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M2CT-22IN1202096 Design for Carbon Conversion Product Pathways with Nuclear Power Plant Integration

September 2022

Elizabeth Kirkpatrick Worsham, Botros Naseif Hanna Bishara Hanna, Lane T Knighton, Stephen G Hancock, Shannon M Bragg-Sitton, William Dunkley Jenson, Aaron S Epiney

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Improving Plant Profitability and Performance with Carbon Capture

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ABSTRACT

Coal is a globally abundant resource that historically has been used for power generation via combustion. As the power industry replaces coal with cleaner methods of generation, energy-rich coal could be used in other chemical and fuel applications. This study presents a coal utilization option in which coal combustion is replaced with a carbon-free nuclear power plant and the coal is upgraded to valuable products for a variety of markets.

Coal is prepared for conversion first by the pyrolysis process, which will optimize solid, liquid, and gaseous products based on the market size and potential product value, maximizing the monetary value of coal. This process is designed using bituminous coal from the Appalachian region as a basis to provide a pathway to preserve or transition coal-related jobs and create new jobs associated with the clean energy transition. Process modeling in the AspenOne Suite will be used to determine each component's sensitivities, costs, inputs, and outputs. Dispatch modeling in the Framework for Optimization of Resources and Economics (FORCE) toolset will optimize the entire system and calculate the net present value for the refinery lifetime. Advanced and light-water reactors are considerations to supply the heat, steam, and electricity to the process.

This paper focuses on the technical and market analysis used to determine the optimal processes and product pathways for the carbon refinery. Product pathways are on activated carbon, formic acid synthesis, and methanol synthesis for further upgrading to marketable chemical and polymer products.

EXECUTIVE SUMMARY

The demand for more carbon efficient power sources and a decrease in natural gas prices has decreased the desire for coal power. This decrease in demand has led to massive job losses in coal mining regions over the past decade. The purpose of this project is to develop a hybrid energy system utilizing coal and a nuclear reactor, which improves the competitiveness of both technologies and decreases carbon emissions.

The final design of the "Carbon Conversion Refinery," combines the valuable carbon content in coal with near-zero carbon heat and electricity from an advanced nuclear reactor. The main goals of this design are to:

- Convert coal to valuable products via pyrolysis and gasification
- Reduce waste by utilizing carbon products in other parts of the refinery
- Capture CO_2 and convert it to products, as opposed to carbon sequestration
- And Maximize revenue from various product streams

The design of a hybrid, closed-loop coal conversion refinery required a significant amount of literature review and decision-making to determine the processes, components, and markets to integrate for the optimal design. This report describes this decision-making process in detail to justify the design choices for the carbon refinery. The processes and markets that will be described in this report are coal conversion to syngas (pyrolysis), conversion of coal liquids to gaseous products (hydrothermal gasification), syngas conversion to carbon products (methanol and polymers), char conversion to carbon products (activated carbon), and carbon utilization (formic acid [FA] and urea synthesis).

The process starts by pyrolyzing coal to produce char, ash, syngas, and a small amount of oils and tars. The oils and tars are further gasified to increase the production of syngas. Char is converted to activated carbon, which can be used for mercury removal from the syngas. Carbon dioxide and sulfur are removed from the syngas, and the syngas is processed into methanol and then further into olefins, resulting in polymer products. Since this is expected to be a nearly closed-loop process for carbon capture, the CO_2 must be utilized versus sequestered. The market chosen for CO_2 utilization was FA, although many opportunities in other markets exist.

Most processes to convert coal to syngas in the literature focus on the direct gasification of coal. This makes sense, because gasification is an exothermic process and the energy in coal can be used directly instead of requiring an external heat source. Pyrolysis is typically used in biomass applications because the biomass yields a higher fraction of oils than gases, which is the inverse result of pyrolyzing coal. The addition of a nuclear heat source eliminates the need for an exothermic process to convert coal to syngas. Pyrolyzing coal is an endothermic process that maximizes the product output because the oxygen-less atmosphere of the reactor will keep gases from combusting. The additional advantage of the pyrolysis process is that it results in multiple product streams: oils, tars, solids, and gases. These product streams can potentially widen the market opportunities for the carbon refinery.

Hydrothermal gasification will be used in the carbon refinery to break down the heavy compounds of tar and pyrolysis oil into syngas. There are two significant reasons why hydrothermal gasification to convert tar to syngas is a better option than finding a market for distilled tar. The first reason is that the pyrolysis of coal results in a small fraction of tars and oils, and the temperature and residence time of the pyrolysis process can be easily adjusted to decrease the fraction further. The second reason is that the market for tar appears to be decreasing in the U.S., and a national policy to ban coal tar could remove those markets at any time. With an efficient hydrothermal gasification process, there should be very little tar product remaining.

Two major pathways for syngas conversion are Fischer-Tropsch and methanol synthesis. The primary application for the Fischer-Tropsch process is fuels, though waxes and olefins can also be obtained. Olefins and gasoline can also be obtained from methanol. Methanol was chosen as the syngas conversion pathway because of the variety of products that can be produced from it. The flexible nature of the modeling means that in the future, Fischer-Tropsch or another conversion process can be added.

Because this study focuses on non-fuel product pathways, the methanol-to-olefins process was chosen, with polymers created downstream. Polymer production was chosen at the request of the Department of Energy because polymers are ubiquitous and are a product that sequesters carbon almost indefinitely, as opposed to fuels that will release carbon after they are burned. The methanol-to-olefins process as well as the olefins-to-polymers process is well-established. Because it is the main product with expected market growth and has a well-developed process for its production, polypropylene will continue to be considered as the polymer product for the refinery. The generation of polypropylene using the MTP process will result in a small fraction of ethylene and gasoline, which can be considered as secondary products for the refinery.

At this carbon refinery, the goal is to utilize the CO_2 generated by the pyrolysis process to produce more value-added products, rather than relying on CO_2 sequestration. Key considerations for this product pathway are that the synthesis utilizes feedstocks already produced at the refinery (hydrogen, oxygen, water, carbon dioxide), the product is either in demand locally or has a generally large market, and the addition of process equipment does not create a significant detriment to the overall profitability of the refinery.

In terms of technical integration, FA synthesis appears to be the best choice for carbon utilization. The process only requires feedstocks already produced at the refinery (hydrogen, carbon dioxide, steam, and electricity), and FA has many markets and uses. It is, however, a low-cost product and may not be as profitable as other options. Ammonia and urea are generally more desirable products because of the growing demand for fertilizers worldwide. The price of ammonia has also recently become extremely variable, corresponding to the variability of the natural gas price. Future work will focus on the near-zero carbon production of ammonia and the CO_2 utilization to produce urea. Urea will not be included in the model but will still be considered as a potential product. The costs and revenues associated with urea production (through ammonia production or purchase) will be estimated based on the resulting CO_2 outputs of the refinery.

Now that the initial design phase is complete, the various processes in Aspen Plus and Aspen HYSYS. Through Aspen modeling and APEN, we can obtain the transfer functions for the feedstocks and cost functions for the equipment. Once these processes are appropriately modeled, they will be transferred to the Framework for the Optimization of Resources and Economics (FORCE) toolset for dynamic modeling and economic analysis. The viability of each case will be evaluated based on two figures of merit: net present value and cost of carbon avoided. Several modeled cases will slightly vary the processes included in the refinery and can be compared to each other as well baseline cases. Results from the carbon refinery will also be compared to the cost and carbon dioxide output of the incumbent processes for creating methanol and polymers. These figures of merit will determine the value of the refinery design in both cost and carbon savings.

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Tables

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ACRONYMS

ac	alternate current
AC	activated charcoal
AE	Alkaline Electrolysis
BLS	Bureau of Labor Statistics
CAGR	compound annual growth rate
CD	coke dust
CHP	chemical heat pump
dc	direct current
EM2	Energy Multiplier Module
FA	formic acid
FOB	Fee on Board
FT	Fischer-Tropsch
HTG	hydrothermal gasification
HTGR	high-temperature gas reactor
HTR	high-temperature gas-cooled reactor
HTSE	high-temperature steam electrolysis
INL	Idaho National Laboratory
LCOH	levelized cost of hydrogen
LD	lignite dust
LDC	lignite dust char
LTE	low-temperature electrolysis
MMR	Micro Modular Reactor
MTO	methanol-to-olefins
MTP	methanol-to-propylene
PAH	polycyclic aromatic hydrocarbon
PEM	polymer electrolyte membrane or proton exchange membrane
PG	plasma gasification
RC	rubber char
RGC	rubber granulated char
SC-HTGR	Steam Cycle High-Temperature Gas-Cooled Reactor
SCWG	supercritical water gasification
SMR	small modular reactor
SOEC	solid oxide electrolyte cells

U.S.	United States
USGS	United States Geological Survey

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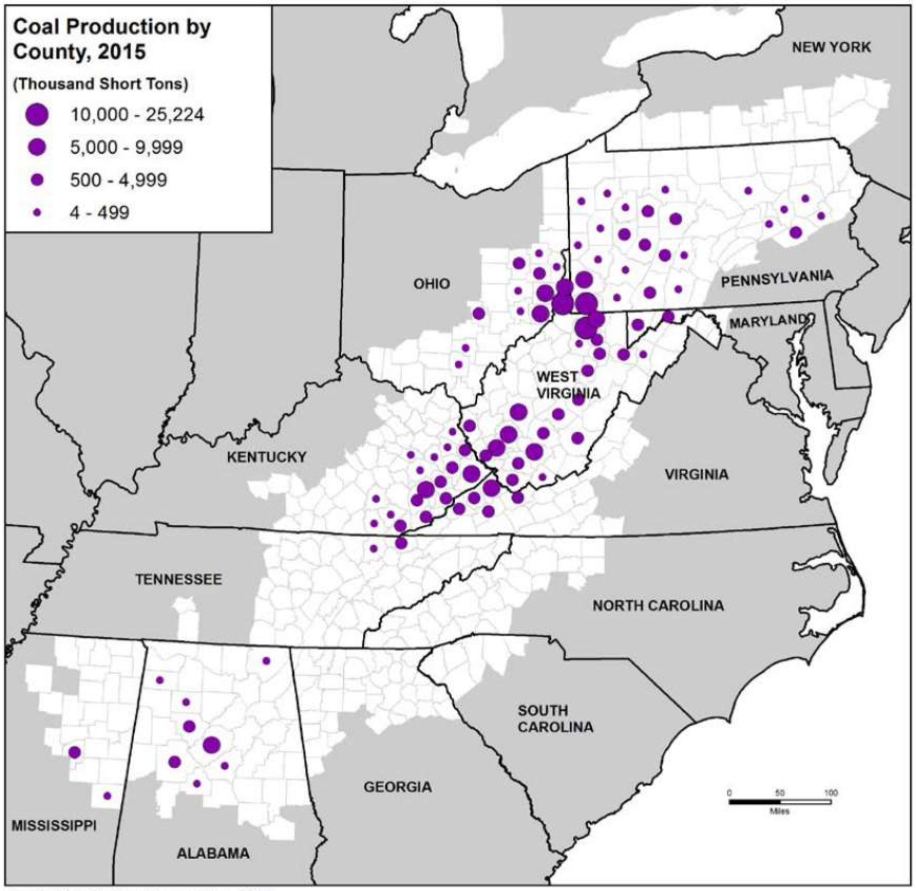
Carbon Conversion Product Pathways with Nuclear Power Plant Integration

1. INTRODUCTION

The expansion in the renewable energy capacity across the United States (U.S.) has created new jobs and supported global carbon dioxide reduction goals in the energy sector. However, the volatile nature of these renewable technologies is forcing traditional baseload power plants, such as coal and nuclear, to operate flexibly at overall lower capacity factors, which reduces revenue, decreases efficiency, and potentially increases maintenance costs. Baseload power continues to be an important part of the electric grid to provide power when electricity from renewable sources is in low supply.

This project focuses specifically on the coal industry in the Appalachian region of the U.S., which is concentrated in the areas of western Pennsylvania, West Virginia, and eastern Kentucky, as shown in Figure 1. Although coal production has decreased across the country, it has decreased significantly in these regions, causing severe impacts on local economies.



Appalachian Regional Commission, 2016
Data source: U.S. Mine Safety and Health Administration

Figure 1. Map of coal production by county in the Appalachian region (Hodge 2016).

This study expands on the previous research done by Worsham et al. (2021) for a hybrid coal and nuclear power system that converted biomass and coal to product feedstocks. Significant changes from the previous research give a valuable and more simplified process design and goals, resulting in a robust process design to convert coal to valuable products using nuclear-generated electricity and steam.

The current research will further develop integrated energy systems through five main objectives:

1. Computationally demonstrate an application for nuclear technology integration with heat, electricity, and steam to generate a material product
2. Computationally demonstrate an application for coal as a valuable feedstock for products other than heat or electricity generation, with zero emissions or toxic solid waste discharge
3. Establish a versatile framework for addressing the conversion of other carbonaceous feedstocks, including biomass, municipal wastes, segregated wastes (with an emphasis on plastics), and lignin from ethanol plants and pulp and paper manufacturing
4. Provide a pathway to preserve and transition coal-related jobs and create new jobs associated with the clean energy transition for communities in the Appalachian Region of the U.S. and expanding to other coal states in the U.S.
5. Evaluate the feasibility of using nuclear energy for coal and carbon conversion using the Framework for the Optimization of Resources and Economics (FORCE) toolset for dynamic modeling and economic analysis, using, for example, the intermittent production of hydrogen and operation of process units that interact with the grid using demand response.

Because of the complexity of this system, there has been a significant amount of literature review and decision-making required to determine the processes, components, and markets to integrate for the optimal design. This paper describes this decision-making process in detail to justify the design choices for the carbon refinery, as well as detail the planned modeling work and case studies. Idaho National Laboratory (INL) previously modeled a case of coal conversion to fuels using pyrolysis and nuclear heat in an unpublished report, which is heavily referenced in this study. However, this case expands on the previous study to model the conversion to non-fuel products, to utilize the resulting CO_2 from the refinery processes, to update the models from this previous study, and to provide a flexible modeling framework for future coal conversion scenarios.

2. PREVIOUS MODELING WORK

There is a large library of information on coal conversion technologies. For example, for many years the Fischer-Tropsch (FT) conversion of syngas produced from coal gasification (or other carbonaceous sources) has been used successfully at commercial scale to produce transportation fuels. The methanol-to-gasoline and methanol-to-olefins (MTO) routes that use syngas to produce motor gasoline and olefins (precursors to plastics and rubbers), respectively, have also been well-established. Methanol synthesis from syngas is a commercial process, as well as the production of various chemicals other than fuels that can be produced using methanol as an intermediate. With most of these processes, the question is not as much what is technically possible but what is economically feasible and an attractive investment for companies and investors. There are, of course, always technical improvements that can be made to improve the overall economics of the process. For this reason, technoeconomic assessments are critical in not just modeling the technical possibility but also showing the relative economic attractiveness of the application. INL and other national laboratories and organizations have over the years performed many technoeconomic assessments on the conversion of coal to valuable chemicals and fuels. Some of these reports and modeling results are publicly available while others have been completed under cooperative research and development agreements, which are not publicly available.

One public study modeled coal-to-liquids processes integrated with nuclear energy from a proposed high-temperature gas reactor (HTGR) (Gandrik and Wood 2010). Figure 2 shows a block flow diagram of the processes modeled in this 2010 study. Coal gasification was modeled and then the resulting syngas was used in a FT synthesis to make liquid propane gas, naphtha (motor gasoline cut), and diesel fuel.

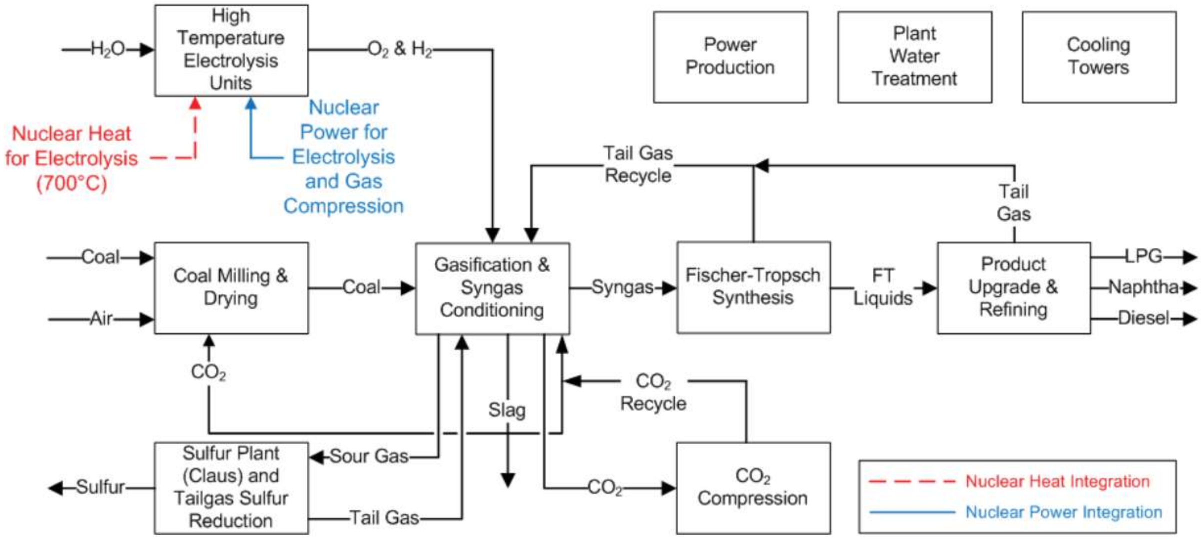


Figure 2. Block flow diagram for the HTGR-integrated coal-to-liquids process (Gandrik and Wood 2010).

Another study completed recently includes an Aspen Plus model of synthetic fuels production via the FT process, replacing coal as the raw material and assuming a pure stream of waste CO_2 is available from an industrial process (the specific source of the CO_2 was not specified at this level of the study) and using nuclear-driven electrolysis to produce hydrogen (Zang, Sun, and Elgowainy 2021). The reverse water-gas shift reaction was used to convert CO_2 to CO using some of the H_2 produced from electrolysis to get the correct H_2-to-CO ratio of the syngas needed for FT synthesis.

3. PROCESS SUMMARY

This status report contains the information gathered so far for the various processes included in the carbon refinery, as detailed in Figure 3. The research team has made significant decisions for methanol synthesis and CO_2 utilization pathways based on the technical aspects of production as well as market analyses. Gathering the data needed to model each process is ongoing, and some processes are discussed further in this report.

