72	1.55
Turbines + Compressor	6.53	6.53	0.54
Misc. Losses	0.33	0.33	0.21
Stack	0.96	0.33	0.25

Values in Table 11 reported in GJ/t NH₃.

Table 12. Energy flows in an ammonia production plant (Barton 2001)

Energy Flow	Share [%]	Share in loss [%]
Product ammonia	71.9	-
Unrecovered process heat	10.5	36.5
Air compressor turbine	7.8	27.1
Syngas compressor turbine	5.7	19.8
Flue-gas heat	2.4	8.3
Refrigeration compressor turbine	1.8	6.3
Miscellaneous	0.6	2.1
Overall	100	100

Table 13. Energy requirement in methane-fed Haber-Bosch process (Smith, Hill, and Torrente-Murciano 2020)

Process Type	Energy input	Energy loss	Efficiency[%]	H2/N2 production			NH3 production		Heat loss/Other
				SMR	WGS	Steam turbine compressor	Purge other	Steam turbine compressor	
1970s design	36.4	17.7	51.2	1.37	5.69	1.81	1.81	2.88	4.15
1980s design, ICI pre-AMV concept	35	15.3	56.3	8.4	1.4	2.1	1.4	1.3	0.7
1995 Low Energy Process	29.3	10.9	63.5	1	1.3	2.2	1.72	4.4	0.33
2010s EC BAT definition example	28.0	9.4	66.4	0.7	-	2.2	-	2.1	4.4

Values in Table 13 reported in GJ/t NH₃.

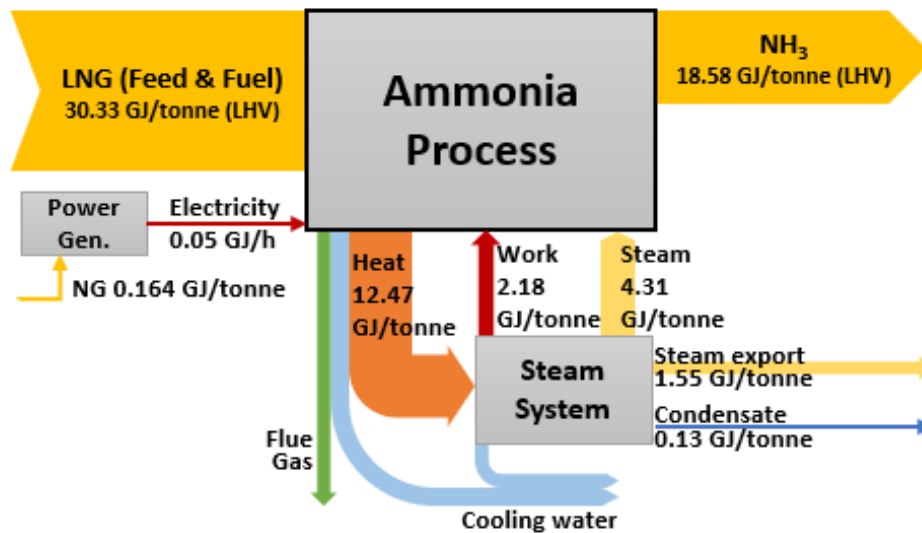


Figure 56. Energy flow diagram for methane-fed ammonia synthesis [reprinted from (Soloveichik 2016, 2017)].

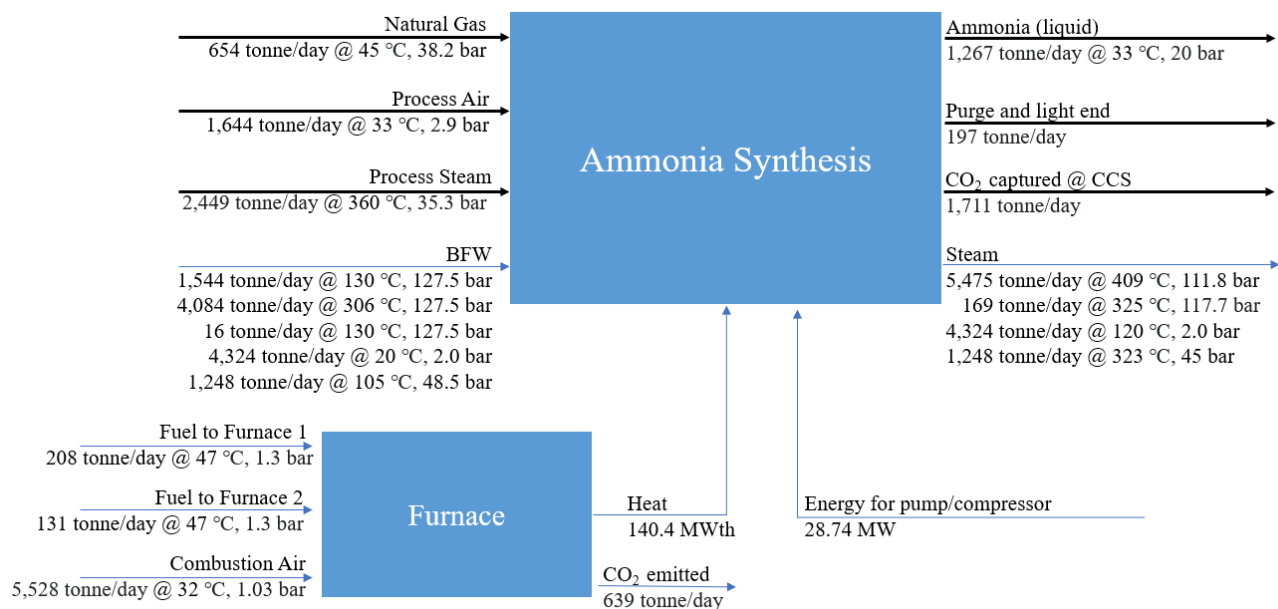


Figure 57. schematic material input and output and energy requirements for Haber-Bosch process

Energy requirements for alternative methods of ammonia synthesis that change the hydrogen source are tabulated in Table 14. Energy requirements for processes with SMR, partial oxidation (POx), gasification, pyrolysis, and electrolysis with different feedstocks are listed. If the process includes carbon sequestration, carbon capture and sequestration (CCS) is added on the process. As a reference, the low heating value of NH_3 , and ideal energy requirements for the ammonia synthesis process using methane-feed SMR and power-supplied electrolysis are listed.

Table 14. Energy requirements for ammonia synthesis in different feedstock and process [reprinted from (International Renewable Energy Agency and Ammonia Energy Association 2022; Smith, Hill, and Torrente-Murciano 2020)].

Feedstock	Process	Typical energy (GJ/t)	Potential (GJ/t)
Natural gas	SMR	28–29	26
Naphtha	SMR	35	–
Heavy fuel oil	POx	38	–
Coal	POx	42	36
Biomass	Gasification	42	37
Natural gas	SMR + CCS	33	29
Natural gas	Pyrolysis	49	46
Coal	Gasification + CCS	–	39
Water	Electrolysis (PEM)	36	33
Water	Electrolysis (SOEC)	30	26
<i>Reference</i>		<i>Energy</i>	
<i>NH₃ Low Heating Value</i>		<i>18.6</i>	
<i>Methane-fed process minimum</i>		<i>22.2 (17.7 feedstock + 4.5 Fuel)</i>	
<i>Electrolysis process minimum</i>		<i>21.3</i>	

Values in Table 14 reported in GJ/t NH₃

4.4.5 Downstream Product and Process

The flow diagram of major downstream nitrogen compounds synthesized from natural gas is shown in Figure 58. The number in each box shows the amount of production by the U.S. in 2020 in the unit of thousand metric tons of gross weight and of contained nitrogen weight (within parentheses), respectively.

Ammonia is usually stored in the form of pressurized liquid, which is referred to as anhydrous ammonia, as opposed to ammonia solution (International Energy Agency 2021). In the U.S., some ammonia is directly used as a fertilizer, but most of it is used for nitrogen compounds such as urea, urea ammonium nitrate solution, ammonium nitrate, ammonium sulfate, ammonium phosphate, and nitric acid (manufactured by the Ostwald process). Most nitrogen compounds originating from ammonia are used as fertilizer. 88% of the ammonia produced in the U.S. in 2020 is utilized as fertilizer.