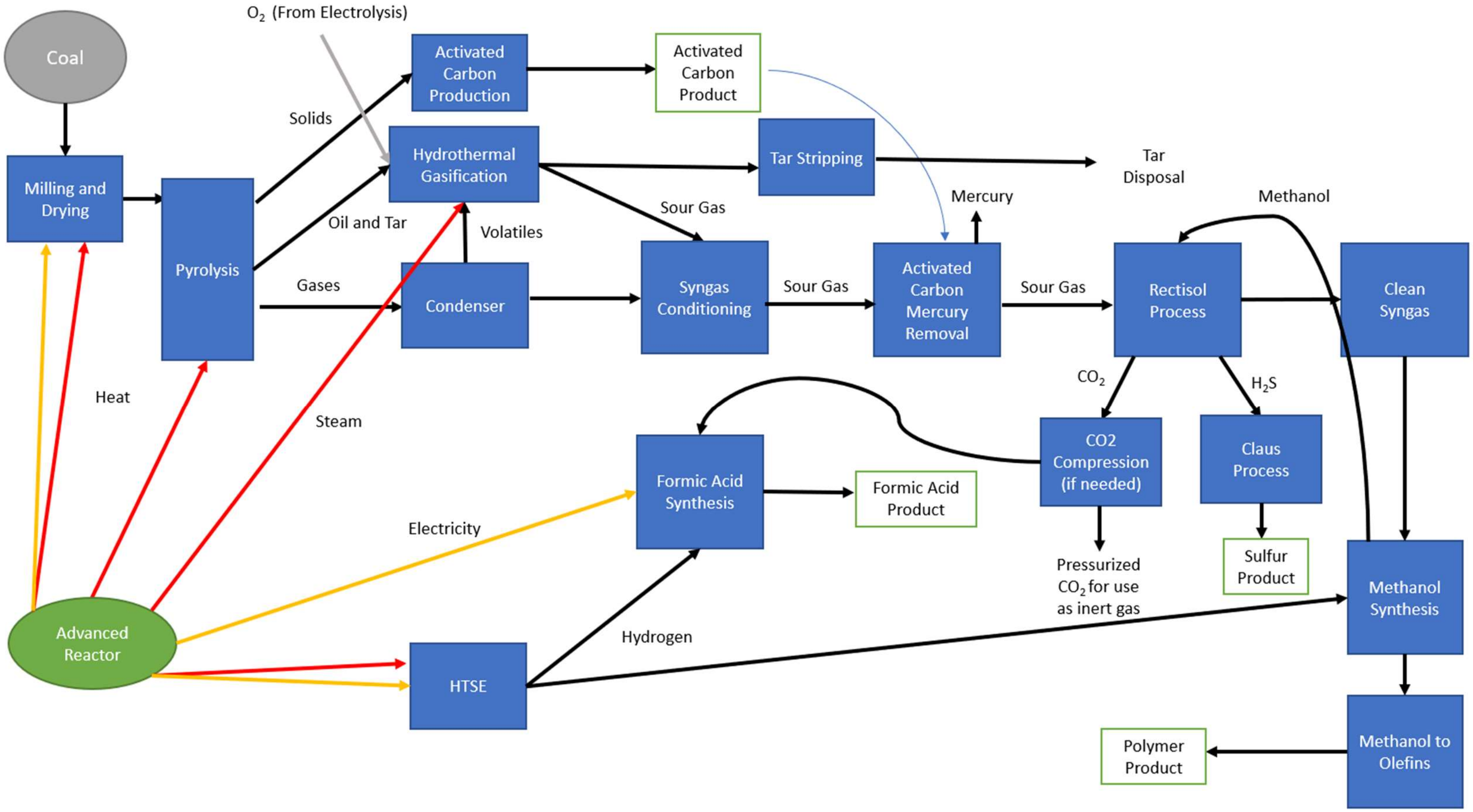


Figure 3. Current design iteration of the carbon refinery model.

3.1 Coal Pretreatment

The first step in the carbon refinery is the coal pretreatment. Coal milling and drying prepare the coal feedstock by removing the water content and reducing the feedstock size to the optimal surface area for pyrolysis. The drying process can utilize residual heat from downstream processes.

There are many studies and existing commercial processes surrounding the processes for pretreating coal to remove impurities, capture mineral and rare earth compounds, and isolate harmful elements like mercury. These processes are standard and well documented and will therefore not be treated in detail in this work. In future iterations of the carbon conversion model, these pretreatments could be implemented at some level for a more complete plant model. The resulting chemical compositions of processes like acid leaching are heavily dependent on the initial coal composition. The models developed in previous INL research use a general subbituminous Wyoming coal, but the final composition will be specific to the coal resource used.

An acid washing coal pretreatment is not included in this model, mainly because of uncertainty in the kind and quality of products that will result from the pyrolysis of the pretreated coal. Previous work studied the effects of acid washing on the pyrolysis products of South African bituminous coal (Roets et al. 2015). The results were overall promising and appeared to be beneficial towards the carbon refinery goals in the current study. Mineral removal efficiencies through acid washing were 76.9–92.8%, and gas yields of the pyrolyzed coal were significantly higher, including an increase in H_2 yields. The main concern for this application is the significant change in tar yields and appearance, which may be important to the carbon refinery's tar market. Tars derived from the acid-washed coal were light to dark brown and powdery. Although a simulated distillation process showed yields of naphtha, kerosene, and fuel oil, it is unknown how tar distillation will affect the products for construction and aluminum markets.

The carbon refinery model in the current study assumes that the coal feedstock is washed when it is received at the refinery and that the only preprocessing is coal milling and drying. This assumption is consistent with previous INL studies involving coal as a feedstock. TEV-672 "HTGR-Integrated Coal and Gas to Liquids Production Analysis" (Idaho National Laboratory 2012a), TEV-1567 "Nuclear-Integrated Methanol-to-Olefins Production Analysis" (Idaho National Laboratory 2012b), and TEV-667 "Nuclear-Integrated Methanol-to-Gasoline Production Analysis" (Idaho National Laboratory 2010), on which the current carbon refinery modeling is based, both model coal milling and drying but no other pretreatment.

Coal washing is a common practice and can occur at coal washing plants located near the extraction site. Coal washing can remove 50–80% of the ash and 30–40% of the total sulfur in coal, reducing soot, SO_2, and NOx from coal burning. Removing coal impurities close to the extraction site reduces the total weight and therefore the space and energy needed for transportation (Longzhong Machinery 2019).

The coal milling and drying model is based on the assumptions used in TEV-1567, TEV-672, and TEV-667. These assumptions are listed here using Illinois bituminous coal (40% fixed carbon). A simplified schematic of the coal drying process is shown in Figure 4. These assumptions are applicable to the current study because the current study uses bituminous coal from the Appalachian region. TEV-672 uses N_2 and CO_2 as inert gases for the drying process, but the current study uses only captured and compressed CO_2 for all inert gas purposes.

Coal is pulverized to below 90 μm using a roller mill. Coal milling power consumption is modeled based on the power calculated by Aspen assuming a Hardgrove grindability index of 60. Drying is accomplished simultaneously using a heated inert gas stream. The gas stream removes evaporated water as it sweeps the pulverized coal through an internal classifier for collection in a baghouse. The inert CO_2, captured from the pyrolysis and gasification process heated using heat derived from a nuclear reactor. The hot inert gas stream dries the Illinois coal down to 6% moisture. CO_2 is also used as the transport gas for the coal from the baghouse to the lock hoppers. Pressurized CO_2 is then used to transport the dry, pulverized coal into the pyrolysis unit. The transport gas is assumed to be 0.15 kg of gas per kg of solids.

The amount of CO_2 vented during feed hopper depressurization is estimated using the ideal gas law (Idaho National Laboratory 2012b).

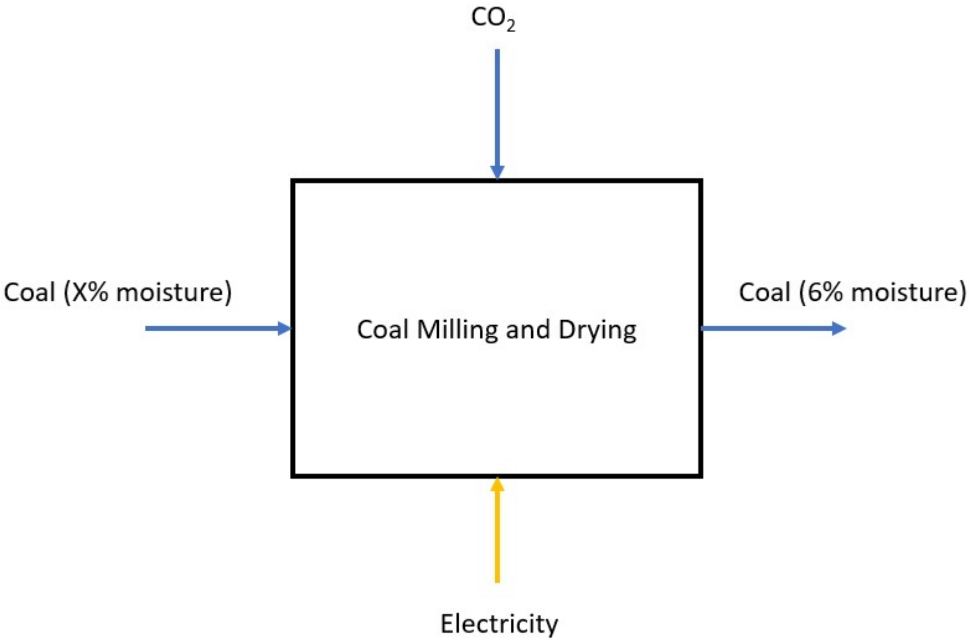


Figure 4. Process diagram for coal milling and drying process.

3.2 Coal Conversion to Syngas

Coal is a carbon-rich feedstock for steam and power production. It is typically considered as a fuel on its own, combusted to produce electricity from a steam cycle; however, it can also be broken down into gaseous and liquid products. Converting coal to these alternative forms can help reduce or control pollutants (National Energy Technology Laboratory n.d.).

3.2.1 Pyrolysis and Gasification

Pyrolysis is an oxygen-free decomposition process operated between 300 and 1300°C, depending on the feedstock and the application, and near atmospheric pressure. In hydropyrolysis, feedstock is pyrolized at 50–200 bar in a hydrogen-rich environment (Sludge Processing 2020c). A graphical depiction of the process is shown in Figure 5. The pyrolysis process can be tailored depending on the desired end products for the available feedstocks. Slow pyrolysis (also called dry carbonization or torrefaction) favors char formation at a heating rate of 10–30°C/minute, to reach about 300°C over 5–10 minutes. Intermediate pyrolysis targets oil and liquid production at a heating rate of 30–300°C/minute to reach 500–650°C. Fast pyrolysis has a very high heat rate at 1200°C and targets oil, liquid, and gas production. Typically in pyrolysis, the effluent from the chemical reactor is gaseous or solid ash. The gaseous product is sent through a cyclone to separate out the char and then through a quench operation to condense the liquid product. The leftover noncondensable gases are usually recycled to the combustor, which provides the heat for the pyrolysis reactor. The refinery-specific pyrolysis process is detailed in 3.2.2.

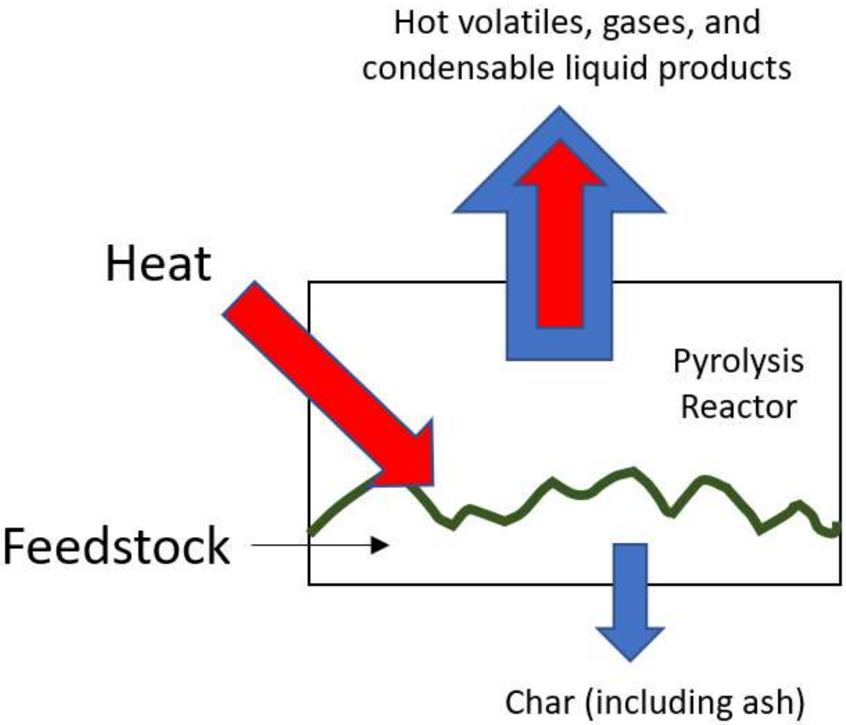


Figure 5. Schematic of the pyrolysis process (Hauserman 2018).

Gasification can be an additional step added onto the pyrolysis process, but both take place within the same chemical reactor (Sludge Processing 2020a). A graphical depiction of this process is shown in Figure 6 and Figure 7. The goal in gasification is to break down all carbonaceous material into either combustible noncondensable gas (such as CO, CO_2, and H_2) or ash. In gasification, the reactor temperature can vary between various sections. First final feed drying occurs and then pyrolysis happens, and the feed is broken down into char and oil fractions. In the final stage, the remaining carbonaceous material is gasified, the final product being a combustible gas that can be used for heating or synthesis purposes. Pyrolysis is done in the absence of O_2, but gasification (also called partial oxidation) is done with substoichiometric amounts of O_2 to partially combust the feedstock in the conversion to CO and H_2. This partial oxidation is exothermic and provides some of the heat to obtain the 1100–1200°C temperature needed. Gasification can be tailored to produce syngas, which is a mixture of CO and H_2 that can be used to synthesize other valuable chemical products.

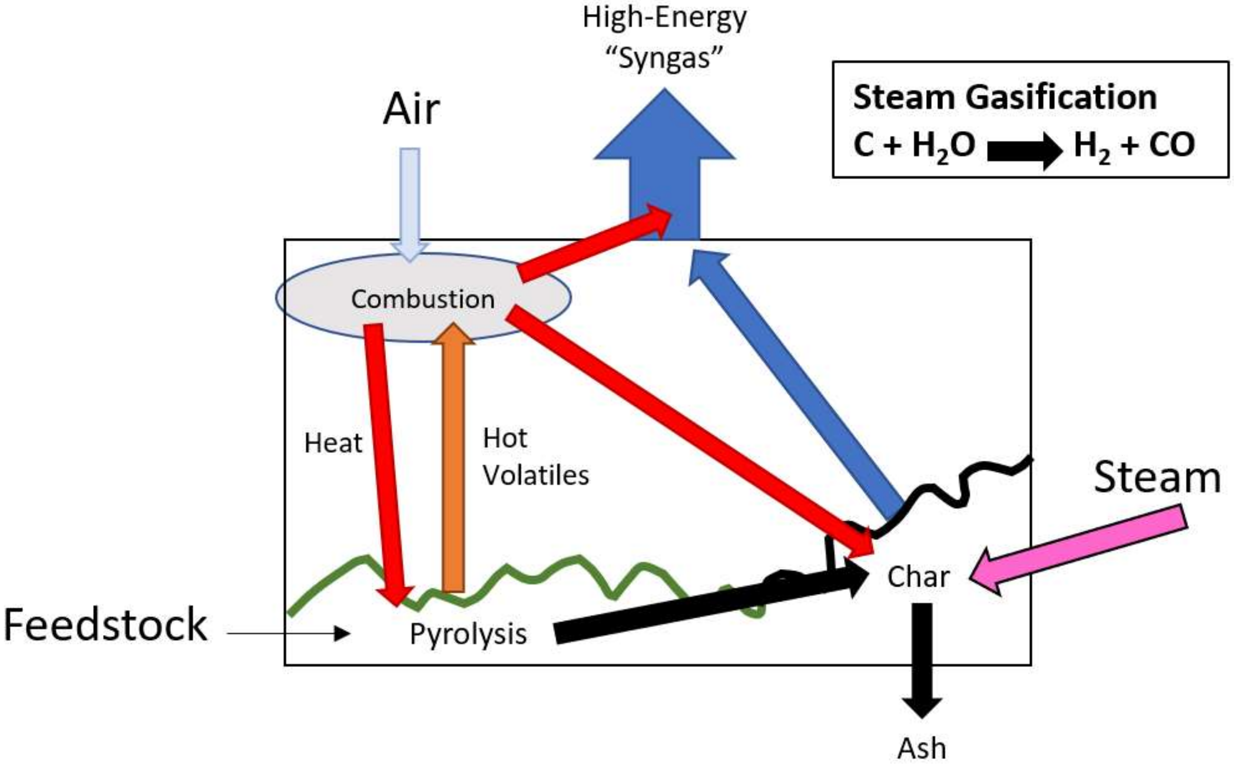


Figure 6. Schematic of the steam gasification process (Hauserman 2018).

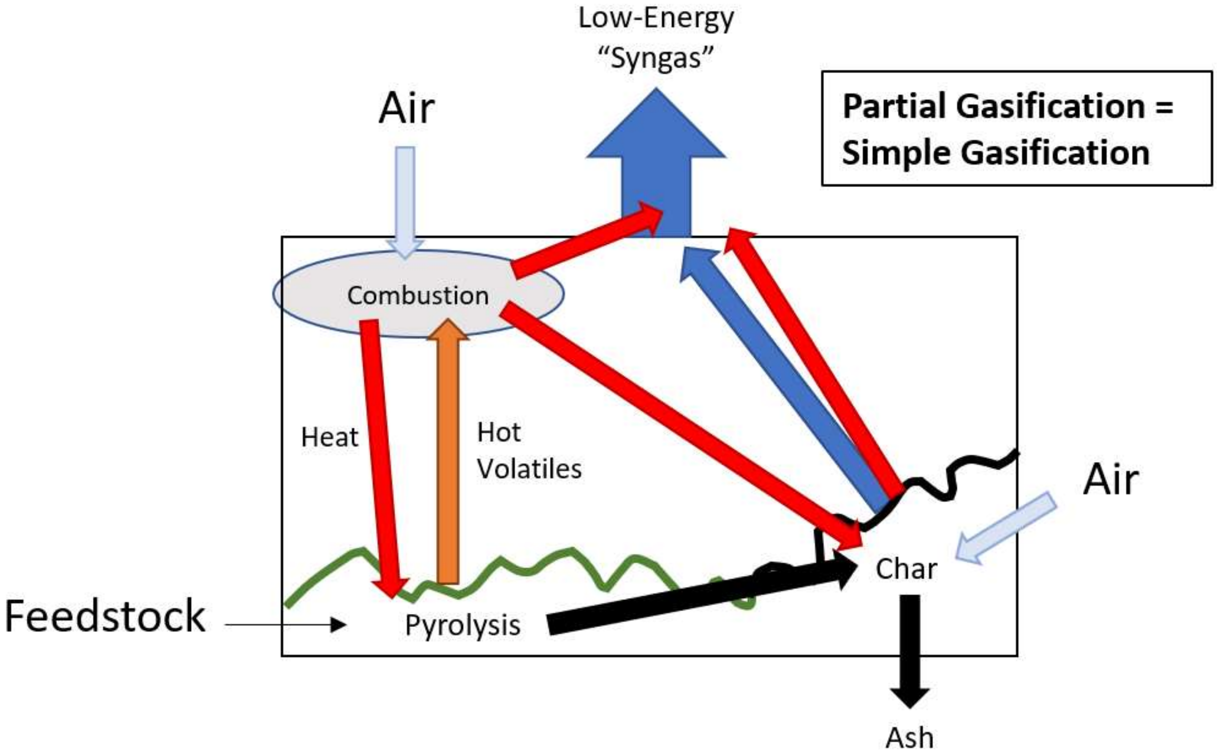


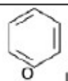
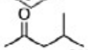
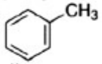
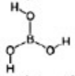
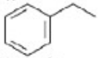
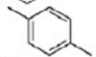
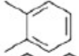
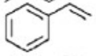
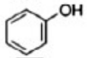
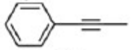
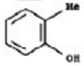
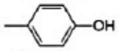
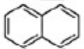
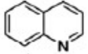
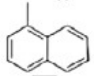
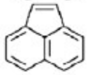
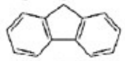
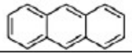
Figure 7. Schematic of the simple gasification process (Hauserman 2018).

Most processes to convert coal to syngas in the literature focus on the direct gasification of coal. This process makes sense because gasification is an exothermic process, and the energy in coal can be used directly instead of requiring an external heat source. Pyrolysis is typically used in biomass applications because the biomass yields a higher fraction of oils than gases, which is the inverse result of pyrolyzing coal. The addition of a nuclear heat source eliminates the need for an exothermic process to convert coal to syngas. Pyrolizing coal is an endothermic process and maximizes the product output because the oxygen deficient atmosphere of the pyrolysis reactor will keep gases from combusting. The additional advantage of the pyrolysis process is that it results in multiple product streams: liquids (oils and tars), solids, and gases. These product streams can potentially widen the market opportunities for the carbon refinery.

3.2.2 Pyrolysis Process Model

Coal pyrolysis is the chemical decomposition of coal at high temperatures. Pyrolysis generates solid products (char), volatile products (tar), and gas products. The dry pulverized coal is subjected to high temperatures in the pyrolizer by direct contact with heat-carrying particles, such as silica sand (Fushimi et al. 2017). The high temperature begins to break down the complex molecular structure of coal in two main pyrolysis steps: primary and secondary pyrolysis. During primary pyrolysis, large functional groups with the weakest bonds begin to break off the main coal structure and break weak hydrogen bonds within the coal to stabilize free radicals. Volatile compounds generated from primary pyrolysis are vaporized and will form the coal tar when condensed. Once the weakest functional groups are removed from the coal structure, new bonds are formed to stabilize the molecular structure of the coal, resulting in the release of small gas compounds, including CO, CO_2, H_2, etc., which will be used for further processing into more useful products. CO + H_2 is known as synthesis gas. The remainder of the coal molecular structure combined with the nonvolatile functional groups form the solid char products (Solomon, Serio, and Suuberg 1992).

The char is separated from the product stream via a cyclone separator as the solids and vapors, including the gas compounds and volatile tar, are quenched and cooled to condense the tar and separate the resulting liquid from the vapor. Alternatively, the tar can be converted further via gasification to increase the yield of synthesis gas and other smaller gas compounds in the vapor stream that could be used for further chemical processing. The tar composition may include compounds in the following groups: aromatic, acidic, phenolic, ketone, and di-aromatic, amongst others (Tursunov et al. 2020), as seen in Figure 8.

Peak. No	Retention time ,min	Compound	Mol. Weight, g/mol	Formula	Structure	Group*
1	2.45-2.47	Benzene	78.114	C_6H_6		AR
2	3.84-3.85	Methyl Isobutyl Ketone	100.16	$C_6H_{12}O$		KT
3	4.47-4.48	Toluene	92.141	C_7H_8		AR
4	7.1	Boric acid	61.831	H_3BO_3		AC
5	7.49-7.50	Ethylbenzene	106.168	C_8H_{10}		AR
6	7.82	P-Xylene	106.1650	C_8H_{10}		AR
7	7.82	o-Xylene	106.1650	C_8H_{10}		AR
8	8.63	Styrene	104.15	C_8H_8		AR
9	11.91	Phenol	94.113	C_6H_6O		AR
10	13.93-13.94	Benzene, 1-propynyl-	116.1598	C_9H_8		AR
11	14.34	Phenol, 2-methyl-	108.1378	C_7H_8O		PH
12	15.07	P-Cresol	108.13	C_7H_8O		PH
13	18.47	Naphthalene	128.1705	$C_{10}H_8$		AR
14	20.14	Quinoline	129.16	C_9H_7N		AR
15	21.67-21.68	Naphthalene, 1-methyl-	142.201	$C_{11}H_{10}$		D-AR
17	25.84	Acenaphthylene	152.196	$C_{12}H_8$		AR
18	29.12	Fluorene	166.223	$C_{13}H_{10}$		AR
19	33.62	Phenanthrene	178.234	$C_{14}H_{10}$		AR
20	33.62	Anthracene	178.234	$C_{14}H_{10}$		AR

AR-aromatic, AC-acidic, PH-phenolic, KT-ketone, D-AR-di-aromatic

Figure 8. A list of compounds found in a tar sample generated by pyrolysis of municipal solid waste and coal at 800°C (Tursunov et al. 2020).

The gas products are made up of a combination of small gas molecules, including CO, CO_2, H_2, H_2O, CH_4, other C_nH_m hydrocarbons, and many sulfur and nitrogen containing gases (Osokina et al. 2017). The distribution and composition of the pyrolysis products vary greatly based on the composition of the coal and pressure and temperature of pyrolysis. Typically, higher temperature pyrolysis results in more gas and tar production and less char as the bonds of the coal molecule are more easily destroyed at higher temperatures. Empirical data is needed to determine the amount and composition of each of the product groups due to the complexity and variation of coal composition, even within the same sample.

The process model is developed to determine the amounts of gas products, tar products, and char generated by pyrolysis as well as the relative composition of the gas products focusing on the most important gases. The model is generated using Aspen Plus software, a part of the AspenOne suite of software. Aspen Plus is preferred over Aspen HYSYS due to its enhanced capabilities dealing with solid coal and chemical compositions in a process stream. The results can then be transferred to Aspen HYSYS for further process modeling of the additional steps in this project. Since the pyrolysis products relate to the coal composition on a percentage basis, the main need for the Aspen Plus model is to determine the amount of external heat required for pyrolysis at the specified temperature. The targeted pyrolysis temperature is 800°C, achieved using heat generated by an advanced nuclear reactor.

The coal is typically characterized within Aspen Plus using a proxanal, ultanal, and sulfanal analysis, which describes the approximate molecular breakdown (Mohan, Pittman, and Steele 2006). For the purposes of this model, the char is also characterized in this manner, with both the coal and char being characterized as nonconventional solids in Aspen Plus. The amount of sand needed for pyrolysis is 20 kg per kg of coal. The heat requirement for pyrolysis is required for recharging the sand. The sand is modeled as a moving stream, and a heater is used in the model to increase the sand temperature by 10°C outside of the pyrolyzer. This is similar to the methodology used in TEV-2132 (O'Brien 2014). The first-pass pyrolysis model uses information readily available in TEV-2132, which uses Wyoming subbituminous coal and analyses and product distributions taken from previous research (Soncini, Means, and Weiland 2013). The data in Table 1 is used as the input for the coal basis analysis. The values for char were taken as estimates from TEV-2132.

Table 1. Coal composition analysis for Wyoming subbituminous coal (Soncini, Means, and Weiland 2013) and char approximation (TEV-2132).

Values	**Wyoming Subbituminous B**	**Char**
Proximate analysis (wt% dry basis)	Proxanal (Aspen Plus)	
Moisture content	10.0	0
Fixed carbon	47.22	67.92
Volatile matter	46.18	20.04
Ash	6.6	12.05
Ultimate analysis (wt% dry basis)	Ultanal (Aspen Plus)	
Ash	6.6	12.05
Carbon	66.21	75.59
Hydrogen	4.2	2.2
Nitrogen	1.2	1.77
Chlorine	0.01	0.004
Sulfur	0.48	0.44
Oxygen	21.3	7.92
Sulfur analysis (wt% dry basis)	Sulfanal (Aspen Plus)	
Pyritic	0.16	0.15
Sulfate	0.16	0.15
Organic	0.16	0.14

The sulfanal values required by Aspen Plus are not typically provided in the data, so these are set equal to the sulfur content in the ultimate analysis, divided equally among the three categories. The moisture is not provided by the data either, so the analysis assumes an insignificant 10% since the coal is dried prior to the pyrolysis process. This only affects the dry coal flow rate since the flow rate of wet coal is specified in the model. The rules that apply to the proxanal, ultanal, and sulfanal categories when setting up the model in Aspen Plus require that the dry basis for proxanal sum to 100, the values of ultanal sum to 100, and the values of sulfanal sum to the value of sulfur in the ultanal category.

The analysis performed by Soncini, Means, and Weiland (2013) for the pyrolysis of Wyoming subbituminous coal provided the pyrolysis details for a mixture of coal with biomass. The product distribution for the data were fit to a polynomial based on the pyrolysis temperature and mass fraction of biomass in the mixture. Since there is no biomass in the current pyrolysis process, the equation becomes a simple linear equation as a function of temperature for each of the major product species. The coefficients for these equations are shown in the Table 2.

Table 2. Common coal pyrolysis products with temperature-dependent production distribution used in the first-pass model (Soncini, Means, and Weiland 2013).

Component	a_0	a_T
Char	6.153E-01	-1.348E-04
CO_2	5.646E-02	3.523E-05
CO	-1.215E-01	4.843E-05
CH_4	-2.051E-02	4.843E-05
C_2H_4	-2.456E-02	4.856E-05
H_2	-2.489E-02	4.289E-05
H_2O	1.681E-01	-1.031E-04
Tar	3.516E-01	-2.105E-04

*The equation for calculating the mass fraction of product, Y_i as a function of temperature is given as:
$Y_i = a_0 + (a_T * T)$, where Y_i is the mass fraction of product, T is the pyrolysis temperature in units of °C and the coefficients a_0 and a_T are given in this table.

The current study assumes that the distribution of ethylene (C_2H_4) includes all other potential C_nH_m hydrocarbon products. The tar composition is simply defined as the remaining mass not converted in the gas products or left behind as char. The stoichiometric coefficients of each of the reactions in the pyrolysis reactor is determined by the molecular weight of the specified component in order to maintain a mass balance around the pyrolysis reactor. Since coal and char are nonconventional solids, the coefficient is one for each of these. The tar is represented using naphthalene, specifically naptha-1, which is a common product in coal tar and is representative of the molecular weight of tar components.

The pyrolysis process model is developed in Aspen Plus using basic included components and calculation blocks. The process is modeled in three main steps: coal drying, coal pyrolysis, and product separation. The coal drying process model first converts the equivalent moisture content in the coal to water flow rate using a stoichiometry reactor and calculator block. The calculator block reads the moisture content of the coal to determine the water mass flow rate and new mass flow rate of the coal. The drying process in the model uses air sweep gas heated to 132.2°C prior to entering the dryer. The air and water are exhausted in a flash component. An air flow rate of 3 kg/kg coal is sufficient to dry the coal with 10% moisture.

The pyrolysis takes place in a stoichiometric reactor with an accompanying sand separator, which is recycled to represent the recharging of the sand temperature following pyrolysis. The sand flow rate is calculated by the sand calculator block as 20 kg/kg dry coal. The stoichiometry of each of the components in Table 2 is the inverse of the molecular weight, with the fraction of coal converted to each component calculated by the linear equation and coefficients given in Table 2.

The final product separation is simply represented by a component splitter sending the char out the bottom, tar out the middle, and gas out the top. This is not representative of the actual process, since no cooling occurs and the tar is still not condensed, but to represent the mass flow and fraction composition of the gas stream.

The heat required from the nuclear reactor is calculated by the power calculating block, which takes into account the heat required for the drying air and pyrolyzer outlet temperature to be 800°C. This process model is used as the basis for the process modeling effort for this project going forward. Figure 9 shows a screenshot of the coal pyrolysis Aspen Plus model.

Table 3 shows the resulting flow rate for each of the pyrolysis products with a corresponding heat input of 100 MW.

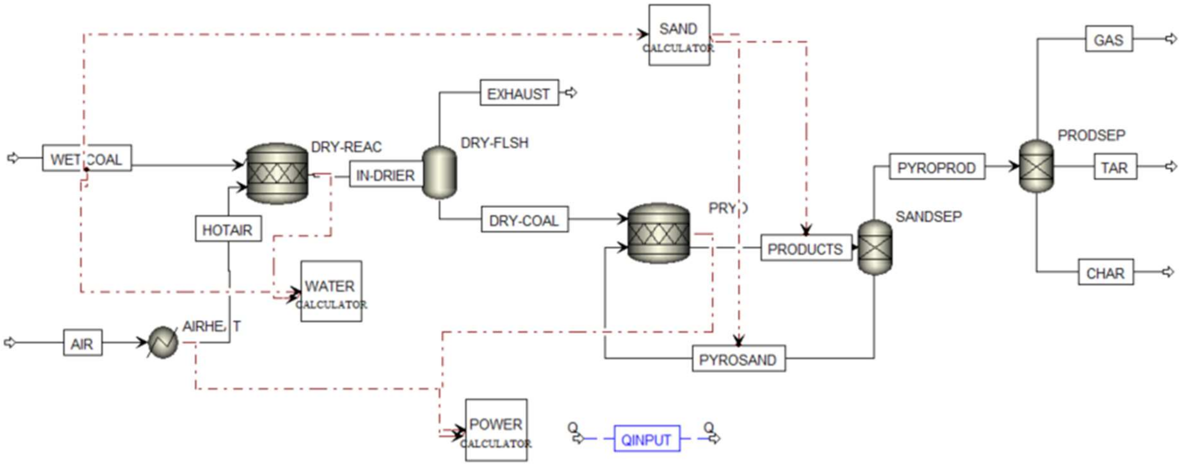


Figure 9. Screenshot of the Aspen Plus pyrolysis modeled as described.

Table 3 shows the results of a first-pass coal pyrolysis at 800°C using 100 MW of external thermal power for the drying process and coal pyrolysis, including the temperature of the stream and mass flow and molar flow of each of the components. The cooling and condensing processes are not included in these results. The inlet wet coal flow is 57.9 kg/sec with an air flow requirement of 156 kg/sec. Coal and char do not have molar flow rates since they are nonconventional solids and do not have a corresponding molecular weight.

Table 3. Results for coal pyrolysis at 800°C with an external heat requirement of 100 MW.

Parameter	**Wet Coal**	**Air**	**Dry Coal**	**Char**	**Tar**	**Gas**
Temperature (°C)	25	20	36.826	800	800	800
			Mass Flows (kg/s)			
H_2O	0	0	0	0	0	4.462
N_2	0	119.665	0	0	0	0
O_2	0	36.335	0	0	0	0
Coal	57.9	0	52.11	0	0	0
Char	0	0	0	26.444	0	0
CO_2	0	0	0	0	0	4.411
CO	0	0	0	0	0	5.062
CH_4	0	0	0	0	0	0.950
C_2H_4	0	0	0	0	0	0.745
H_2	0	0	0	0	0	0.491
NAPHT-01	0	0	0	0	9.547	0
			Mole Flows (mol/s)			
H_2O	0	0	0	0	0	247.658
N_2	0	4,271.69	0	0	0	0
O_2	0	1,135.51	0	0	0	0
CO_2	0	0	0	0	0	100.223
CO	0	0	0	0	0	180.718
CH_4	0	0	0	0	0	59.228
C_2H_4	0	0	0	0	0	26.540
H_2	0	0	0	0	0	243.554
NAPHT-01	0	0	0	0	74.482	0

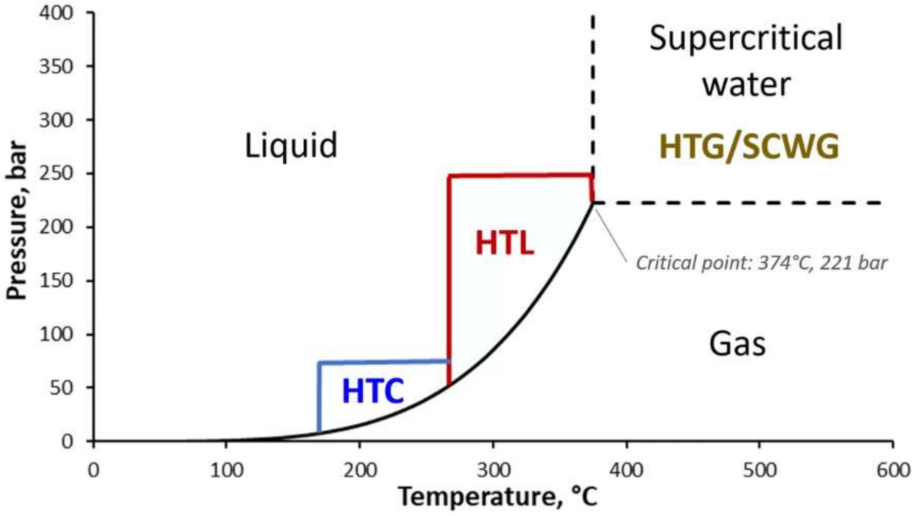
Molar flow is included in addition to mass flow to demonstrate that a substantial amount of CO and H_2 are produced from coal pyrolysis forming synthesis gas. Future work with the pyrolysis model may require the heat load to decrease as well as the temperature as other processes are included in the overall analysis. This will require a change in the fractional conversion of coal to each of the products at the new pyrolysis temperature.