Urea, which contains a high amount of nitrogen, 46% by weight, is widely used as fertilizer. Urea is made through combining ammonia and CO₂. It is usually manufactured at an ammonia plant because CO₂ produced as a byproduct in an ammonia plant can be directly used for the urea synthesis. Two chemical reactions are involved in the synthesis of urea. First, ammonia and carbon dioxide can react to form ammonium carbamate in the condition of 14 MPa and 170–190°C. In the second reactor, ammonium carbonate is dehydrated, forming urea. Impurities are removed by a distillation tower and an evaporator. Under high temperature and low pressure in the distillation tower, the ammonium carbamate is decomposed back to ammonia and carbon dioxide, and light gases are flown off. Urea solution from the distillation tower is concentrated in the evaporation step. Concentrated urea solution is sprayed out in the prilling tower, resulting in crystallized solid form of urea (Chemical Engineering World; 2020).



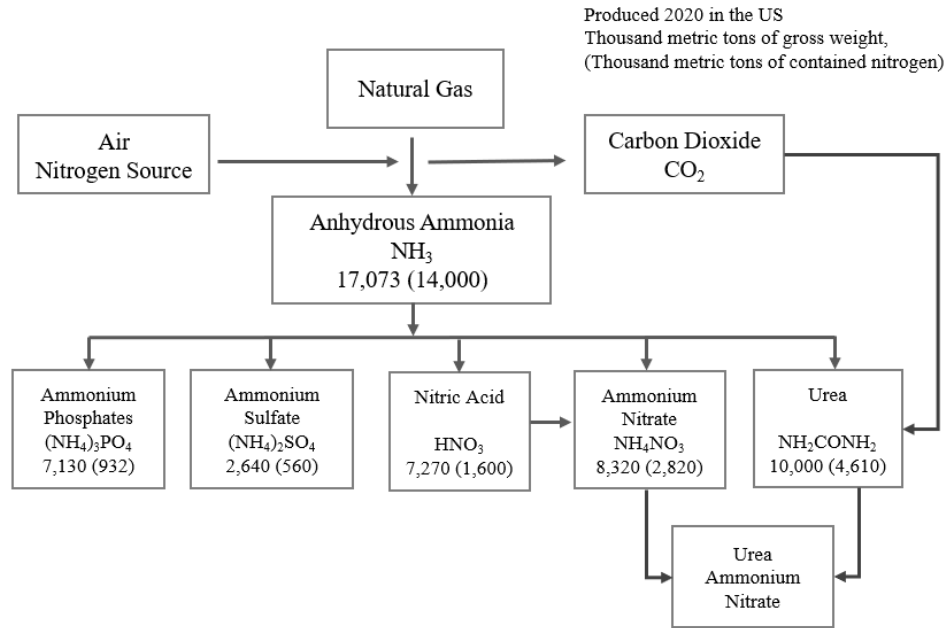


Figure 58. Major downstream nitrogen compounds from natural gas in the U.S. 2020 (United States Geological Survey 2021).

4.4.6 Opportunity for Nuclear Reactor Integration

Pupuk Kaltim, Indonesia’s largest company, has a project to build a nuclear-powered ammonia plant of 1 million tonne per year capacity by 2030 with a Danish industrial consortium—Topsøe (SOEC, ammonia synthesis), Copenhagen Atomics (modular reactor), and Alfa Laval (heat exchange and desalination). In the project, a 1GW SOEC facility to produce hydrogen will be powered by 25 units of modular thorium MSR that deliver 100MW. These MSRs will be the size of a 40-ft shipping container. Copenhagen Atomics is expected to reach an electricity price below \$20/MWh in a mass manufacturing scenario (Njovu 2023; Rouwenhorst 2022). Another consortium for nuclear-power ammonia synthesis includes Terrestrial Energy, the developer of a thorium-fueled Integral Molten Salt Reactor (ISMR) and KBR (Rouwenhorst 2022). There are some ideas to employ floating nuclear power plants. Denmark Seaborg, Korea Hydro & Nuclear Power Co. and Samsung Heavy Industries have signed an agreement to develop floating nuclear power plant using Seaborg’s compact molten salt reactor technology. Once a ship is moored, the power plant can be connected to onshore electrical grid and used for hydrogen and ammonia synthesis (Kim 2023). In addition, UK-based CORE POWER released a report about floating nuclear power to produce e-fuels offshore. They suggested four main steps to produce ammonia: Seawater desalination, PEM, nitrogen separation from air, and Haber-Bosch process. Figure 59 presents the flow-through of a 1 mtpa production of ammonia suggested by CORE POWER. For a nuclear reactor, energy source of all of process mentioned above, they have partnered with Terrapower in the development of a specifically marinized molten salt reactor (MSR) which uses high assay low enriched uranium fuel (Megginson 2022). In contrast to CORE POWER findings, INL studies show that high-temperature electrolysis (THE) is a better electrolysis method. It is worth noting that HTE makes it possible to integrate the heat of the Harber Bosch reactor with 30% of higher efficiency. HTE is quickly rising to commercial readiness, progressing to TRL 7-8 by the time that advanced nuclear reactors are built within the next 10 years (Wendt et al. 2022).

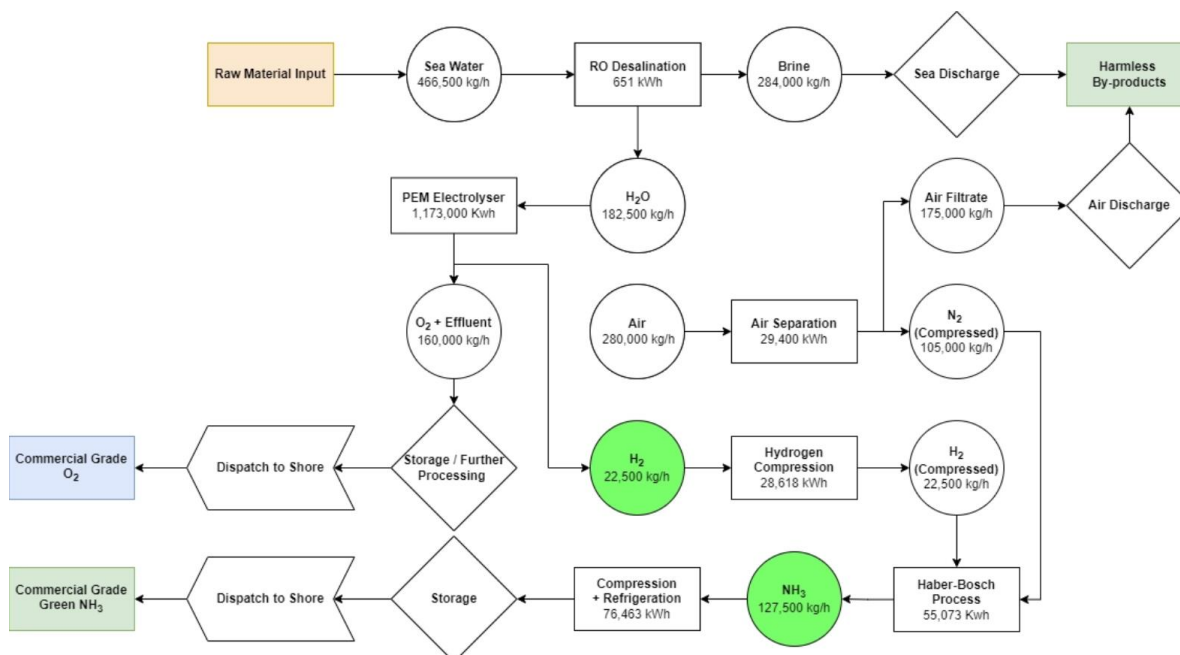


Figure 59. Flow-through of a 1 mtpa production of ammonia by CORE POWER.

4.5 Chlor-Alkali

Chlorine ranked among the top ten chemicals produced in the U.S. by weight, and 2021 production stood at approximately 11 million metric tonnes (Mansfield, Depro, and Perry 2000; Pellegrino 2000; United States Environmental Protection Agency 2022). Chlorine is one of most energy-intensive mass-produced chemicals (Brueske, Kramer, and Fisher 2015). Notably, process temperatures are low (74–105°C) and electricity use is high, potentially making chlorine production well-suited for pairing with lower temperature nuclear reactors.