3.3 Hydrothermal Gasification

Hydrothermal methods (hydrothermal carbonization is sometimes referred to as wet torrefaction, liquefaction, and gasification) of converting carbonaceous material are used when the water content of the material is very high. Hydrothermal gasification is the highest temperature operation of the hydrothermal methods, and like gasification, the process targets the production of combustible and usable noncondensable gases, such as CO, H_2, CO_2. Syngas (CO and H_2) selectivity can be high with the addition of specific catalysts (hydroxides, metals, and activated carbon). When hydrothermal gasification (HTG) is operated at supercritical conditions, it is also known as supercritical water gasification (SCWG) because in this variation the process is operated at a temperature and pressure above the supercritical point for water and involves the gasification of wet carbonaceous material at around 400–700°C and 280–

300 bar (around 4,060 psi). Post-gasification cleanup steps include a salt separator separating inorganic solid residues, such as potassium, phosphorous, and an ammonia-rich water stream. These products are principle ingredients for fertilizer (nitrogen, phosphorous, potassium or N-P-K). Relevant applications could include those with very wet organic feedstock, such as organic effluent from industry, liquid residues from methanation units, liquid effluents from livestock manure, and sewage treatment plant sludge.

Figure 10 shows the temperature and pressure operating condition regimes for the three different hydrothermal conversion processes, hydrothermal carbonization, hydrothermal liquefaction, and SCWG. The figure shows the critical point for water of 374°C and 221 bar beyond which the process needs to run.



Hydrothermal processes and approximate regions of operation with reference to the pressure:temperature water phase diagram. (HTC: Hydrothermal carbonisation, HTL: Hydrothermal liquefaction, HTG/SCWG: Hydrothermal gasification/supercritical water gasification.)

Credit: Judd Water & Wastewater Consultants

Figure 10. Temperature and pressure operating condition regimes for three different hydrothermal conversion processes: hydrothermal carbonization, hydrothermal liquefaction, and HTG or SCWG (Sludge Processing 2020b).

The advantages of hydrothermal gasification include the ability to take very wet feedstock and eliminate the predrying prerequisite as with pyrolysis and conventional gasification. Also, because the water is beyond its critical point, the water stays liquid due to the high pressures. Hydrolysis reactions become very relevant in the material decomposition. At supercritical conditions water is able to act as a solvent of organic compounds because of the decreased dielectric constant, which may be a result of hydrogen bond distortion. Acid-base reactions may be catalyzed by the increased ionization to H+ and OH^- in the supercritical water. Hydrogen peroxide or nitric acid can be added to increase the reaction rate and yields. The ionic hydrothermal gasification reactions may have better mass transfer, diffusivity, and selectivity versus the free radical pyrolysis reactions. The disadvantages of supercritical HTG include the high capital and operating costs involved with the high pressure and corrosion prevention and mitigation requirements of the process.

One study looked at the SCWG of lignite coal for hydrogen production at 500–650°C and 200–300 bar catalyzed with potassium hydroxide and calcium oxide (Zhang et al. 2010). The process was tuned for maximum hydrogen production. Lignite is a low-rank coal with a high moisture content and low carbon content (25–35%). Lignite is the youngest of the coal categories and as such hasn't been exposed to high heat and pressure to concentrate the carbon content like the other categories of coal. Coal is ranked by its heating value, which correlates proportionally to carbon content and inversely to moisture content. From low heating value to high heating value, the coal categories are lignite, subbituminous, bituminous, and anthracite. Low-rank lignite coal could be a possible candidate for supercritical HTG because of its existing high moisture content and the incentive to trade the cost of the high pressure required for supercritical HTG and the costs of predrying requirements for conventional pyrolysis (when the main goal is char and liquid production) or gasification (when gas production is the main goal).

3.3.1 Supercritical Water Gasification for the Gasification of Tars and Oils

Hydrothermal gasification is a process designed for treating wastewater with a catalyst, resulting in treated water and a carbon-rich gas. Recently, researchers have explored this process for the direct gasification of biomass and upgrading bio-oil from pyrolysis.

There have been some studies of the results of hydrothermal gasification on coal and petroleum products. Morimoto et al. (2008) explored the use of hydrothermal extraction and gasification to dewater brown coal, resulting in treated water, hydrogen, methane, and CO_2 products. The hydrothermal extraction yielded 30% at 300°C and 46% at 350°C. Over 97% of the extraction product was gasified through catalytic hydrothermal gasification at 350°C.

Miri, Shahraki, and Motahari-Nezhad (2019) studied syngas production from the hydrothermal gasification of pyrolyzed fuel oil. This process included a CO_2 sorbent to increase the H_2 output in syngas. CaO is a CO_2 sorbent in the gasification process because of its abundance compared to other sorbents. Figure 11 provides a schematic of the Aspen model used for the study.

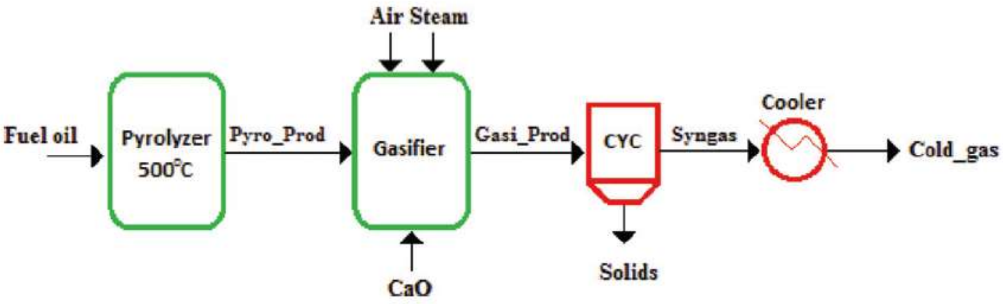


Figure 11. A schematic diagram of the Aspen Plus model (Miri, Shahraki, and Motahari-Nezhad 2019).

The study found that an increase from 700 to 850°C shows an increase in H_2 concentration, with a slight decrease at 900°C. The effect on CO_2 was exactly opposite. At 900°C and a 0.5 CaO-to-fuel ratio, gas composition was recorded as a function of steam to fuel. Increasing the steam-to-fuel ratio from 0.5 to 1, H_2 and CO_2 concentrations increased because the additional steam improves the water-gas shift and steam reforming reactions. The steam-to-fuel ratio had a lower effect on H_2 concentration than on the other gases, and it is better to prevent an over-injection of steam because it can increase tars. Increasing the CaO-to-fuel ratio from 0.5 to 1.0 greatly reduced the amount of CO_2 produced and increased H_2 production. The carbonation reaction also decreased the CO fraction. Hydrothermal gasification, especially with the addition of a CO_2 sorbent, has a great potential to convert coal pyrolysis oil to syngas and reduce the need for CO_2 capture.

Hydrothermal gasification will be used in the carbon refinery to break down the heavy compounds of tar and pyrolysis oil into syngas. With an efficient hydrothermal gasification process there should be very little tar product remaining. As is detailed in Section3.3.3, the market demand for coal tar is decreasing due to health concerns. Syngas is a much more desirable product to maximize in the refinery.

3.3.2 Alternative Option: Coal Tar Distillation

Fractional tar distillation refers to separating components in a chemical mixture by taking advantage of the difference in their boiling points (Satyendra 2018). Since the quality of the coal tar is dependent on the coal pyrolysis process and the specific composition of the feed coal, and since there are large numbers of chemical compounds available in coal tar, the design and composition of the tar distillation plant varies with the type of tar and compounds required to be distilled. Hence, it is rare that two tar distillation plants are similar. Furthermore, separating crude coal tar into its different components would cost more than the compounds are worth (Britannica 2022). Therefore, the refining processes are designed to produce only the most valuable compounds and send the residual for bulk sale.

Although no two tar-producing plants are the same, they all rely on the same basic steps (Cheremisinoff, Rosenfeld, and Davletshin 2008). In general, two distillate streams are produced in coal tar pitch manufacturing. The first distillate represents about 20% of the tar, usually referred to as chemical oil. The second and heavier distillate is the creosote fraction, used to make wood preservative feedstock and sold into the carbon black manufacturing market. This stream accounts for roughly 30% of the crude tar. The remaining fraction (roughly 50%) is carbon pitch (also called coal tar pitch), sold in the aluminum and graphite industries. Coal tar pitch essentially drives the domestic tar distillation business. Tar is heated to 100–400°C at atmospheric pressure in distillation stills to produce the coal tar pitch (See Figure 12).

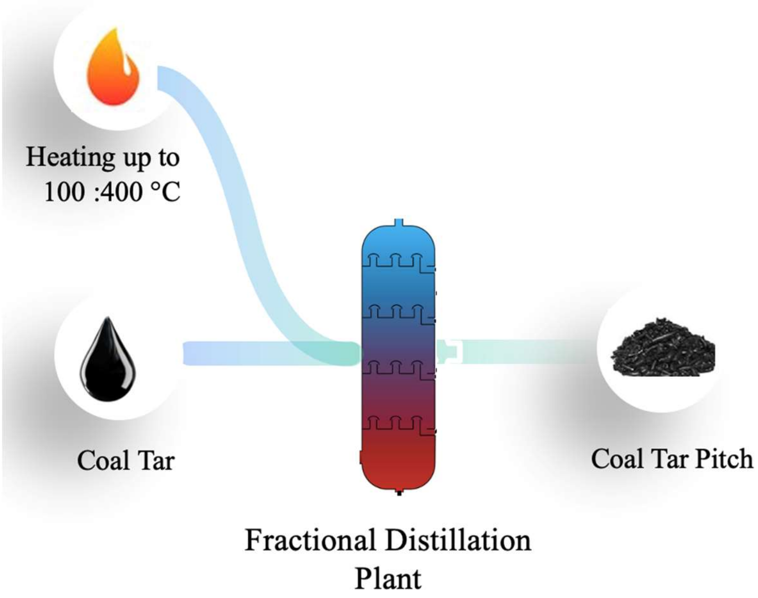


Figure 12. A simple representation of producing the coal tar pitch via fractional distillation.

3.3.3 Market Considerations

Coal tar pitch is used as a binding agent in the manufacturing of graphite electrodes (used in electric arc furnaces in steel plants) and carbon anodes (utilized in aluminum smelters). Coal tar pitch is the best raw material for carbon electrodes for aluminum production and other uses because of its economic feasibility and durability as a binder (Emergen Research 2021). The rising aluminum demand is a significant driver of the global carbon tar market. Aluminum is regarded as a valuable material for vehicle components due to its strength and low weight and the implementation of stringent regulations regarding vehicle emissions making manufacturers adopt lightweight aluminum components. The production of 100 lb of aluminum requires around 10 lb of coal tar pitch. Global annual primary aluminum production was 5,744 metric tons in May 2021 (Technavio 2021).

Manufacturers worldwide have switched from traditional steel production to electric arc furnace steel production, which requires graphite electrodes. Therefore, the global carbon tar market will also be driven by the steel industry's steady growth (Future Market Insights 2018).

While coal tar pitch also enjoyed a significant percentage of the roofing market for more than 50 years, its share has significantly shrunk during the last 20 years due to the confirmation of potential carcinogenicity in coal tar pitch volatiles or fumes (Mellott n.d.).

Driveways and asphalt pavement sealants also contain 20–35% coal tar pitch. The United States Geological Survey (USGS) estimates that 85 million gallons of coal-tar-based sealant—enough to cover 170 square miles—is laid down each year. But the shiny, black sealant contains toxic compounds known as polycyclic aromatic hydrocarbons, or PAHs, that can seep into the environment. As a result, several cities have banned the sale and use of PAHs, and some localities are suing coal tar sealant manufacturers to get them to pay for the costly environmental cleanups (Keller 2021).

Scientific investigations by the National Institute for Occupational Safety and Health have established that, when heated, coal tar pitch yields PAHs that are suspected or known carcinogens. To reduce these emissions at the coal and coke facilities where the coal tar originates, efforts were subsequently made to remove as much of the potential carcinogen as possible during processing. This resulted in an overall reduction of the coal tar pitch available to the marketplace and, therefore, an increased base cost for coal tar pitch (Mellott n.d.).

Due to its applicability as a binding agent, 81% of coal tar is used for electrode production in the aluminum industry (Global Monitor 2020). The global market is mainly impacted by production in China and the U.S. Koopers Inc. recently shut down plants in the U.S., UK, and China due to oversupply in the market. From

Table 4, primary production of aluminum peaked in 2019 but decreased over 19% though 2021 (U.S. Geological Survey 2022). Secondary production is also on the decline. Primary smelters operated at 49% capacity in 2020, down from 60% in 2019 due to global overcapacity. There are only six smelters operating in the U.S. in Missouri, Indiana, Kentucky (two), South Carolina, New York (2022).

Prices increased from $0.897/lb in 2020 to $1.40/lb in 2021 due to lasting effects of the COVID-19 pandemic, which caused supply chain disruptions. Aluminum production employment decreased from 32,900 in 2019 to 30,000 in 2021.

Coal tar is also used in road construction products (McIntyre 2022). Several locations have banned coal tar in sealcoat products, including the District of Columbia ; Austin, Texas; Dane County, Wisconsin; Washington; and several municipalities in Minnesota and other states (Coal Tar Free USA 2017).

Table 4. U.S. aluminum market statistics (U.S. Geological Survey 2022).

	2017	**2018**	**2019**	**2020**	**2021**
Production:					
Primary	741	891	1,093	1,012	880
Secondary (from old scrap)	1,590	1,570	1,540	1,420	1,500
Secondary (from new scrap)	2,050	2,140	1,920	1,630	1,700
Imports for consumption:					
Crude and semimanufactures	6,220	5,550	5,280	4,320	4,800
Scrap	700	695	596	542	700
Exports:					
Crude and semimanufactures	1,330	1,310	1,110	905	820
Scrap	1,570	1,760	1,860	1,850	2,000
Consumption, apparent	5,680	4,900	4,980	3,980	4,300
Supply, apparent	7,730	7,040	6,910	5,620	6,000
Price, ingot, average U.S. market (spot), cents per pound	98.3	114.7	99.5	89.7	140
Stocks, year-end:					
Aluminum industry	1,470	1,570	1,600	1,490	1,700
London Metal Exchange, U.S. warehouses	254	186	120	235	100
Employment, number	31,700	31,600	32,900	30,100	30,000
Net import reliance as a percentage of apparent consumption	59	50	47	39	44

1,000s of metric tons unless otherwise noted

U.S. refinery net production of asphalt and road oil showed little gain in 2021 and has been in steady decline since 2005 (U.S. Energy Information Administration 2022b). Production in the U.S. fell by 34% between 2005 and 2021. The production trend for the Appalachian area is nearly flat; although, it did grow by less than 9% from 2005 through 2021 (U.S. Energy Information Administration 2022a).

Because of health concerns and the decline in U.S. aluminum production, carbon black can be produced by thermal decomposition of the coal tar. Carbon black is widely used as a colorant and reinforcing filler in tires and rubber products (Fortune Business Insights 2020). The tire manufacturing industry in the U.S. was worth $148.4 billion annually. The rising tire market reflects the consumer demand for lightweight vehicles. The U.S. is a leading automotive industry, accounting for nearly a fifth of the global industry (Expert Market Research 2022). The carbon black market is expected to grow at a compound annual growth rate (CAGR) of about 5.2% in the forecast period of 2022–2027.

The global market size for carbon black is $25.95 billion annually with a CAGR of 6.0% (Grand View Research 2018b). The tire production segment is expected to have a 4.3% CAGR with additional growth coming from use in plastics. The manufacturing process induces harmful emissions; as such, the industry is highly regulated. Carbon black was added to California's list of substances known to cause cancer in February 2003. The fee on board (FOB) price in March 2022 was $2,645 per MT (ChemAnalyst 2022a). The FOB price is referring to the price up to the shipping point, where buyers are responsible for costs after the product is loaded on a vessel for international export. In recent quarters, new vehicle production has been weak, so replacement tires have been leading the industry. Imports of carbon black from Asia and Europe have declined some as a result of high freight costs.

3.3.4 Benefits for Hydrothermal Gasification at the Refinery

Hydrothermal gasification will be used in the carbon refinery to break down the heavy compounds of tar and pyrolysis oil into syngas. There are three significant advantages of hydrothermal gasification to convert tar to syngas versus finding a market for distilled tar, namely, 1) the pyrolysis of coal results in a small fraction of tars and oils, and the temperature and residence time of the pyrolysis process can be easily adjusted to decrease the fraction further, 2) the market for tar appears to be decreasing in the U.S., and a national policy to ban coal tar could remove those markets at any time, and 3) it appears to be more economically favorable. With an efficient hydrothermal gasification process, there should be very little tar product remaining. Overall, syngas is a much more desirable product to maximize in the refinery.

3.4 Syngas Cleaning

The refinery will utilize a method of syngas conditioning proposed in TEV-1567. The conditioning process eliminates the need for water-gas shift reactors by adding H_2 from the electrolyzer directly into the syngas stream. The optimal H_2-CO ratio to the methanol synthesis reactors is:

$$\frac{H_2 - CO_2}{CO + CO_2} = 2.10$$

The authors of TEV-1567 found that, when the shift reactors are eliminated, the CO_2 concentration entering the Rectisol® unit is reduced from 30% in the baseline case to 6% and the CO_2 concentration in the purified syngas is reduced from 3% in the baseline case to 1%. Correspondingly, the H_2-CO ratio decreased from 2.45 to 2.20. Rectisol® capacity and utility usage were also reduced by more than 50% compared to the baseline case.

3.4.1 Mercury Removal

One potential method for absorbing mercury from flue gas is activated carbon. Although this method is very effective, removing almost all the mercury from flue gas, this method can be restrictive for large applications due to the cost of activated carbon. However, with the refinery's ability to produce its own activated carbon, a small portion could be diverted from the output stream, at the expense of an opportunity cost of selling this activated carbon as opposed to the material cost of purchase.

Marczak et al. (2019) studied the mercury removal efficiency from subbituminous and lignite combustion flue gas using various sorbents, one of which was activated carbon. In this current study, bituminous coal is pyrolyzed rather than combusted, so the results will not be exactly applicable but likely somewhere in between the sorbent results for subbituminous coal and lignite combustion.

The high specific surface of activated carbon gives it an equilibrium sorptive capacity more than 50 times higher for mercury than coke, lignite, and lignite dust char. In testing, it removed 92.9% of mercury from the subbituminous coal and 80.3% of mercury from lignite flue gas. The rubber char and granular rubber char sorbents were only slightly more effective, as shown in Figure 13.

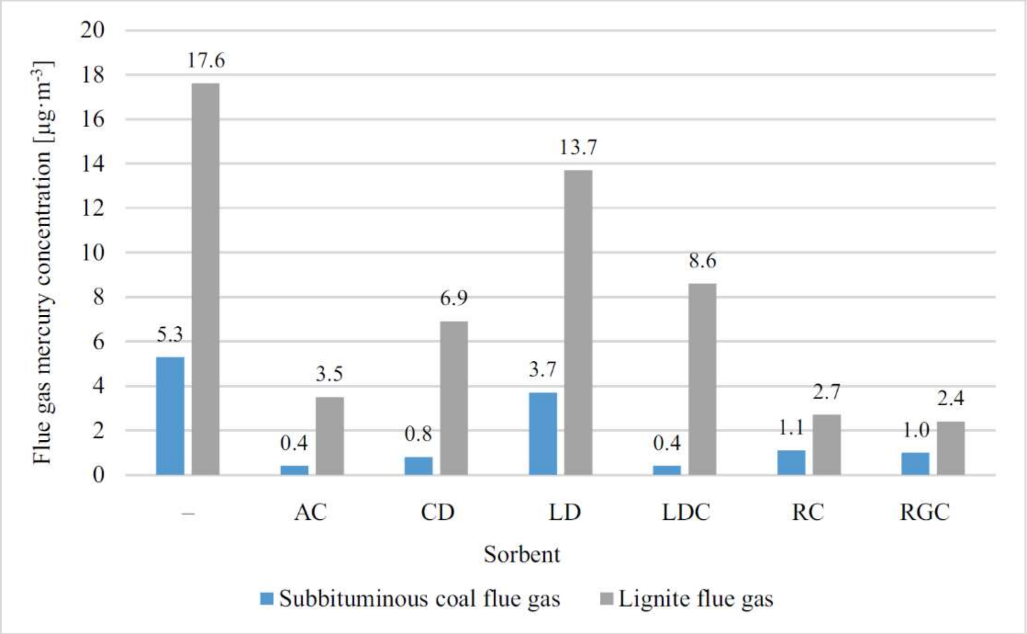


Figure 13. Concentration of mercury in raw flue gas compared to cleaned flue gas emitted to the atmosphere (Marczak et al. 2019) using activated carbon (AC), coke dust (CD), lignite dust (LD), lignite dust char (LDC), rubber char (RC), and rubber granulated char (RGC).

3.4.2 CO_2 Removal

Two commercial processes for the removal of CO_2 are being considered for the carbon refinery: Selexol™ (Figure 14) and Rectisol® (Figure 15). Both processes remove CO_2 and H_2S from flue gases, and the names refer to the solvents used in the process. Selexol™ is a mixture of dimethyl ethers of polyethylene glycol, and Rectisol® is chilled methanol, which will be produced as a product of the refinery. Another significant difference between these processes is that Rectisol® is much more energy intensive because of the refrigeration required to maintain the solvent.

Mohammed et al. compared these two processes for the precombustion removal of CO_2 and H_2S in an integrated gasification combined cycle plant. The Rectisol® process was able to remove more CO_2 and sulfur than the Selexol™; although, the estimated capital cost of Rectisol® is expected to be higher due to the complexity of the process. There are also additional risks involved in the Rectisol® process because of the toxicity of methanol as a solvent. The authors recommended that Rectisol® would be more suitable for downstream applications in which high syngas quality is required, while upstream removal from Selexol™ would offer better performance at the integrated gasification combined cycle plant. From this conclusion, it is likely that the Rectisol® process will be necessary to integrate into the carbon refinery.

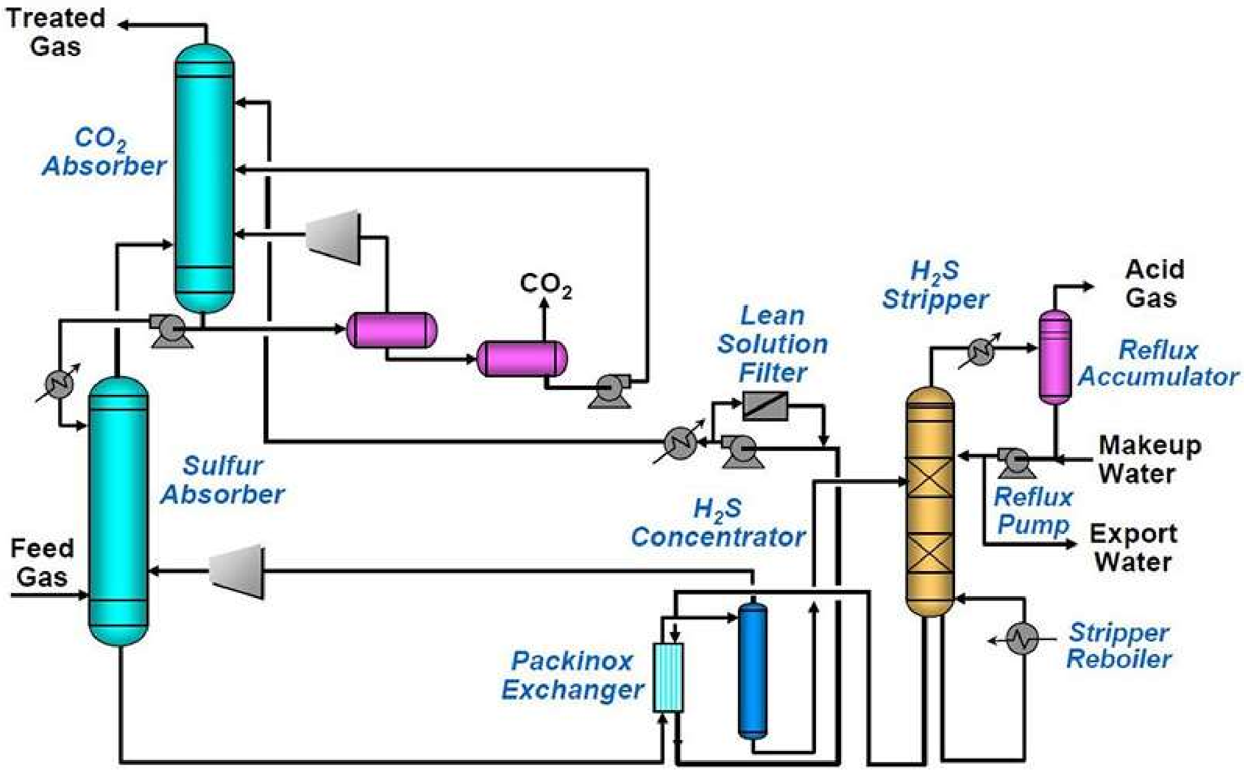


Figure 14. A schematic of the Selexol™ process (National Energy Technology Laboratory, n.d.).

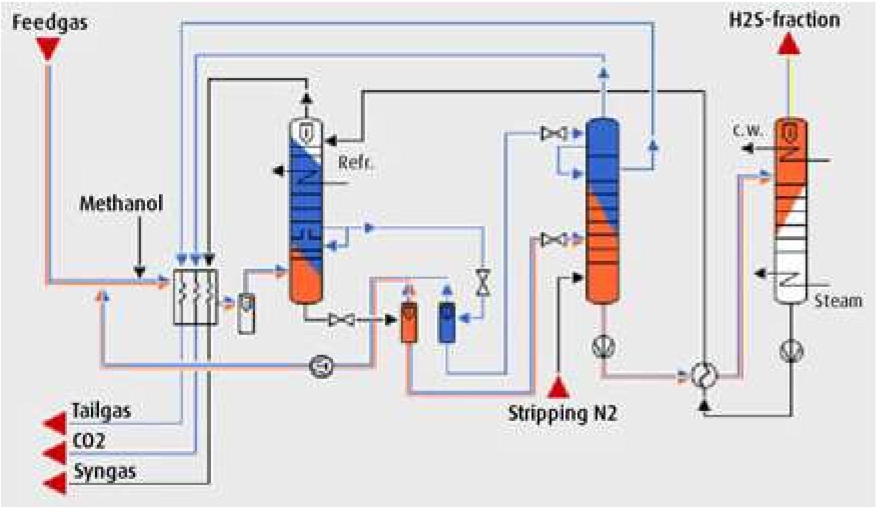


Figure 15. A schematic of the Rectisol® process. Includes refrigerant (Refr.) and cooling water (C.W.) streams. (Linde Engineering n.d.).

3.4.3 Sulfur Recovery

An optional addition to syngas cleaning is sulfur recovery through the Claus process, as shown in Figure 16. The addition of the Claus process would produce a stream of pure sulfur, which could be another marketable product for the refinery. The Claus furnace combines H_2S gas and oxygen to form sulfur dioxide and water, which is shifted to produce pure water and pure sulfur. Another benefit to adding sulfur recovery is that it will reduce gaseous waste products to the atmosphere, which is another goal of the refinery.

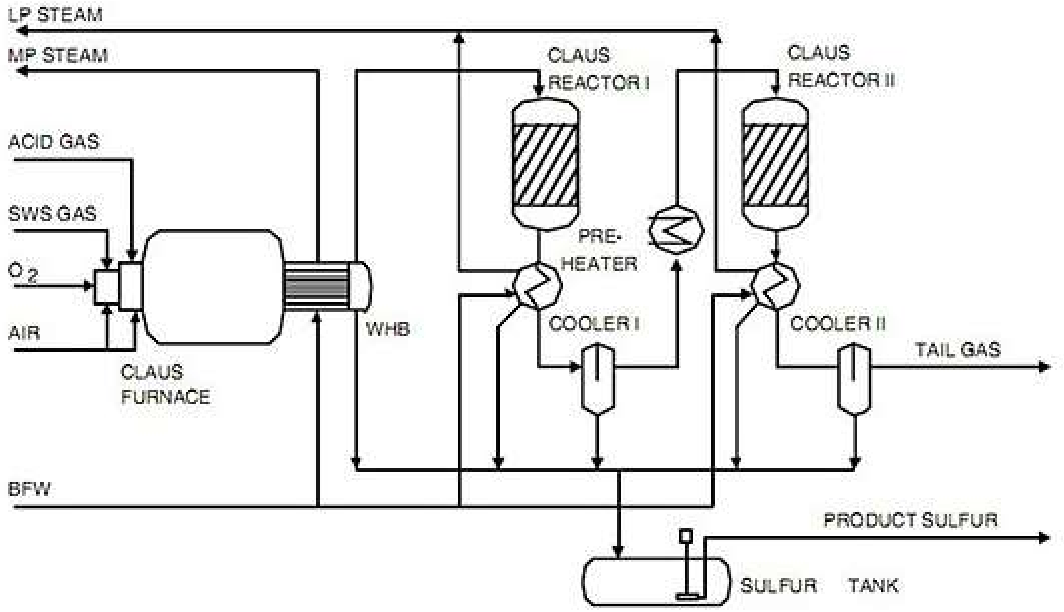


Figure 16. A schematic of the Claus process (low pressure [LP], medium pressure [MP], waste heat boiler [WHB], boiler feed water [BFW], sour water stripper [SWS]) (National Energy Technology Laboratory, n.d.).

3.5 Conversion of Syngas to Products

Two major pathways for syngas conversion are Fischer-Tropsch and methanol synthesis. The primary application for the Fischer-Tropsch process is fuels, though waxes and olefins can also be obtained. Olefins and gasoline can also be obtained from methanol. Methanol was chosen as the syngas conversion pathway because of the variety of products that can be produced from it, as shown in Figure 17. The flexible nature of the modeling means that, in the future, Fischer-Tropsch or another conversion process can be added.

Syngas produced during pyrolysis and gasification will be converted into methanol. Methanol is chosen as the syngas conversion pathway because of the variety of products that can be produced from it, as shown in Figure 17. Because this study focuses on non-fuel product pathways, the methanol-to-olefins process, with polymers created downstream, is the goal of the methanol pathway. The methanol-to-olefins and olefins-to-polymers processes are well-established. The market analysis in the following subsections narrow down options for product pathways.

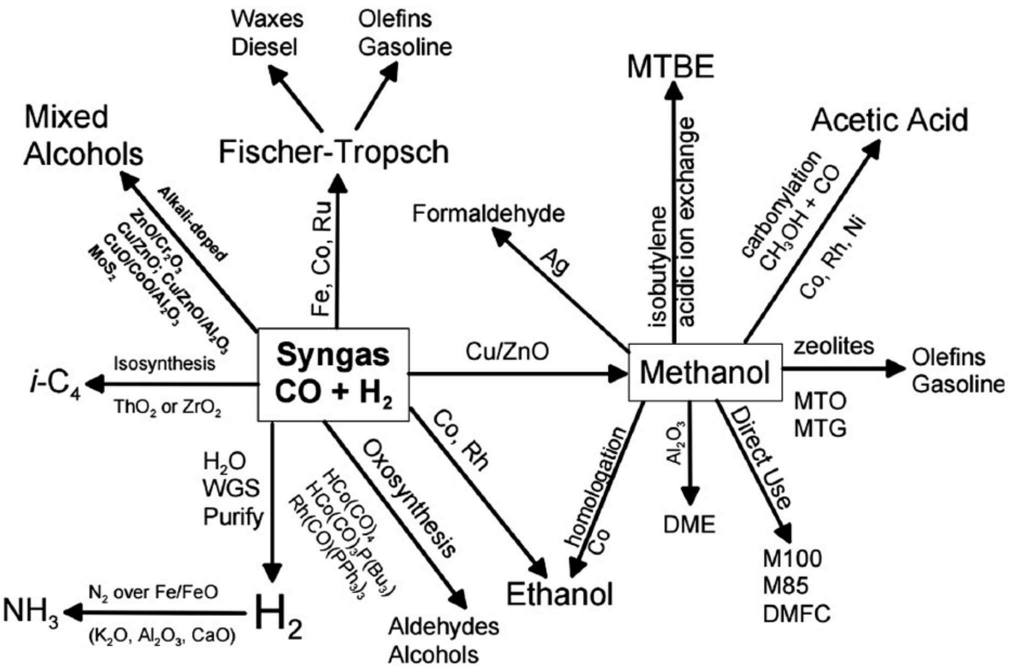


Figure 17. Some established fuels and chemical products pathways using synthesis gas (Spath and Dayton 2003).

3.5.1 Syngas Conversion to Methanol

The synthesis of methanol from syngas is an established process, but the syngas is typically obtained through steam reforming of methane (natural gas). The major compounds in syngas, CO and H_2, are combined in a reactor to form methanol and water. It also generally results in excess H_2, which can be purged and reused in the refinery. The process is described in Figure 18.

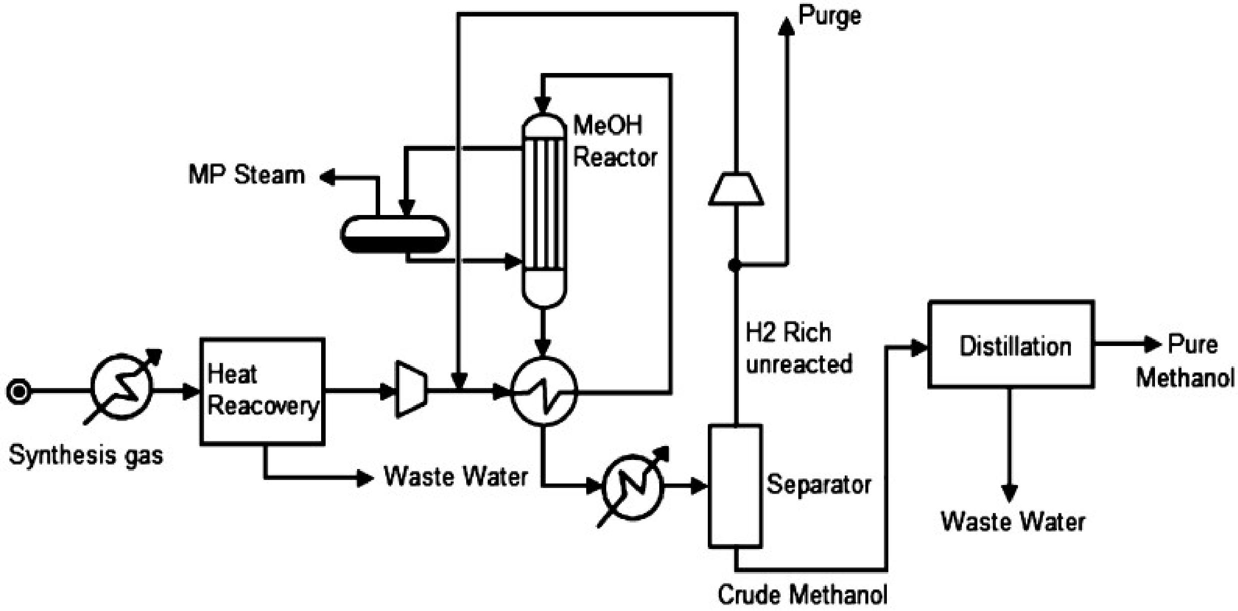


Figure 18. A schematic of the process to convert syngas to methanol (Alarifi, Elkamel, and Croiset 2013).

3.5.2 Methanol Conversion to Olefins and Polymers

There are several pathways to obtain ethylene and propylene from methanol. The first is the MTO process patented by Universal Oil Products (UOP), now Honeywell UOP. The advanced methanol to olefins (MTO) process yields a greater than 89% yield and a flexible 1.25-to-1.8 propylene-to-ethylene ratio. Processes like this one that prioritize the production of olefins over gasoline and liquefied natural gas (LNG) are advantageous because the profit margin for olefins is higher (DuBose 2015). Another process is the dimethyl ether methanol-to-olefins process, which produces about a 1-to-1 ratio of ethylene to propylene (Ye, Tian, and Liu 2021). An alternative to these processes methanol-to-propylene (MTP), which prioritizes the production of propylene. The process, patented by Lurgi, delivers polymer-grade propylene from a zeolite catalyst and produces about 66% propylene with the next highest fraction of gasoline at 25% (Air Liquide Engineering and Construction 2022). The MTP process is shown in Figure 19.

The polymerization process, shown in Figure 20, requires hydrogen, a comonomer, and a catalyst. The double bonds in ethylene and propylene are broken down in the presence of the catalyst, and the atoms connect into chains. The compositions of the components and conditions of the reactor determine the amount of branching and chain length (Sharpe 2015). This process is a good fit for the refinery because the nuclear power source will provide hydrogen to the polymerization process without emitting carbon.