4.5.1 Market

Chlorine is used directly for disinfection of water supplies, the paper industry, production of vinyl chloride, the disinfectant sodium hypochlorite, and other chemicals and pharmaceuticals. It is also used as a reactant in various industries (Mansfield, Depro, and Perry 2000, Pellegrino 2000). Electrolysis of brine is the dominant method of production, representing 99% of installed capacity (The Chlorine Institute 2022). During electrolysis, sodium hydroxide is co-produced at a rate of about 1.1 times by mass. Due to this, the markets for chlorine and sodium hydroxide both significantly impact plant economics (sodium hydroxide is also known as caustic soda or lye, and is alkaline). Consequently, plants are known as chlor-alkali plants. U.S. plants are heavily concentrated along the Gulf Coast, and include about 39 plants throughout the country that produce chlorine and sodium hydroxide as primary products by electrolysis (The Chlorine Institute 2022).

4.5.2 Production Process

Electrolytic production of chlorine requires significant electric power as well as heat. Chlorine is produced by the electrolysis of sodium chloride (table salt) dissolved in water (brine). The brine may be supplied directly, or solid sodium chloride may be dissolved to produce brine. Electrolysis produces chlorine anions and sodium cations along with hydroxide anions and hydrogen gas (H₂). Chlorine ions are attracted to the anode and form chlorine gas (Cl₂), while the sodium ions are attracted to the cathode and form sodium hydroxide with the hydroxide ions. Industrial facilities isolate chlorine ions from other collected species to prevent production of undesired compounds and to reduce the amount of hydrogen

mixed with the chlorine gas (Pellegrino 2000). Hydrogen is produced at a rate of 0.03 kg per kg of chlorine (McMillan et al. 2016).

The vast majority of electrolysis cells in the U.S. are of two types: diaphragm and membrane. Both types accomplish the necessary separation of the products of electrolysis. Diaphragm cells utilize a barrier constructed from a mixture of asbestos and polytetrafluoroethylene, through which sodium ions pass and which may be integrated with the cathode and produce a sodium hydroxide solution of 10–15% with significant salt content. Membrane cells, a newer technology, utilize an ion-exchange membrane constructed of fluorinated polymers through which sodium ions pass and produce a sodium hydroxide solution of 30–33%. Both types of cells have similar electric consumption per unit product, while the cell process temperature is 90–105°C in diaphragm cells and 74–91°C in membrane cells (Pellegrino 2000). Both cell types require additional thermal energy for post-cell evaporation of sodium hydroxide to reach the standard commercial concentration of 50%. However, because membrane cells produce more highly concentrated sodium hydroxide, it is expected that plants using membrane cells require less thermal energy for post-cell evaporation. Furthermore, membrane cells produce sodium hydroxide nearly free of salt, making the product ready for uses requiring salt-free sodium hydroxide without further purification. Diaphragm cells also contain asbestos fibers and must be disposed of as hazardous waste, which is a relative disadvantage (Pellegrino 2000). As of 2020, diaphragm cells were the most common in the U.S. (50% of installed capacity) while membrane cells (49%) were slated to become the most common within a few years per announced changes at chlorine plants. Mercury cells, a third type of electrolysis cell, are operated at a single site and represented only 0.5% of installed capacity (The Chlorine Institute 2022). The overall process is shown in Figure 60, showing the process flow for a plant using the diaphragm cell.

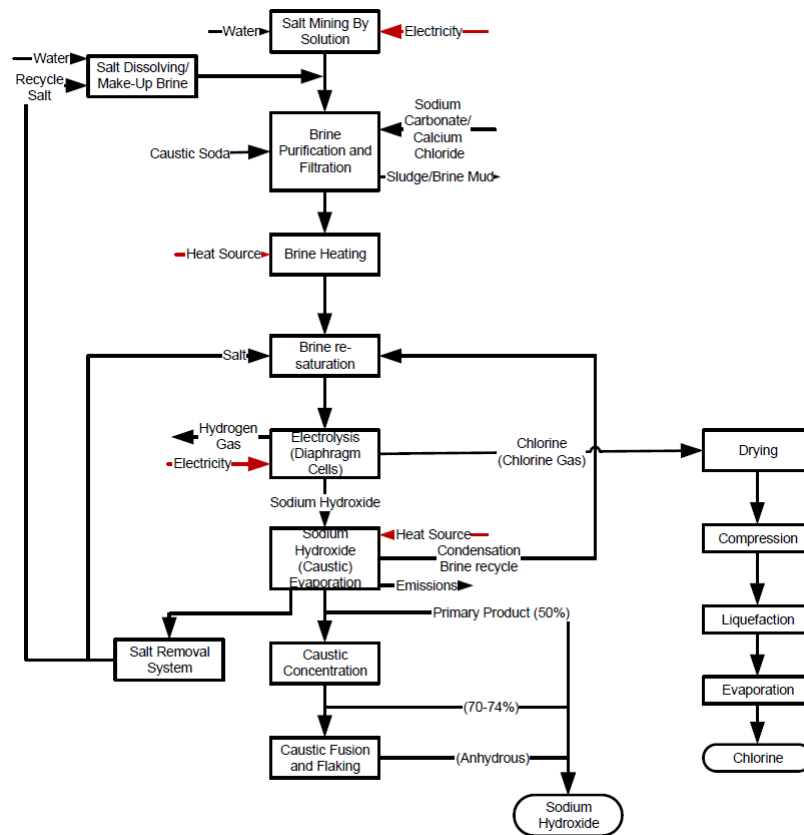


Figure 60. Process flow diagram for a chlor-alkali plant based on the diaphragm cell. From (McMillan et al. 2016), based on (Pellegrino 2000; Tilak V. Bommaraju 2002).

4.5.3 Energy Requirements and Opportunity for Nuclear Reactor Integration

In electrolytic chlor-alkali plants in general, heat is used to bring the brine to the process temperature of up to 105°C and to evaporate sodium hydroxide for its concentration. Additionally, heat may be used to evaporate the brine for purification. Chlorine plants do not export energy (Pellegrino 2000).

Using the totals for the U.S. chlor-alkali industry, Colin McMillan 2016 determined that an “average” diaphragm cell plant producing 828 metric tonnes of chlorine per day has a daily heat demand of 2.7 TJ. In existing plants, some portion of this heat is delivered by steam, typically at 177°C and 0.82 MPa (Colin McMillan 2016). If all heat is delivered via steam, an estimated 576 tonnes per day would be required². Dividing the daily heat demand by the daily production quantity, 3.26 MJ of thermal energy is required to produce 1 kg of chlorine. Due to the co-production of sodium hydroxide, it follows that plants utilizing diaphragm cells will require higher thermal energy than those using membrane cells as diaphragm cells produce a lower concentration of sodium hydroxide (Pellegrino 2000). Thus, an extra evaporation step to generate the standard commercial concentration must require more energy. Consequently, the energy requirement given earlier (2.7 TJ/day) is expected to be an overestimate for membrane cell plants.

The plant also demands an average of 141 MW of electric power (Colin McMillan 2016) continuously, which translates to 14.4 MJ (4 kWh) of electric energy required to produce 1 kg of chlorine. Electricity consumption values found in (Pellegrino 2000) are for the cell only, at about 2.8 kWh/kg of chlorine, and so do not reflect all the electric needs of the plant (for example, compression of chlorine gas is not included). Finally, external electrical demand at a given plant might be lower than the above values per kg, if previously announced efforts to utilize hydrogen (produced by the process) to generate electricity have been successful (Pellegrino 2000).

4.5.4 Decarbonization Potential

Due to use of fossil fuels for heat, the “average” diaphragm cell plant emits 2,014 metric tonnes of CO₂ per day, or 2.43 kg of CO₂ per kg of chlorine (McMillan et al. 2016). These figures do not appear to include emissions from electricity generation; thus, as average grid generation emits considerable carbon at present, and any existing on-site electricity generation is likely to be fossil-fuel-fired (although this may be offset by use of byproduct hydrogen), the decarbonization potential from supplying all heat and electricity from a co-located nuclear reactor is likely even greater than prior literature estimations.

5. CONCLUSIONS

This report provides an analysis of process-efficiency and thermal integration improvements for industrial processes at specific energy requirement levels by considering clean energy delivery and use by industry to reduce GHG emissions. It specifically considers the possibility of replacing fossil-fuel combustion in the selected industries with clean nuclear energy.

The US energy consumption in 2022 was 105 EJ (~99 quads with the industry consuming ~33 quads). The EIA projects the total U.S. energy consumption for the next 5 years will be about 104 EJ (98 quads) in 2027, with the industrial sector consuming about 36 EJ (~34 quads) or about 35% of the U.S. energy consumption. (reference EIA 2023 AEO) Annual energy consumption in the industrial sector is forecast to increase to about 40.8 EJ (38.5 quads) by 2050—a ~17% increase, exceeding 7% of total energy consumption in the United States.

The industrial sector was the third-largest source of direct U.S. GHG emissions in 2022, behind electricity generation and transportation, accounting for roughly 30% of total emissions (EIA 2023). In

² Assuming a delivery temperature of 105°C, slightly higher than the process temperature range of 90–105°C given by Pellegrino 2000. Calculated using specific enthalpies of 2783.54 kJ/kg for steam input to a heat exchanger and of 440.79 kJ/kg for steam at the output of the heat exchanger.

2022, the industrial sector GHG emissions were 1,393 million metric tonnes. These emissions are expected to decrease by ~7% to 1,282 million metric tonnes by 2050.

The NE-IES program at INL is establishing thermal integration requirements for industrial processes at specific energy requirement levels. Multiple simultaneous efforts have been put forward to develop the understanding necessary to engineer solutions to industrial decarbonization. The industrial sector could realize decarbonization benefits by integrating manufacturing with the nuclear reactors and installation of Small Modular Nuclear Reactors (SMNR) for the supply of clean electricity and heat.

Understanding the interest and concerns of industry to incorporate and integrate with industrial applications is critical for identifying the opportunities and degree of SMNR growth and R&D requirements. Through an industry sector survey, it was determined that 1. industry representatives are primarily interested in the integration methods needed to interface nuclear reactors with industry and 2. a major concern centers around the economics of that integration. These responses motivate the project to develop the specific requirements for integration schemes.

The process and thermodynamic performance, scale, electricity and heat-use patterns of facilities were evaluated for the refining, ammonia, chlor-alkali, methanol and paper and pulp industries. The common feature of these industries is they convert raw materials into products by means of physical and chemical changes that require large quantities of thermal energy and electrical power. Heat demands range from low-temperature steam (0.25 MPa) used for refining and pulp & paper processes up to high-temperature-unit operations (up to 950°C) used for methanol, refinery and ammonia operations.

The scale of heat demand for the average facility ranges from a heat input of ~75.9 TJ/day (73,000 MMBtu; or 905 MW) for production of 88,000 bpd gasoline, jet fuel and diesel fuel from refining to 26 TJ/day (25,000 MMBtu; or 300 MW) for roughly 5,000 tonnes per day of pulp and paper processing. Discussion of additional technical characteristics and considerations is provided in the main body of the report and the appendices.

Table 15 briefly summarizes the various requirements of ammonia, chlor-alkali, methanol, oil refining, and pulp and paper production. These industries produce over 305 million tonnes of CO₂ and are industries that currently project as significant contributors to the current and future economy. These systems have been broken down into specific processes to identify specific energy requirements throughout the plant. Through this analysis method, the IES program at INL is prepared for continued detailed study of these processes: identifying specific integration strategies, novel control methods for the complex systems, and technoeconomic assessments of these novel deployments.

Table 15. Summary of identified industry CO₂ emissions and process conditions.

Industrial Product	Annual CO₂ Emissions	Temperature Needs	Pressure Needs (if steam)
Ammonia	4.4 million tonnes	50°C–1,025°C	—
Chlorine & Sodium Hydroxide	28.7 million tonnes	177°C	0.82 MPa steam
Methanol	4.1 million tonnes	170–1,700°C ^b	3.6 and 10 MPa steam
Oil Refining	238.2 million tonnes	300–800°C	0.27, 1.2, 4.1 MPa steam
Pulp & Paper	34.3 million tonnes	125–325°C	0.45, 1.2, 2.6 MPa steam

^a 2023 estimate for the annual equivalent CO₂ emissions from oil/tar sands in North America.

^b Including some potential methanol conversion pathways.

The practical limit of clean heat sources depends on the temperature output of the source. Current high temperature gas-cooled SMRs can provide upwards of 850°C, and with materials development, 950°C may be attainable with demonstration of metal alloys performance at these temperatures. Substitution of one-third of the projected 2027 industrial energy demand could be met by about 230

SMRs with a capacity rating of 150 MWt forecast. This study indicates the scale of the largest industrial energy users is amenable to the scale of SMR applications.

An advanced reactor summary is also included in this report with a focus on presenting information that can drive interested industries toward appropriate reactor vendors. The A-NPP summary details prospective reactor types: A-LWRs, HTGRs, SFRs, and MSRs. This summary can be improved and updated as reactor developers approach final designs. Future work will include determining specifically how to interface these advanced reactors with industrial production of ammonia, chlor-alkali, methanol, oil refining, and pulp and paper. Further focused analysis is warranted to identify and quantify opportunities for the integration of SMNRs with industrial energy requirements to meet clean energy demands.

Several technical challenges and opportunities to integrate SMNR clean energy sources for industrial electricity and heat applications were identified and are discussed in this report, including:

- Quality of heat (or temperature of the working fluid) as defined by the user application
- Industry process heat-transfer modes
- Scale of heat and electricity source versus heat and electricity user demand, which may be mitigated by selecting the appropriate source or by industrial clustering (also referred to as an energy park)
- Transport requirements between the heat source and industrial process-unit operations, which involves distance and the materials needed for that transport
- Thermal energy storage needs and options
- Hybrid heat/electricity production.

The following list is an abbreviated summation of the report observations and finding:

1. Five key industries (ammonia, methanol, refining, chlor-alkali and pulp & paper) were selected for process-level energy (thermal and electricity) analysis. Based on the EIA GHG emissions inventory, they industries constitute nearly 22% of U.S. GHG inventory industrial-sector emissions, which equates to about 7% of U.S. total emissions in 2022. Most of the remaining 75% of industrial GHG emissions is therefore tied to smaller facilities that fall under the EPA reporting limits for large GHG emitters.
2. Within these industries, CHP and conventional steam boilers account for the majority of the heat loads. These heat supply systems and other fossil-fired heating systems could be substituted with clean heat sources from SMNRs for generating electricity, steam, and heating other heat-transfer media. Options for clean heat sources include emerging SMRs, as their scales are applicable to individual industry needs. Clean heating systems could replace the combustion gas systems by using heat circulation systems such as those described in this report.
3. Several industrial heat users, such as oil refineries, pulp/paper manufacturing, methanol, ammonia plants and chlor-alkali plants, have duties in excess of 10 TJ/day (9,500 MMBtu; 120 MWt). SMR technologies are expected to be well-matched to this scale of demand.
4. SMNR applications could potentially supply heat to the majority of the industrial applications analyzed here.
5. The design of heat transport from a SMNR source to the industrial user may be optimized with a heat circulation system that uses a liquid heat transfer media—such as a molten salt or Dowtherm™—to deliver thermal energy over relatively long distances. Heat transfer to a hot gas or steam loop may then optimally interface with the heating coils or boiler tubes that are used in most industrial processes.

6. Hybrid thermal/electricity generation of a SMNR may help balance hourly, daily, and/or seasonal electrical cycles.
7. Electrification of industry warrants further consideration. Thermal energy storage concepts such as those being developed for concentrating solar systems may help coordinate grid profiles with industry heat use profiles. Direct electrical heating is technically feasible but could add to grid-response dynamics and challenges.
8. Hydrogen production for use as a substitute fuel gas by industry could reduce industry GHG emissions. Hydrogen could also replace carbon that is used as a reducing agent in steel manufacturing. Hydrogen that is produced by water splitting from electrolysis would provide carbon-free hydrogen for these uses.
9. SMNRs were identified as an option for process heat and hydrogen production for feedstock use. The number of SMNRs theoretically required to meet the heat and hydrogen requirements of the industries analyzed will vary due to their wide range of demand. The potential number of SMNRs that could be built may be limited to siting restrictions and licensing restrictions which is a subject of an INL study.
10. Petroleum refineries use ~9,130 metric tonnes/day of hydrogen. This hydrogen is produced from fossil-based natural gas and supplied by merchant (offsite) steam methane reforming hydrogen plants. All of the refinery merchant hydrogen demand could be met by ~309 light-water SMR modules.
11. Substitution of hydrogen for coke in U.S. steel production would use an additional 6,690 metric tonnes/day of hydrogen. All of the merchant hydrogen for the steel industry could be met by 226 light-water SMR modules.