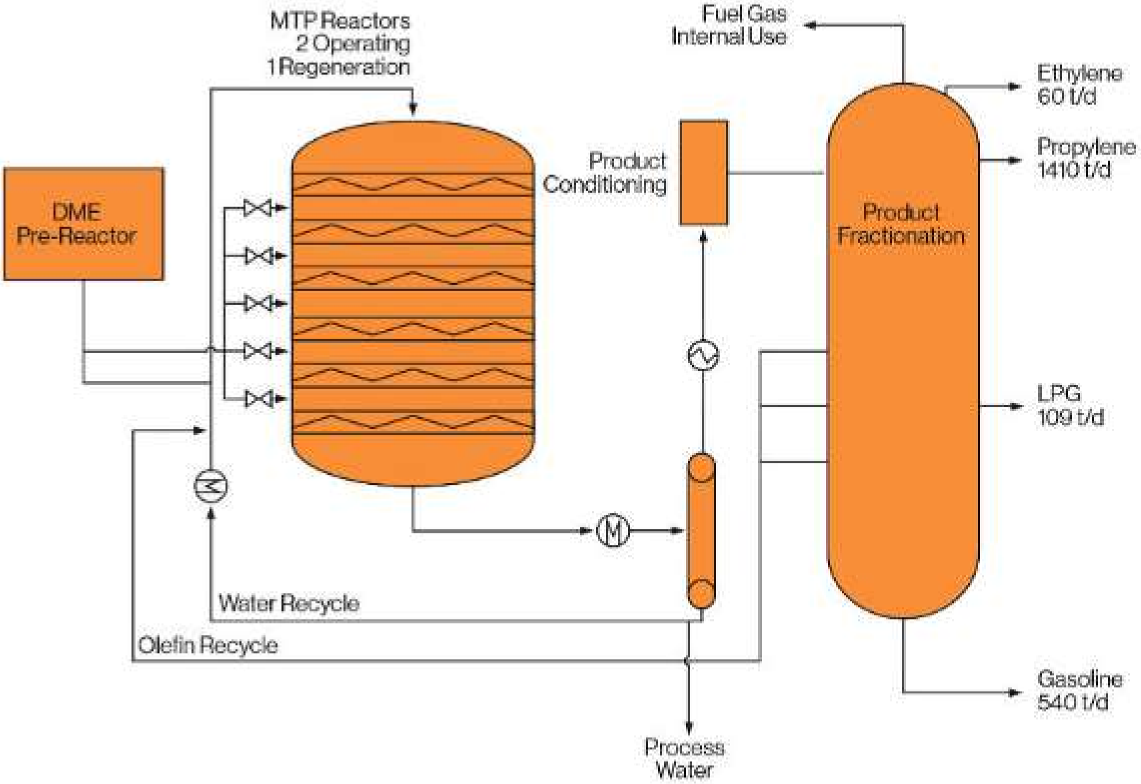


Figure 19. MTP process diagram (Air Liquide Engineering and Construction 2022).

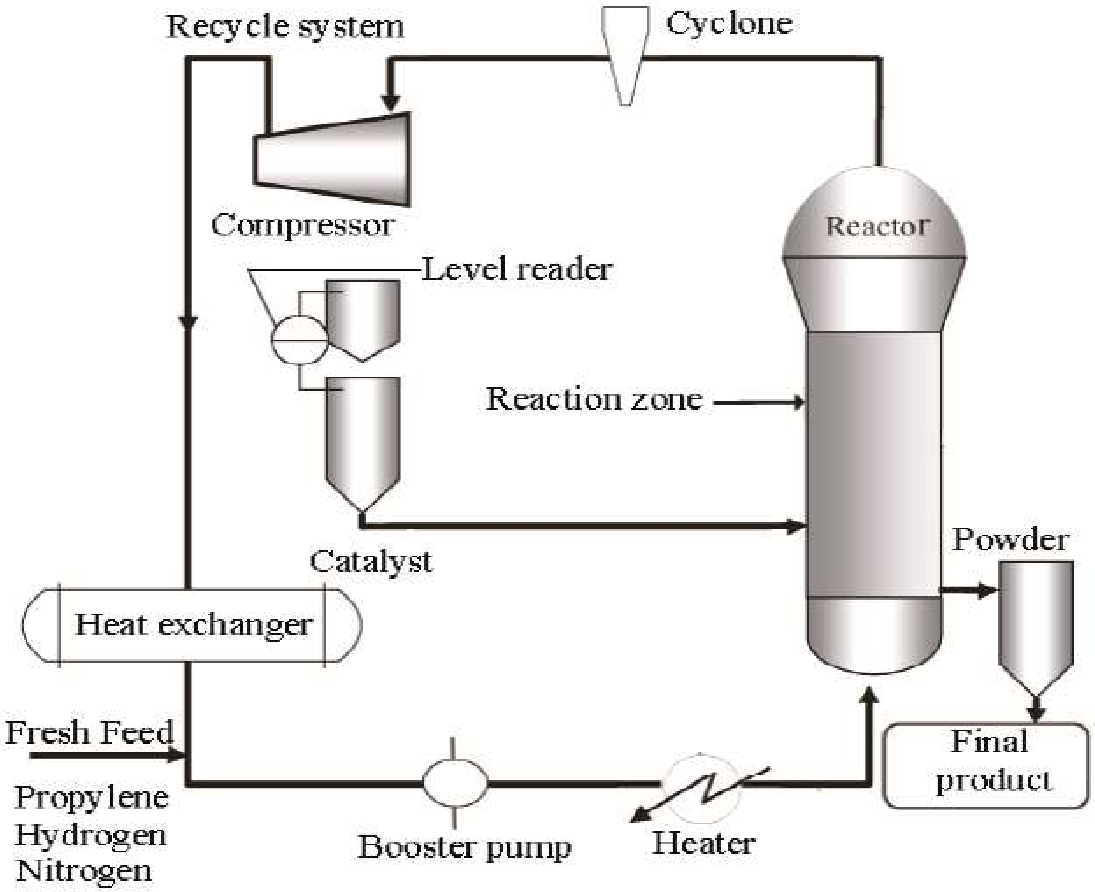


Figure 20. Propylene polymerization process diagram (Khan, Hussain, and Mujtaba 2014).

3.5.3 Market Analysis

Methanol is a valuable commodity that can be formed from many carbonaceous sources and can be converted to fuels, chemicals, and plastics. While methanol could be sold directly from the refinery, the goal is to drive as much of the downstream processes as possible using nuclear heat and electricity.

Polyethylene

The total market size for polyethylene is estimated at $111.8 billion with an expected CAGR of 3.2%. The North American FOB price in March 2022 was $4,110 per ton (ChemAnalyst 2022b). According to Grand View Research (2019), increased environmental protection and health warnings are dampening demand. As such, biobased polyethylene is beginning to show up on the market. Along with biobased feedstocks, coal and shale gas are other means of production. Products like packaging, cable coverings, buckets, lids, and containers are popular uses of polyethylene. Large plastics producers, like Dow Chemical, BASF, Chevron Phillips, and Huntsman, are major players in this market, which could make it difficult for smaller companies to compete.

Plastics industry employment statistics apply to both polyethylene and polypropylene markets since Bureau of Labor Statistics (BLS) industry data does not address the two products separately. Data for 44 states was available from BLS without disclosure concerns. In 2021, there were 11,471 plastic product manufacturers across the United States, according to Figure 21. California was home to 1,102 establishments with a combined total of 38,680 employees. Ohio led the nation with 44,406 employees and 667 establishments. The combined Appalachian region had almost 221,000 employees working in the plastics industry at over 3,600 establishments, according to Figure 22 (Bureau of Labor Statistics 2022).

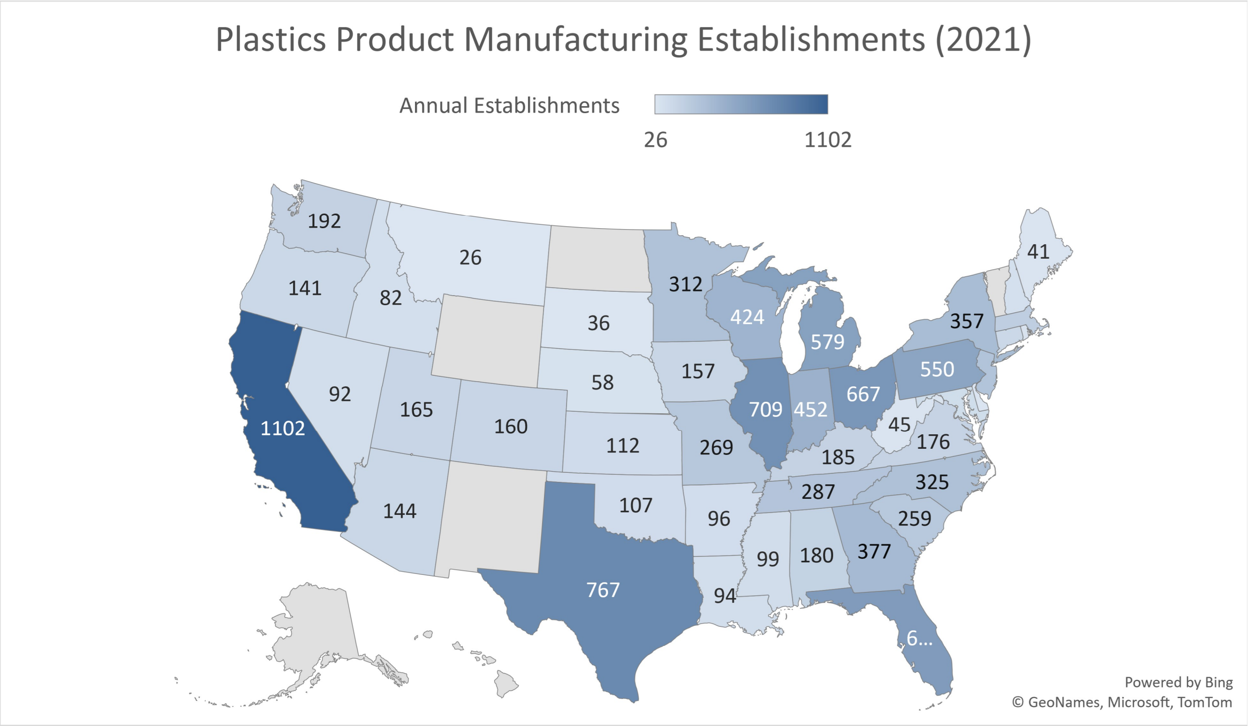


Figure 21. Locations of plastic product manufacturing establishments (Bureau of Labor Statistics 2022).

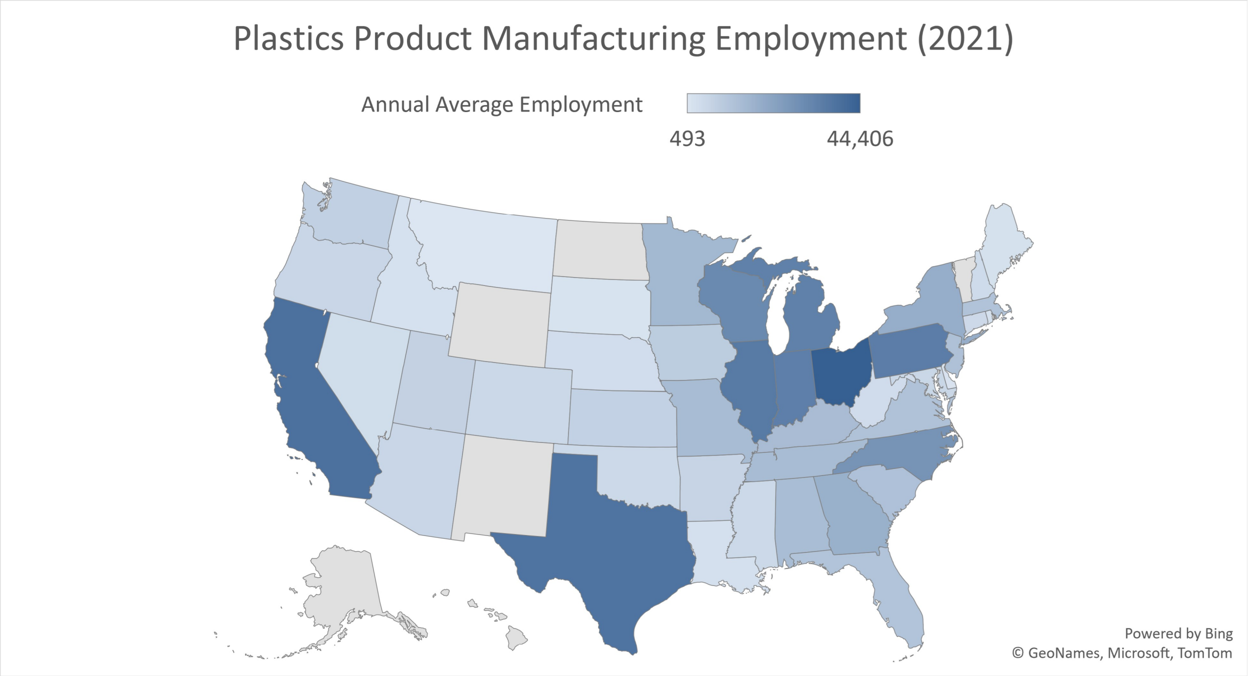


Figure 22. Locations of plastic product manufacturing employment (Bureau of Labor Statistics 2022).

Polypropylene

The annual market size of the polypropylene is estimated at $117.8 billion. The North American price for the product was $1,957 per ton in March 2022 (ChemAnalyst 2022c). Polypropylene market growth is expected to follow the production of lightweight vehicles. Grand View Research (2021c) expects the market to increase by 3.4% CAGR. Packaging accounted for 35.8% of global revenue. Other uses are found in medical devices and construction. Electronics industries use the product as a lightweight alternative to metal construction. Healthcare-related manufacturers are using polypropylene for safety kits that include masks and gowns. The pandemic put many of these products in short supply and now provides a stable base for market performance. Grand View Research indicated the market is comprised of small- to medium-sized companies but also includes large companies, like SABIC, Exxon Mobil, China Petrochemical Corp, BASF SE, Eastman Chemical, and LG Chem.

Polyisobutylene

The global market size for polyisobutylene is $1.87 billion annually. Based on findings presented by Grand View Research (2021b), the polyisobutylene market is expected to grow at 3.2% CAGR in the U.S., slightly behind the global growth rate of 4.0%. Manufacturers of adhesives, sealants, fuel additives, and lubricants are frequently using polyisobutylene. The product is also used in tubeless tire applications to prevent oxygen transfer (seeping air). Telecommunication-related industries also use polyisobutylene for a cable insulation material, which puts the product in high demand for Asian and U.S.-based auto and electronics producers. Lubricant applications made up more than half of industry revenues.

Butyl Rubber

The global market size for butyl rubber is $5.21 billion (Grand View Research 2017). Emerging economies in Brazil, Russia, India, and China are consuming more tires as vehicle sales increase. According to Grand View Research (2017), the butyl rubber market achieved an 6.9% CAGR. From Figure 23, annual motor vehicle production in the U.S. fell by 28% between 2016 and 2020 according to the Bureau of Transportation Statistics (2022). The largest decline was in passenger cars, which fell by 51%. Commercial vehicle production fell by 17% between 2016 and 2020. Recent supply chain constraints caused by the COVID-19 pandemic are likely causing further disruption in motor vehicle production.

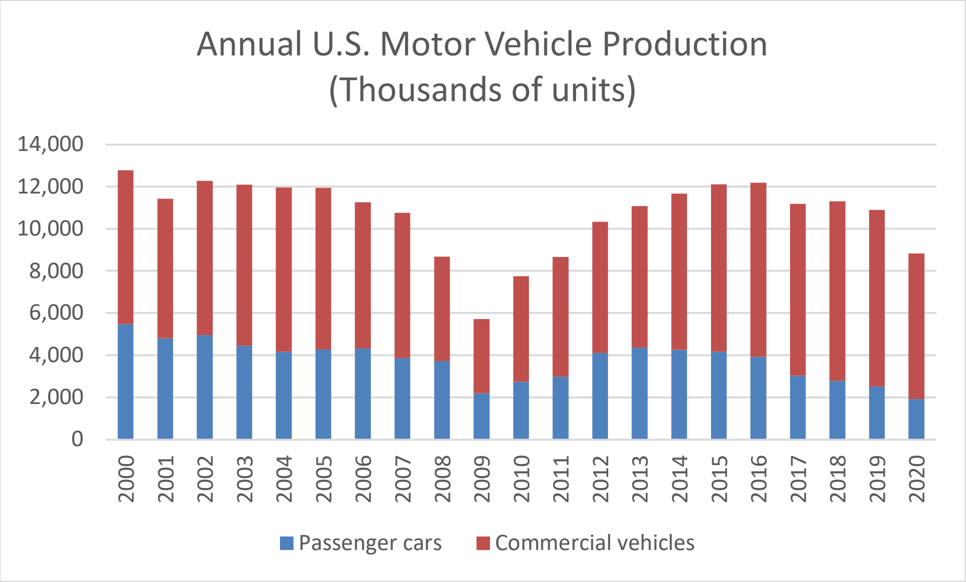


Figure 23. Annual U.S. motor vehicle production from 2000–2020 (United States Department of Transportation 2022).

According to the U.S. BLS, in 2021 there were an average of 473 tire manufacturing establishments across the United States (Bureau of Labor Statistics 2022). The BLS was able to release employment and establishment data on 25 states without disclosure concerns. California led the country in the number of tire manufacturing establishments (38) but only showed a total of 384 employees. In contrast, South Carolina had 16 establishments but led the country with 9,720 employees. Although Virginia and West Virginia did not show a presence of tire manufacturing facilities, the surrounding states showed a significant tire manufacturing presence. Figure 24 and Figure 25 show the number of tire manufacturing establishments and average employment according to BLS records.