As the U.S. pursues its decarbonization goals, innovative integration methods will be needed to reduce the environmental impact of these significant industries. Replacing carbon-emitting energy sources of industry with integrated SMNR systems will enable direct thermal substitution within processes, electrification and making electricity generation “green,” or through novel chemical processes to produce an identical product. This report aids researchers in correctly determining how necessary energy streams might be replaced with clean energy sources of SMNRs within these industries.

Moving forward, this work will be extended through detailed nuclear integration studies. Primary modeling of industrial processes will use chemical modeling software tools including Aspen Plus or Aspen HYSYS by AspenTech. The IES program over the next year intends to evaluate the feasibility of integrating nuclear heat from various advanced reactors to industrial heat, power, and chemical feedstock requirements. These studies will likely identify research gaps that the program will use industrial interfacing to address and promote solutions for. As opportunities are identified, the specific decarbonization benefits and economic potential both through new energy sourcing and through tax credits from the Inflation Reduction Act will be evaluated.

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APPENDIX A

Question 1

Select the industrial process(es) that are of interest to your company.

- | | |
|---|--|
| <input type="checkbox"/> Hydrogen Production | <input type="checkbox"/> Ammonia |
| <input type="checkbox"/> Concrete Production | <input type="checkbox"/> Minerals |
| <input type="checkbox"/> Synthetic Fuels Production | <input type="checkbox"/> Desalination |
| <input type="checkbox"/> BioFuel Production | <input type="checkbox"/> Oil Refining |
| <input type="checkbox"/> Carbon Sequestration | <input type="checkbox"/> Mining |
| <input type="checkbox"/> Glass Production | <input type="checkbox"/> Drilling |
| <input type="checkbox"/> Paper Production | <input type="checkbox"/> Petrochemicals |
| <input type="checkbox"/> Steel | <input type="checkbox"/> Chemicals |
| <input type="checkbox"/> Polymers | <input type="checkbox"/> Oil production. |

Question 2

Describe current carbon-reduction goals and strategies proposed by your company, if applicable.

Question 3

Is integration of integrated energy systems with an advanced nuclear reactor of interest to your industrial process?

- Yes No Possibly

Question 4

Within what timeframe do you envision integrating your system with IES thermal energy storage (assuming the commercial system was immediately available)?

- Immediately 1–5 Years 6–10 Years >10 Years I don't know N/A

Question 5

Rank your company's primary research needs that would help accelerate the implementation of IES at your company. Drag and drop the options below in order of priority.

Drag and drop the options below in order of priority. 1 = Highest priority / 5 = Lowest priority			
Priority No.	Priority No.		
_____	Economic Viability	_____	Black Start Capability
_____	System Safety	_____	Decarbonization
_____	Integration Points	_____	Product diversification
_____	System Control (i.e., transients control)	_____	Capital investment

Question 6

Please provide the following.

	1 = Highest priority 3 = Lowest priority		
	1	2	3
Temperatures, pressures, mass flow rates, and process information, if applicable			
Steam pressures and temperatures	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Temperatures and pressures for processes which consume conventional heating fuel (e.g., natural gas)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Processes in your facilities that use external heat and/or electricity	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Question 7

What are the external steam, heat, and electricity loads (i.e., kWe or kWth loads) required by your plants (either typically, or any specifically those that would be best fits for IES)?

	Typical (kWe) Load	Typical (kWth) Load	IES Interest (kWe) Load	IES Interest (kWth) Load
External steam				
Heat				
Electricity				

Question 8

What is the priority for the following forms of energy output from an IES or thermal energy storage assisted system would best fit your operation or process requirements and goals for incremental decarbonization?

	High Priority	Medium Priority	Low Priority	N/A
Electricity	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Heat augmentation via heat exchangers (i.e., not sensitive to heat transfer fluid)	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Heat transfer fluid	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Hot oil	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Hot water	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Steam	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Other, please describe:	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Question 9

Describe a generalized energy demand schedule for your plant and the energy form (electricity, steam pressure and temperature, etc.) under normal operating conditions (e.g., 24/7/365, batch-style periodic in short duration).

Question 10

Is your company interested in learning more about how advanced reactor demonstration capabilities and reactor coupling with industrial processes (i.e., integrated energy systems) can decarbonize your facility, company, and processes? Optional: Please include any information in support of your selection in the box provided below.

Yes

No

Possibly

Question 11

If there are factors we neglected to consider that are extremely important, please include them below.

Question 12

Is your facility currently set up to sell excess electricity generation to the grid?