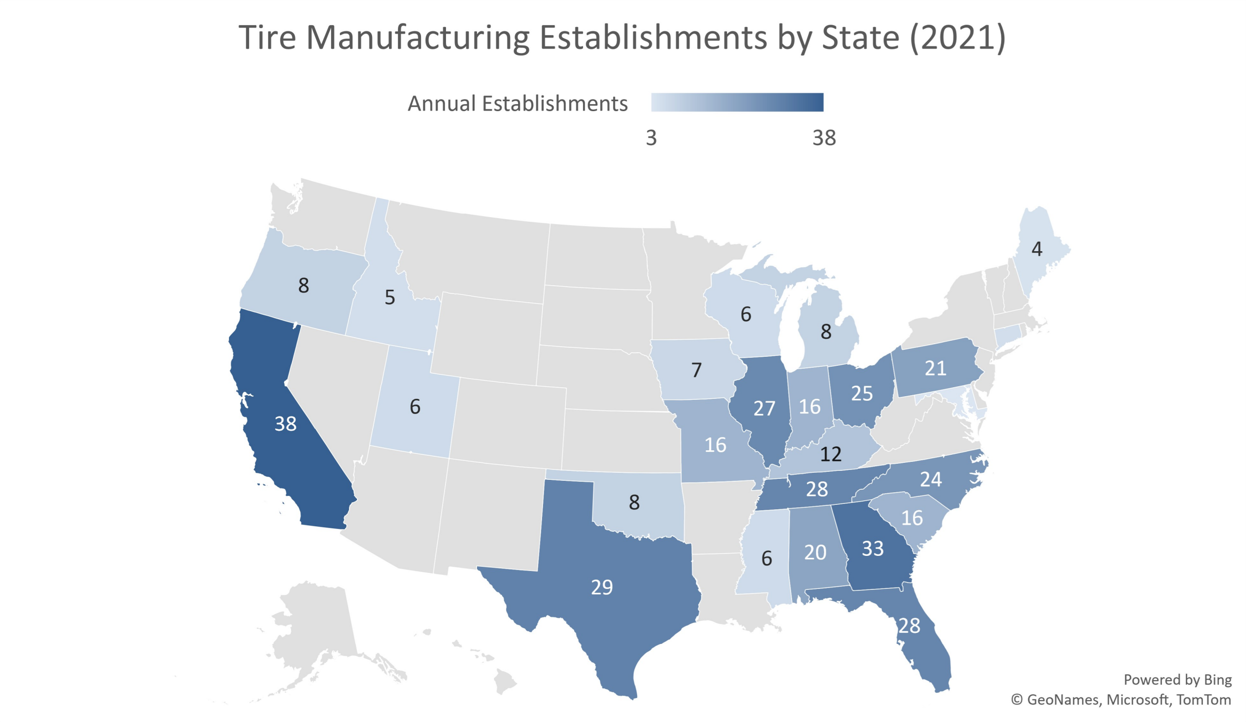


Figure 24. Locations of tire manufacturing establishments (Bureau of Labor Statistics 2022).

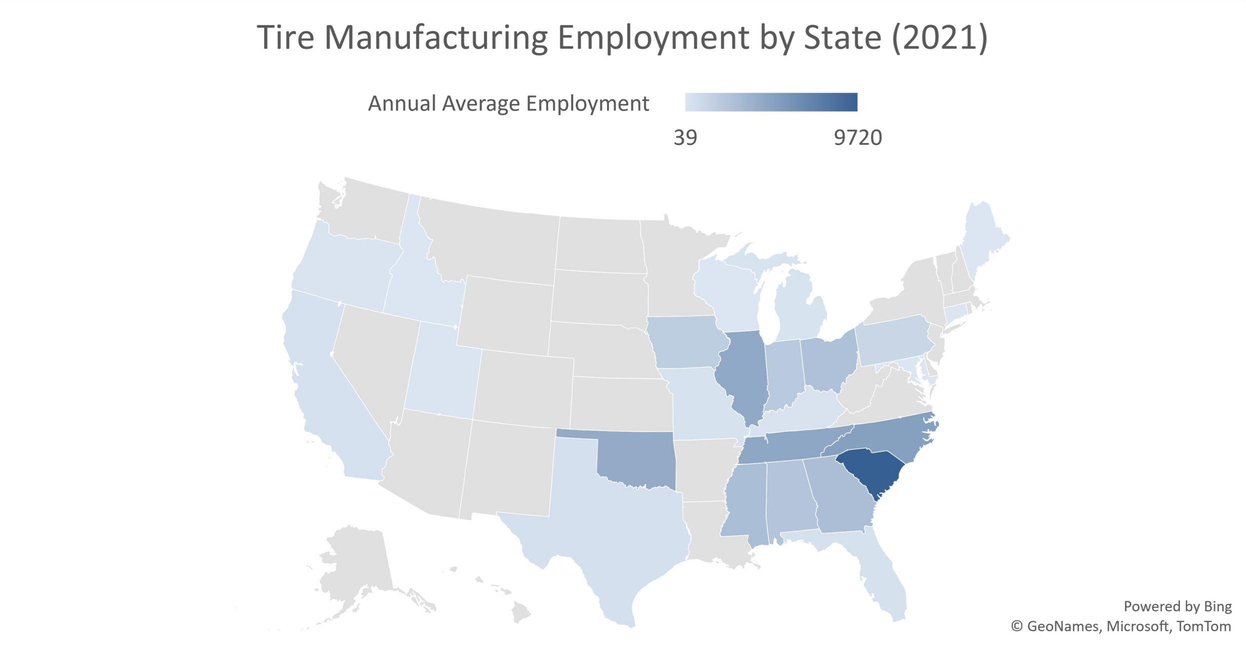


Figure 25. Locations of tire manufacturing employment (Bureau of Labor Statistics 2022)

3.6 Electrolysis

The electrolysis process uses energy in the form of electricity to split water into hydrogen and oxygen. At the carbon refinery, hydrogen and oxygen would be invaluable commodities in the various chemical conversion processes that could be employed to generate valuable products. Hydrogen is required for the production of syngas; for example, many chemicals as well as the coal have a much higher carbon to hydrogen content than biomass and as such any product from coal will need to be adjusted to increase the hydrogen to carbon ratio depending on the downstream chemical conversion process used. Hydrogen produced from electrolysis can be used to fill this need. Also, hydrogen is used as a reducing agent in fuel refining processes such as hydrofining and hydrocracking to remove sulfur and other contaminants, reduce the aromatic content, and to crack larger carbon chains into smaller target product chains. In FT, hydrogen is used to convert heavy waxes, which are the crude product of FT synthesis, into lighter and more usable transportation fuels. Oxygen can be used in chemical conversion processes or for oxy-firing fossil-fueled industrial heating. With oxy-firing, nitrogen in the air is not introduced to the process, which enables cleaner burning without a potential for NO_x and also enables an easier separation of CO_2 from the offgas. The separated CO_2 could be used as well for chemical conversion processes, as discussed in the next section.

Electrolysis is extremely energy intensive such that a large majority of the production costs of hydrogen via electrolysis is attributable to the electricity cost. As such, electrolysis processes could pair well with nuclear power where very large amounts of carbon-free electricity can be available to generate carbon-free hydrogen (and oxygen as a co-product). There has been significant work worldwide, especially in the past decade, to research technology, methods, manufacturing and supply chain solutions to decrease the cost of making hydrogen via electrolysis, especially using carbon-free electricity. Three general types of technology are currently being employed to produce hydrogen, including alkaline, polymer electrolyte membrane / proton exchange membrane (PEM) also commonly called low-temperature electrolysis (LTE), and solid oxide electrolyte cells (SOEC) also commonly called high-temperature electrolysis or high-temperature steam electrolysis (HTSE). The fourth up and coming technology is proton conducting solid oxide electrolysis cells, which is mostly in the laboratory research phase at present. Alkaline electrolysis is the most mature technology, with few advances happening to increase efficiency. PEM-LTE has begun to overtake alkaline electrolysis in commercial applications due to various advantages. HTSE-SOEC has the potential to increase the efficiency and reduce the cost of hydrogen production beyond PEM technology. HTSE, by virtue of being able to utilize thermal energy to be able to gain a better efficiency that PEM can uniquely pair well with large sources of thermal energy such as nuclear power plants to produce large amounts of hydrogen at higher efficiency.

3.6.1 Low-Temperature Electrolysis

Low-temperature electrolysis requires ambient temperature water, as opposed to HTSE which requires water high temperature pre-heat, which is preheated by the heat from the stack. HTSE is a good fit where it is desired to produce large amounts of centrally produced hydrogen near a source of thermal energy (nuclear power, industrial heat, or solar-thermal power plant). LTE might be a better fit in distributed scenarios where it is desired to produce smaller amounts of hydrogen from distributed generation sources such as photovoltaic solar and wind turbines.

Commercial options for LTE are Alkaline Electrolysis (AE) and Proton Exchange Membrane (PEM) Electrolysis. AE technology is more established than PEM; although, PEM is approaching technical maturity and economy of scale (International Renewable Energy Agency 2018). PEM electrolyzers have a faster response time than AE, which is why they are generally preferred in studies of future projects (International Renewable Energy Agency 2019). Both technologies are worth investigating for this project.

Scaling an electrolysis unit could have an effect on the system electricity and water demand. The Fraunhofer Institute provides a recent and detailed analysis of scaling for both PEM and AE technologies. Table 5 and Table 6 show the effects of scaling from a 5-MW electrolysis unit to a 100-MW unit. Although the data shows a slight increase in specific energy demand due to scaling, this difference is likely due to rounding as opposed to an actual difference in performance. In the sensitivity studies, electricity and water demand will not scale due to increases in hydrogen production.

Table 5. Scaling results for AE (Holst et al. 2021).

Case	Unit	5 MW	100 MW
Water demand	kg/h	958	19,152
Specific water demand (electricity)	kg/MW	191.6	191.52
Specific water demand (hydrogen)	kg/kgH_2	9.3	9.26
Hydrogen production rate	kg/h	103	2,069
Specific hydrogen production rate	kg/MWh	20.6	20.69
Specific energy demand	kWh/kgH_2	52.8	53.4

Table 6. Scaling results for PEM electrolysis (Holst et al. 2021).

Case	Unit	5 MW	100 MW
Water demand	kg/h	896	17,930
Specific water demand (electricity)	kg/MWh	179.2	179.30
Specific water demand (hydrogen)	kg/kgH_2	9.14	9.11
Hydrogen production rate	kg/h	98	1,969
Specific hydrogen production rate	kg/MWh	19.6	19.69
Specific energy demand	kWh/kgH_2	54.5	55.1

Scaling up of the electrolysis system does provide some cost benefits; however, the cost of electrolysis is dominated by the electricity cost at high operating capacities (International Renewable Energy Agency 2018). As electrolysis technologies continue to advance, this initial investment cost is expected to become less significant.

Figure 26 illustrates how the levelized cost per kg of H_2 of an electrolysis unit changes as the annual operating hours increase. The levelized cost of hydrogen (LCOH) starts to level out around 3,650 hours. This introduces an important consideration when sizing the H_2 unit; if it is operated at a low utilization rate, sizing down the electrolyzer and introducing storage may be a more cost effective option.

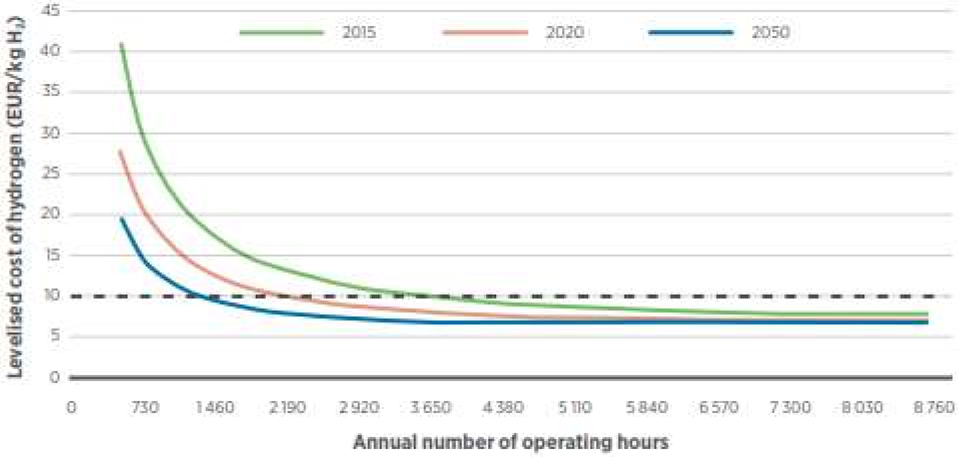


Figure 26. Estimated levelized cost of hydrogen versus annual operating hours (International Renewable Energy Agency 2018).

Scaling has a significant impact on the cost per kW of an electrolysis unit. There are many components of the electrolyzer that do not scale up as the size of the unit increases, as shown in Figure 27 and Figure 28. Notably, the specific costs for engineering, instrumentation, compression, and balance of plant cathode greatly decrease.

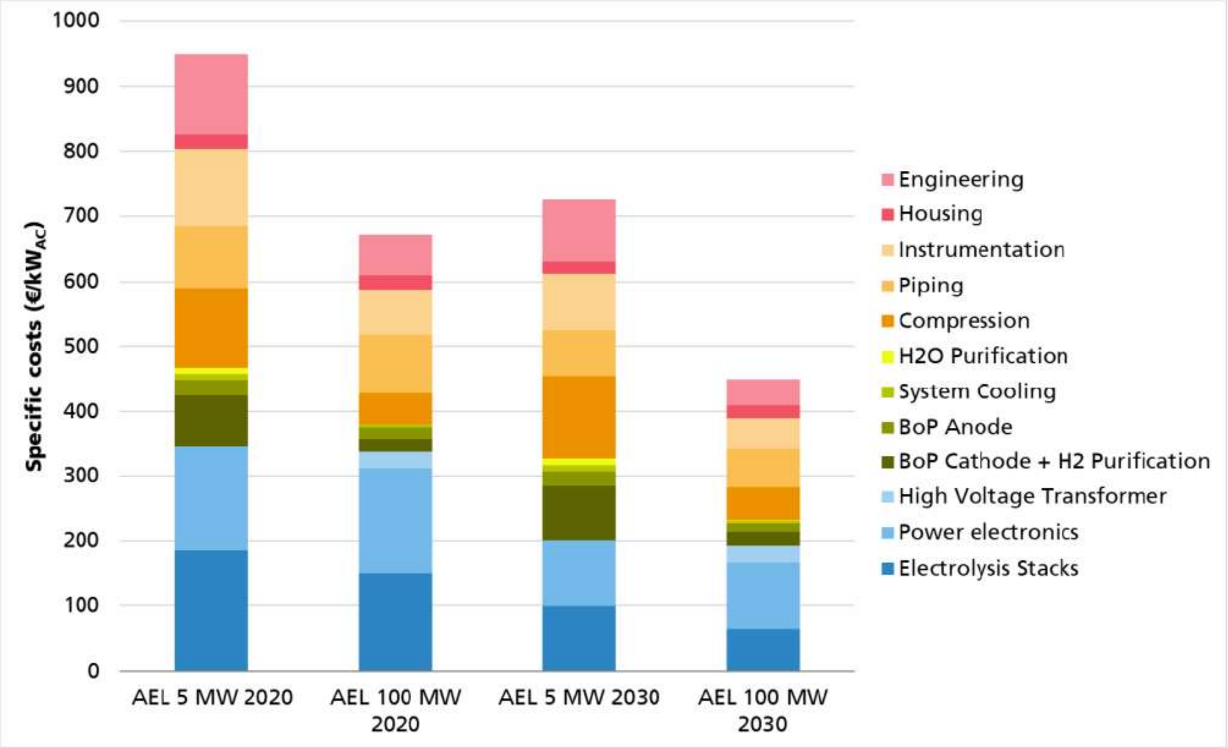


Figure 27. Specific costs of 5-MW and 100-MW next generation alkaline electrolysis systems (including mechanical compressors) for the design scenarios 2020 and 2030.

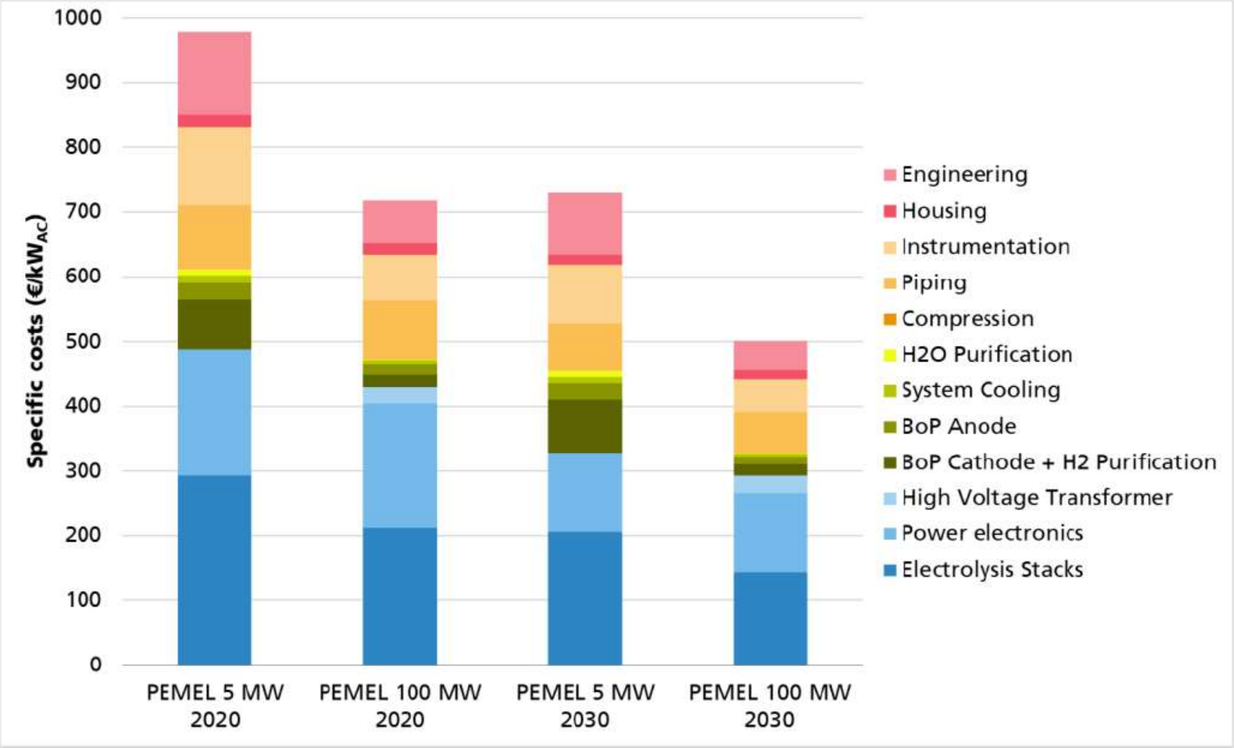


Figure 28. Total PEM electrolysis system cost for all analyzed scenarios. Mechanical compressors are not required (Marius Holst et al. 2021).

The total costs of the 5-MW and 100-MW units were estimated from Figure 27 and Figure 28 and converted from 2020 euros to 2020 USD. The two units were then used as references to solve for a scaling factor in the following equation:

$$Capital\ Cost_{100\ MW} = Capital\ Cost_{5\ MW}\left(\frac{100\ MW}{5\ MW}\right)^{Scaling\ Factor}$$

The results of this calculation for PEM and AE are listed in Table 7. In general, the AE unit is less expensive than the PEM unit. This is likely due to its relative maturity on the market. Both technologies have a scaling factor close to 0.9.

Table 7. Capital cost and scaling factors for LTE (Marius Holst et al. 2021).