Yes

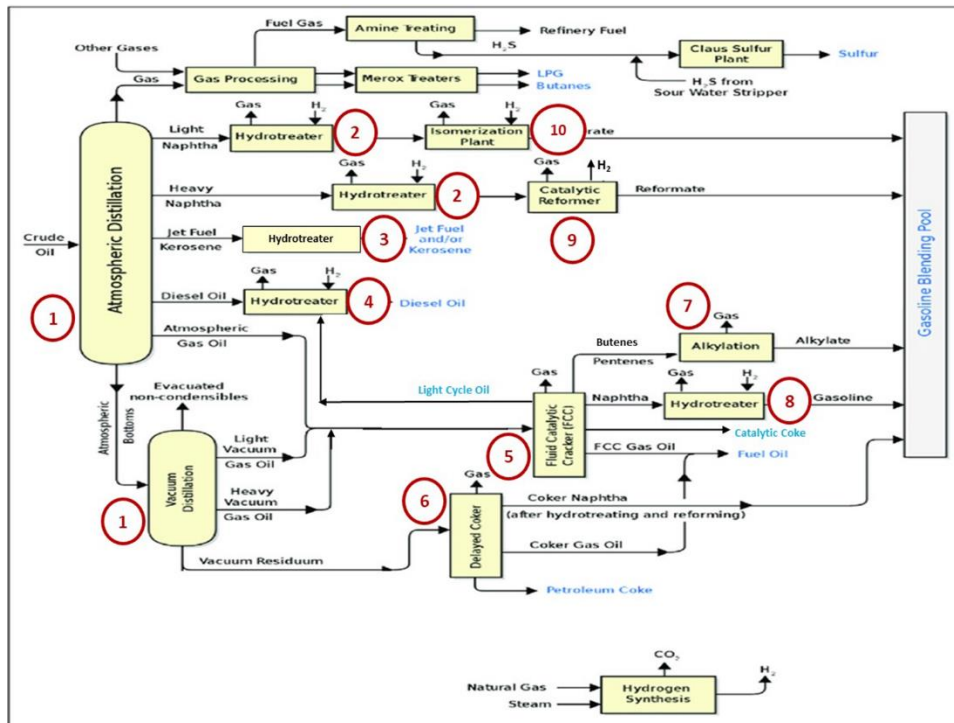
No

APPENDIX B

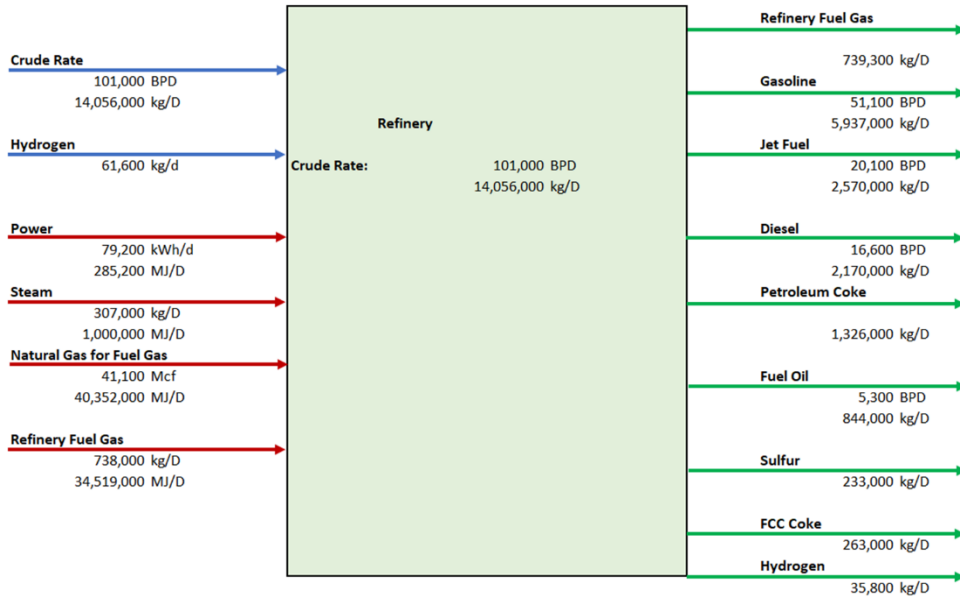
Refinery Mass and Energy Block Diagrams

The refinery configuration is for an upgrading refinery. The mass and energy balances are related to the refinery process a crude slate of Arabian Medium crude. The PRELIM model was used to develop the information.

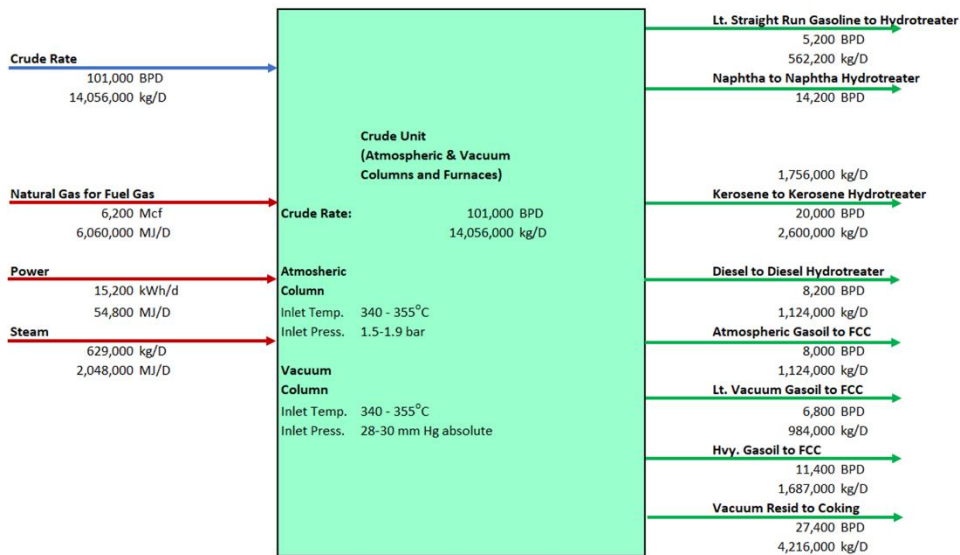
Refinery Overview



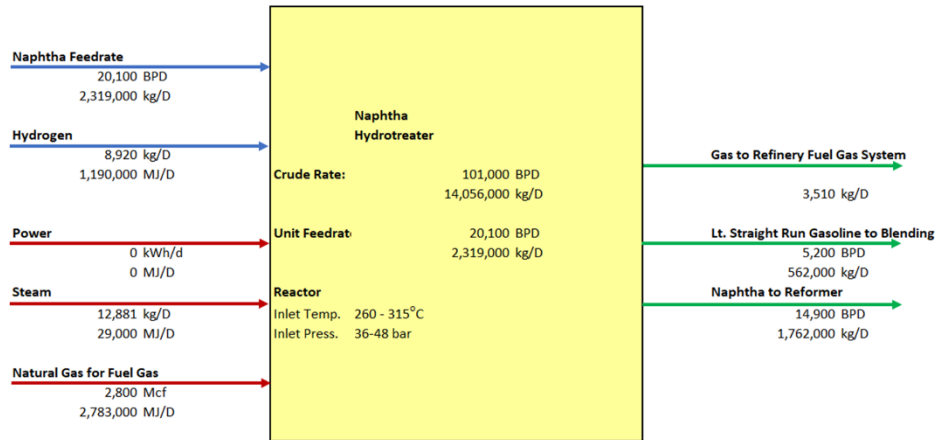
Refinery Mass and Energy Flows



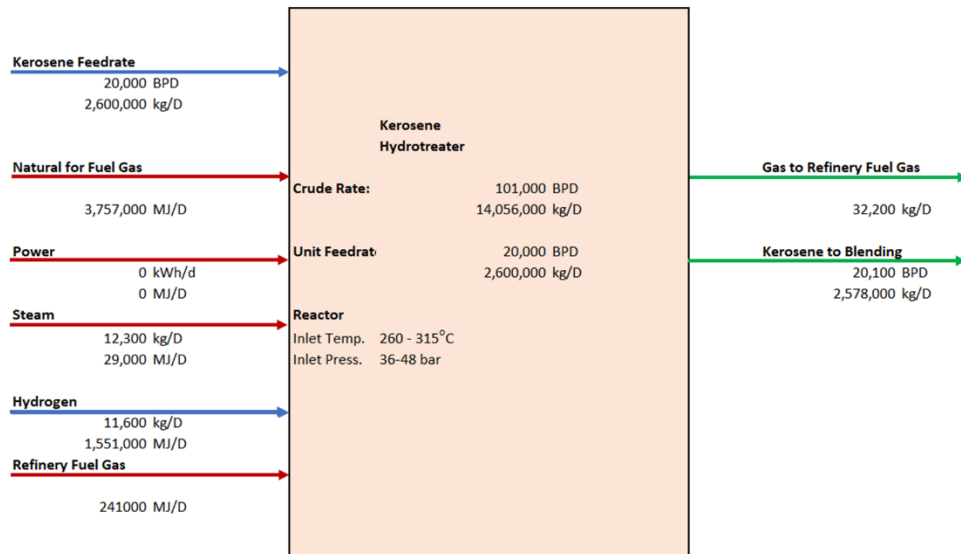
1 - Crude Unit



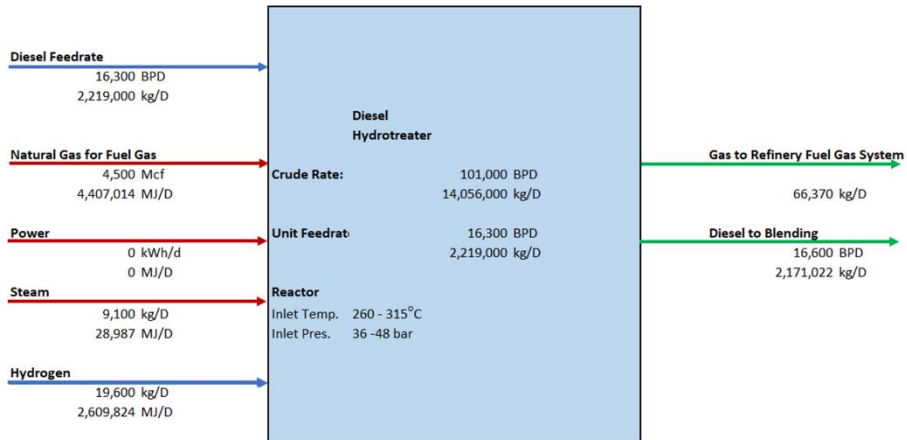
2 – Naphtha Hydrotreater



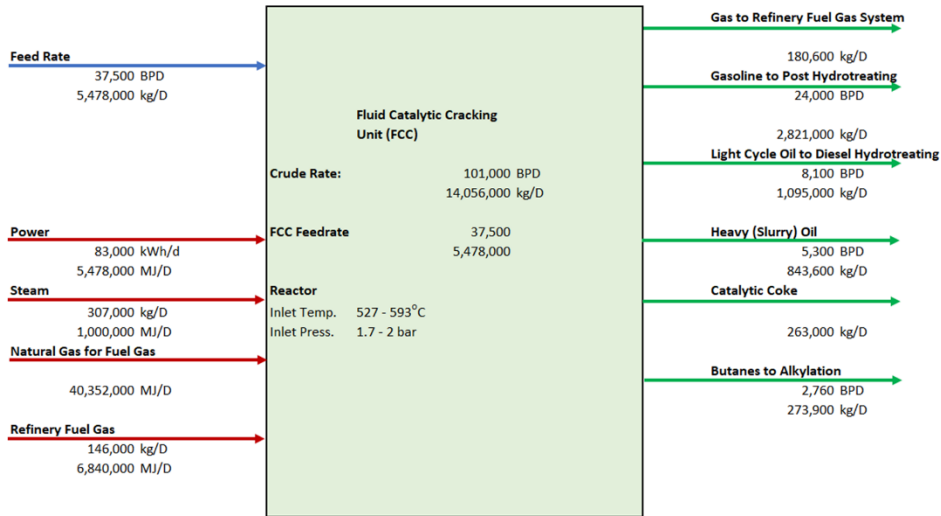
3 – Kerosene Hydrotreater



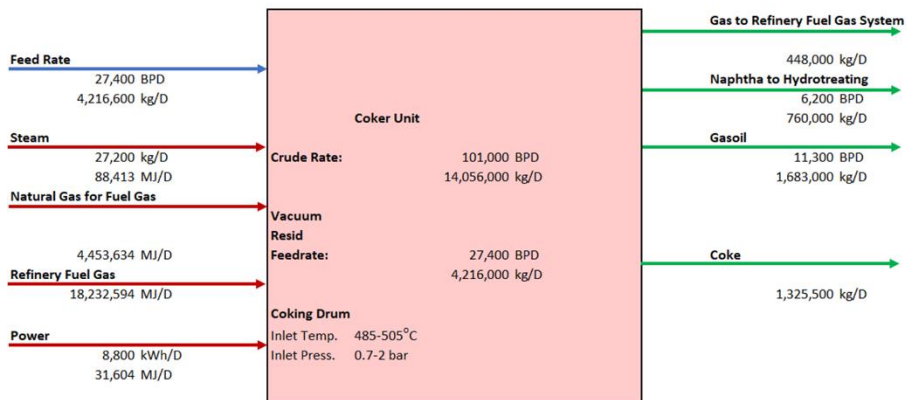
4 – Diesel Hydrotreater



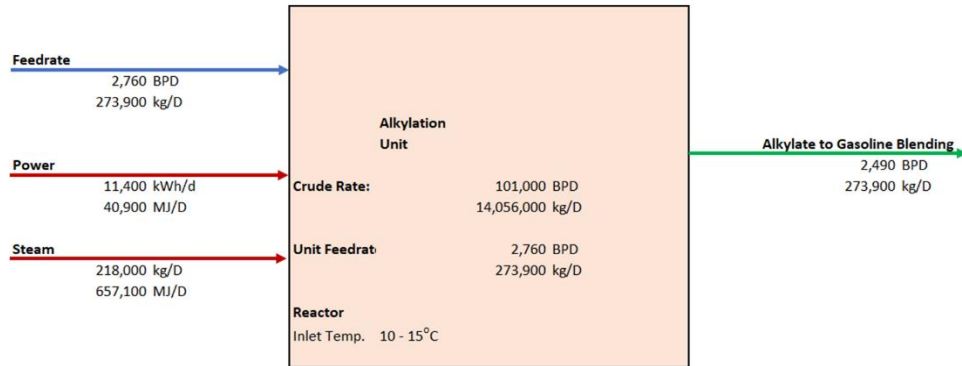
5 – Fluid Catalytic Cracking Unit (FCC)



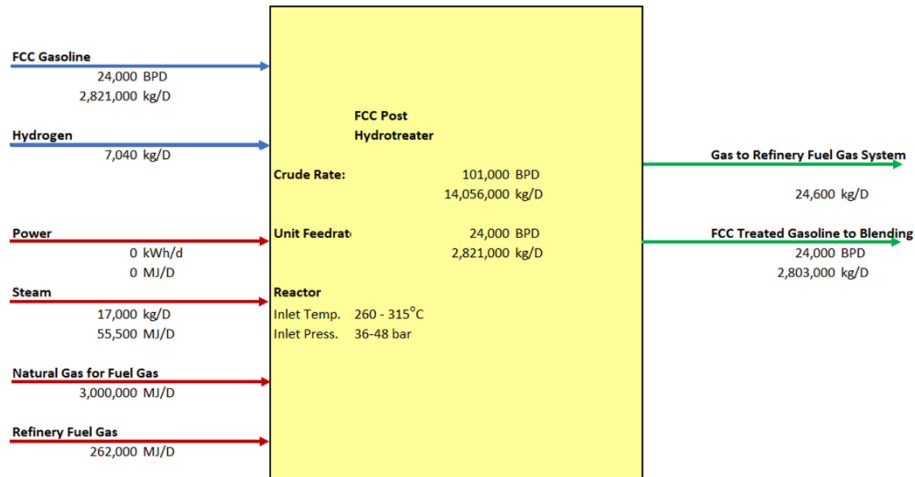
6 – Coker



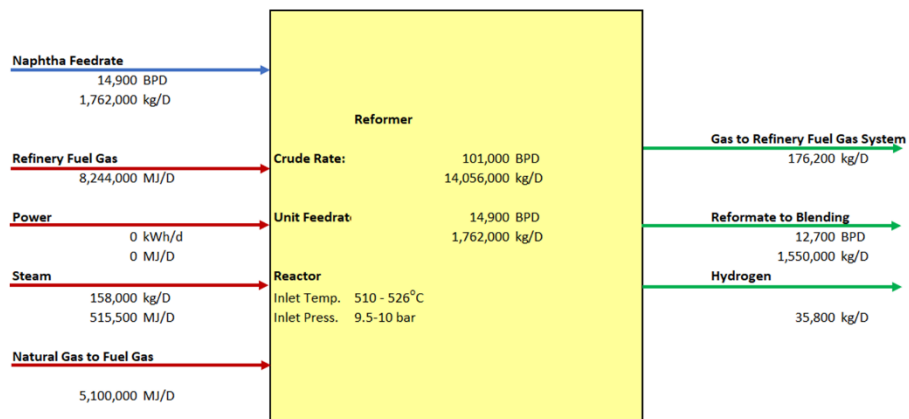
7 – Alkylation Unit



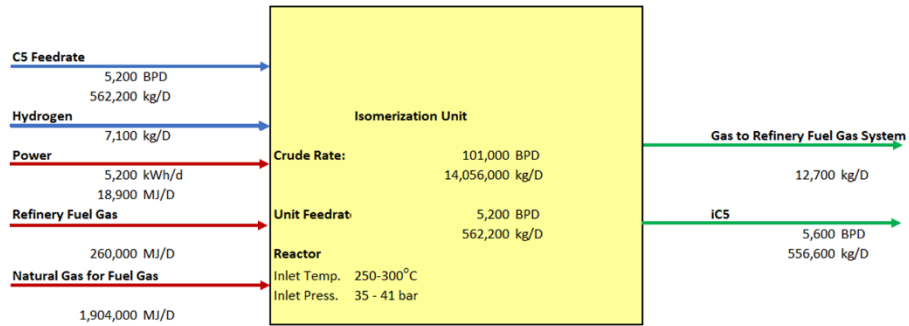
8 – FCC Post Hydrotreater



9 – Reformer

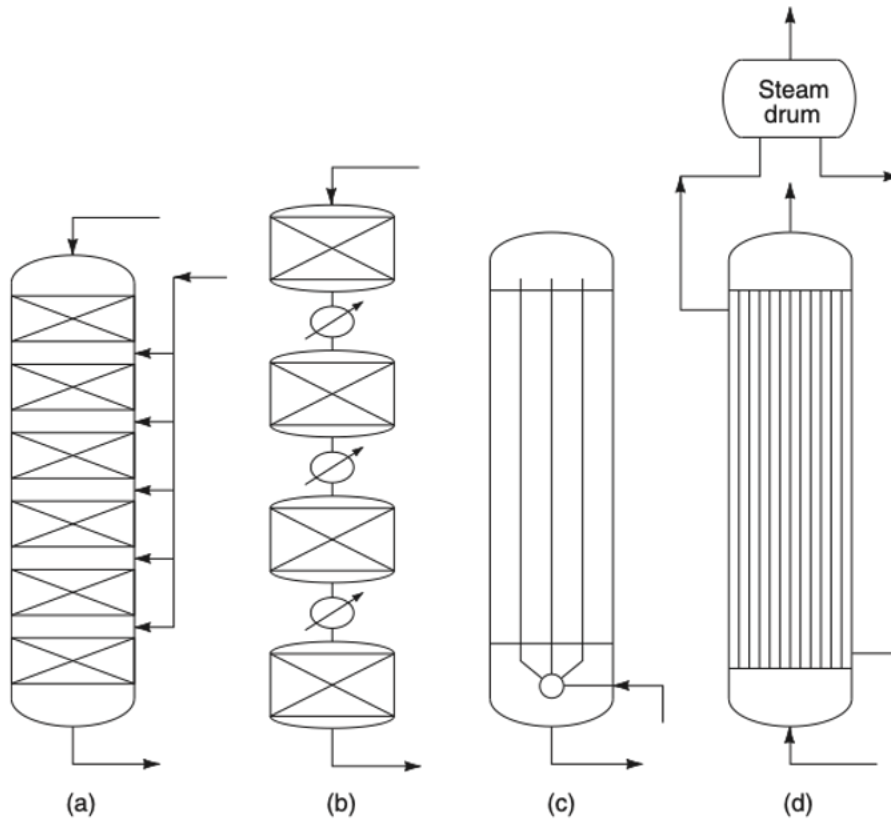


10 – Isomerization Unit



APPENDIX C

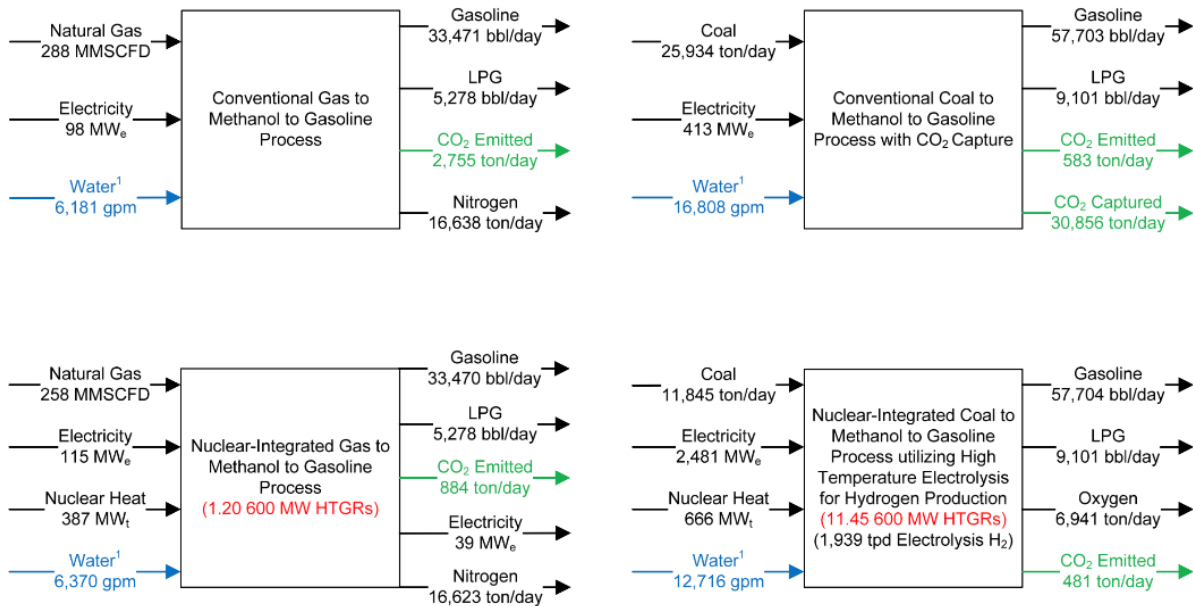
Types of Methanol Reactors



- A) Quench Reactor: These involve multiple gas-injections points into catalysts beds. The catalyst beds are adiabatic and the temperature profile depicts a sawtooth behaviour. The reactor is often chosen for its reliability

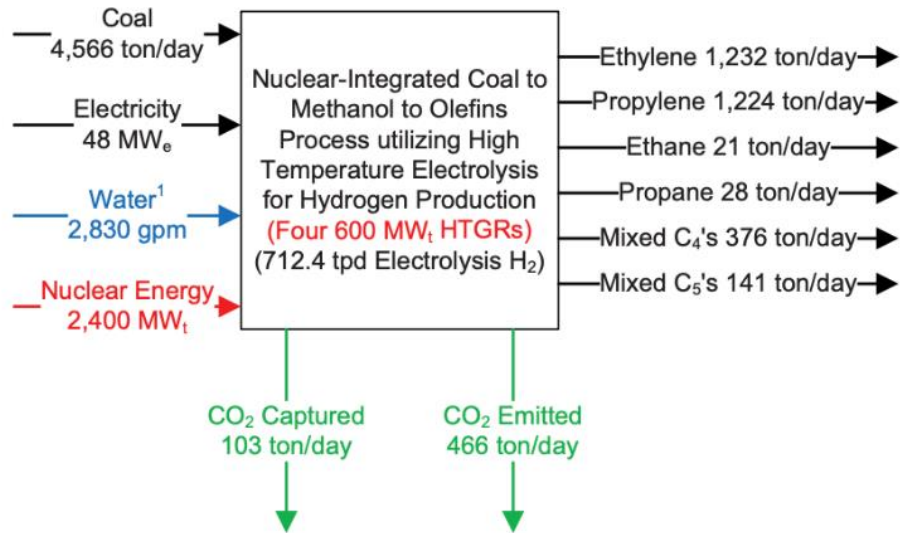
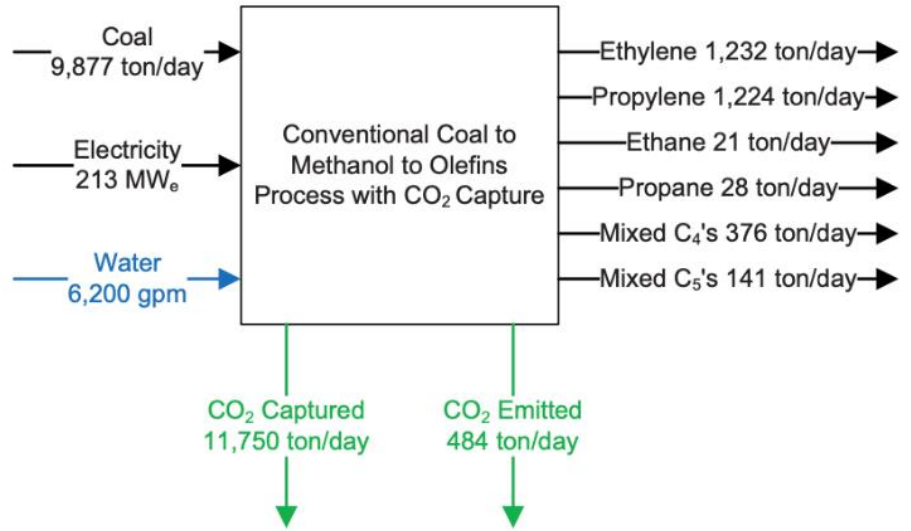
- B) Adiabatic Converters: Heat exchangers are used to control temperature. Multiple vessels and heat exchangers exacerbate the investment cost of the technology
- C) Tube-cooled Reactor: Serves as an inter-changer, consisting of a tube-filled vessel with a catalyst on the shell side. A major advantage is the reduced volume requirement for catalyst.
- D) Steam Raising Reactor: Available in multiple configurations: radial, axial steam flow with catalysts either on the shell side or the tube side. Improved thermodynamical efficiency witnessed due to near isothermal operation. Reduced by-product due to lower temperatures on catalysts.

Material balance summary for MTG pathway with HTSE and HTGR (with coal and natural gas as feedstock).



¹Does not include heat rejection requirement for the nuclear plant.

Material balance summary for MTO pathway with HTSE and HTGR (with coal as feedstock).



¹Does not include heat rejection requirement for the nuclear plant or HTSE water requirements.