	5 MW	**100 MW**	**Scaling Factor**
AE	~$1084/kW	~757/kW	0.880
PEM Electrolysis	~1117	~820	0.897

3.6.2 High-Temperature Steam Electrolysis

A recent report published by INL shows detailed performance and cost estimates for a hypothetical near-term large-scale HTSE plant integrated with a 1-GW nuclear power plant, where the hydrogen plant is assumed to use all the energy output of a typical light boiling-water reactor, including thermal and electrical energy (Wendt and Knighton 2022a). One advantage of HTSE is that, by using thermal energy from a large source (like a nuclear power plant), the efficiency gain versus PEM can be realized. The thermal energy is used to overcome the large heat of vaporization of water to generate steam. Then recuperating and topping heat exchangers are used to elevate the temperature to the needed ~800°C for HTSE.

Figure 29 shows a sensitivity study reproduced from this report on the LCOH produced by HTSE. This figure shows that using baseline conditions analyzed a levelized cost of hydrogen of \$1.86/kg-H_2 could be achievable. The figure also shows the potential LCOH movement dependent on various key parameters such as the price of the electricity used for electrolysis, direct capital costs of the electrolysis system, electrolysis stack costs etc.

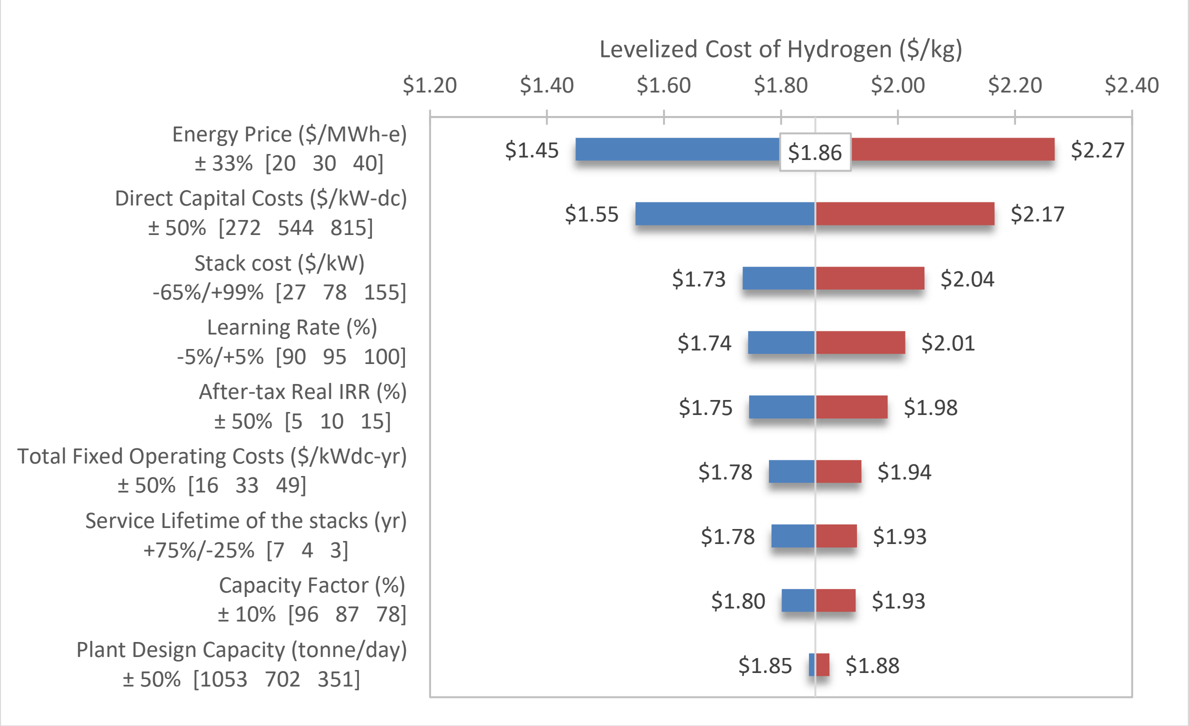


Figure 29. Sensitivity of LCOH to selected constant hydrogen production case input parameters.

Importantly Figure 32 copied from the reference report shows the competitiveness of producing hydrogen via HTSE with the incumbent method of industrial hydrogen production, steam methane reforming, as a function of electricity price to the electrolysis plant and natural gas prices in MMBTU. This chart shows that at baseline assumptions of electricity price of \$30/MWh, that HTSE produced hydrogen using some heat from a light water reactor (LWR) could be competitive with hydrogen produced via steam methane reforming depending on the price of natural gas. These charts do NOT take into account recently congressionally passed hydrogen production tax credits (PTC) as a result of the Inflation Reduction Act (IRA) of 2022. The IRA provides for up to \$3/kg-H_2 PTC for 10 years which could definitely make HTSE extremely competitive with steam methane reforming while the credit is valid. In the 10-year timeframe allotted for the PTC it is expected that HTSE technology can improve to the point where it could be competitive on its own after the PTC expiration.

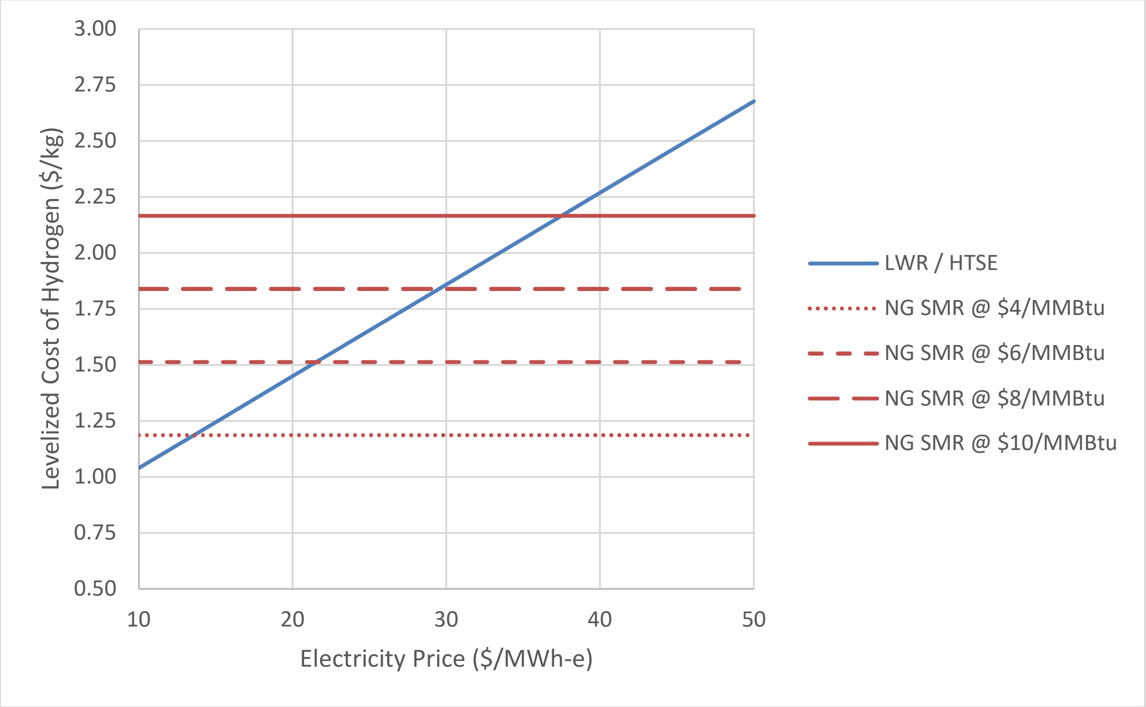


Figure 30. LWR-integrated HTSE plant LCOH as a function of electricity price. Also shown is the NG-SMR LCOH corresponding to selected natural gas pricing levels.

Table 8 shows the performance and cost information of a 1-GW-scale HTSE plant from the referenced report. This shows that an LCOH of as low as \$1.86/kg-H_2 could be possible with near-term SOEC technology paired with an existing light-water reactor (LWR) at large-scale hydrogen production

Table 8. Summary of 1-GW design-scale HTSE plant performance and costs (Wendt and Knighton 2022a). Reproduced with permission.

Parameter	Value	Notes
Plant design capacity	702 metric tonnes hydrogen per day	
Power requirement	1,000 MW-dc 1,076 MW-ac	Direct current (DC) power corresponds to stack power input Alternating current (AC) power corresponds to total power requirement balance of plant (BoP, ac power to rectifier, pumps, compressors, topping heaters, etc.)
Thermal requirement	188.2 MW-t	Provided directly by nuclear process heat
Efficiency (higher heating value - HHV)	90.2%	Includes both thermal and electrical energy consumption
Stack pressure	5 bar	Based on maximizing system efficiency by trending operating pressure and steam utilization versus system efficiency
Steam utilization (conversion of reactant steam)	80%	Based on maximizing system efficiency by trending operating pressure and steam utilization versus system efficiency
H_2 product pressure	20 bar	
H_2 product purity	99.9 mol% H_2	Water condensation from cooling and compression only; no pressure swing adsorption (PSA) and temperature swing adsorption (TSA) steps included
Electricity required	36.8 kWh-e/kg-H_2	Process model result
Thermal energy required	6.4 kWh-t/kg-H_2	Process model result
Technology horizon	NOAK, 95% learning rate	95% corresponds to a 5% cost reduction with every doubling of the number of units produced
Stack cost	\$78/kW-dc	Value reported from design for manufacturing (DFMA) analysis of an electrode-supported cell stack with 1,000 MW/year manufacturing rate (James and Murphy 2021)
Service life	4 years	Assumes annual stack replacements to restore the HTSE plant design capacity rating at the start of each operating year, which is consistent with the current technology case (Peterson, Vickers, and DeSantis 2020)
Direct capital cost	\$544/kW-dc	Includes the capital cost of the nuclear process heat delivery system; for HTSE applications not including nuclear process heat input, the capital expenses (CAPEX) would be reduced accordingly
Total capital investment	\$703/kW-dc	Includes indirect costs (site preparation, engineering & design, contingency, land, etc.)

3.7 CO_2 Utilization

At this carbon refinery, the goal is to utilize the CO_2 generated by the pyrolysis process to produce more value-added products, rather than relying on CO_2 sequestration. Key considerations for this product pathway are that the synthesis utilizes feedstocks already produced at the refinery (hydrogen, oxygen, water, carbon dioxide), the product is either in demand locally or has a generally large market, and the addition of process equipment does not create a significant detriment to the overall profitability of the refinery.

CO_2 is already a valuable feedstock used directly and indirectly across the food, fuel, and chemical industries. Expanded interest in CO_2 utilization in recent years has resulted in even more opportunities to prevent CO_2 from being released into the atmosphere as a waste gas. Figure 31 describes some of the processes in which CO_2 can be transformed.

Table 9 shows some of the applications for CO_2 utilization and their production rates.

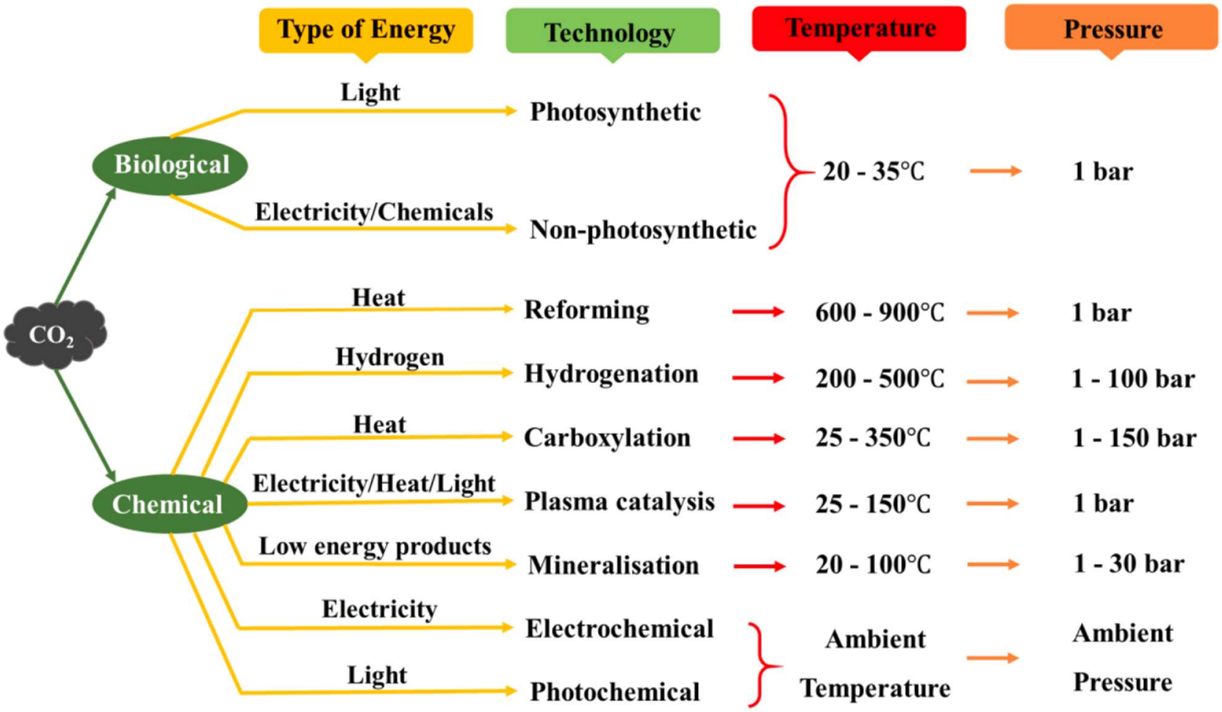


Figure 31. Pathways for CO_2 conversion (Kamkeng et al. 2021).

Table 9. Products and applications for carbon dioxide utilization (Kamkeng et al. 2021).

Utilization Mode	Application and Product	CO_2 Used (MT/yr)	Production (MT/yr)
Direct Uses	Enhanced oil and gas recovery	25.0	25.0
	Food preservation	8.2	8.2
	Industrial gases	6.3	6.3
	Carbonated drinks	2.9	2.9
	Total	42.4	—
Indirect Uses	Urea	132.0	180.0
	Inorganic carbonates	70.0	250.0
	Methanol	10.0	60.0
	Formaldehyde	5.0	25.0
	Dimethyl ether	5.0	20.0
	Tertiary butyl methyl ether	3.0	40.0
	Algae	2.0	1.0
	Polymers	1.5	15.0
	Acrylates	1.5	3.0
	Carbamates	1.0	6.0
	Formic acid	0.9	1.0
	Organic carbonates	0.5	5.0
Total		232.4	—

The five options selected to explore for carbon utilization are formic acid, acetic acid, urea, methanol, and formaldehyde for their recent interest or commercialization, large market opportunities, or INL mission interest. Each of these products is analyzed in this section from a technical and financial perspective as well as an overall market perspective.

The first technical aspect for evaluating these products is the rate of CO_2 utilization. The goal of the carbon capture and utilization process in the refinery is to utilize all CO_2 that would otherwise be emitted or sequestered. A product with a high CO_2 utilization has the benefit of requiring smaller equipment and could fit into a smaller market size. Alternatively, a product with a lower CO_2 utilization rate could have a high price and large market that would justify additional capital costs for its production. Table 10 shows the carbon utilization rates for six products along with other material inputs.

Table 10. Carbon dioxide and hydrogen demands for carbon utilization products (CarbonNext 2017).

Application or Product	Ton of CO_2 Used per Ton of Product	H_2 Requirement	Other Noncatalytic Inputs
Formaldehyde (CH_2O)	1.467	0.067	N/A
Methanol (CH_3OH)	1.375	0.188	N/A
Formic acid (CH_2O_2)	0.96	0.043	N/A
Urea (CH_4N_2O)	0.73	0	Ammonia
Acetic acid (CH_3COOH)	0.47	0	Methane

3.7.1 Formic Acid

Formic acid (FA) is a high-demand product with a variety of markets and uses. FA is typically produced through the carbonylation of methanol to form methyl formate, followed by the hydrolysis of methyl formate. The hydrolysis process produces an aqueous FA product of about 85% purity.

Recently, the market for FA as a hydrogen carrier has gained traction, with commercial processes in development. There are two major CO_2 reduction processes in development: CO_2 electrolysis with water and the synthesis of CO_2 and H_2. Both processes could be easily integrated into the carbon refinery with readily available sources of steam, electricity, hydrogen, and carbon dioxide.

Rumayor, Ramos, and Irabien (2018) compared a model of a CO_2 electrolyzer to a synthesis process modeled by Pérez-Fortes and coworkers, based on a lab-scale patented design from Schaub et al. The comparison considered the production of 1 kg FA at a commercial concentration of 85 wt%. From Table 11, the major differences between the two processes are the amount of electrode or catalyst utilized and steam consumed. In the electrolytic reduction case, most of the steam is consumed in the distillation process. The recirculated case consumes about a third of the steam of the single pass but still more than twice that demanded by the synthesis process. The synthesis process also consumes half the electricity of the recirculated process, even including the electricity for hydrogen electrolysis. The main benefit of the electrolytic reduction process appears to be the great amount of hydrogen produced through the process. In the carbon refinery, the hydrogen electrolysis process will be designed to meet the demand of all refinery components. The electrolytic reduction process could be useful for the refinery if it were to replace hydrogen electrolysis to provide hydrogen to other processes; however, the electrolytic reduction processes still demand more steam and electricity than the FA synthesis and hydrogen electrolysis processes combined to produce 1 kg FA.

Table 11. Comparison of strategies to convert CO_2 into FA (Rumayor, Dominguez-Ramos, and Irabien 2018).

	Electrolytic Reduction of CO_2 (single pass)	**Electrolytic Reduction of CO_2 (recirculated)**	**Synthesis of CO_2 and H_2 Using Homogeneous Catalysts**	**Conventional FA Production**
Electrode or catalyst (10^{-6}kg)	9.92	14.9	3.75	15.60
CO_2 consumed (kg)	0.96	0.96	0.83	0
H_2O consumed	0.59	1.41	0.56	0.60
H_2O produced	0.18	0.18	0.06	0.18
H_2 produced (10^{-3}kg)	3	92	-0.06	0
Electricity consumed	4.59	11.9	4.07	0.29
Steam consumed (MJ)	65.18	25.67	10.03	22.77

Moving forward, we will consider the CO_2 and H_2 synthesis process for FA production. Because of the interest in FA as a hydrogen carrier, several commercial processes for this production route are in development. Using water electrolysis for hydrogen production will also allow the refinery to be designed around the hydrogen needs of the processes. If hydrogen was produced by the electrolytic reduction of CO_2, the process would be reliant on the amount of CO_2 emitted at the refinery, and the size of the system could result in more FA production than is marketable or profitable for the refinery.

Model Parameters

Pérez-Fortes et al. (2016) compared the synthesis of H_2 and CO_2 via renewable electrolysis to a conventional FA process, as shown in Figure 32. The inputs and outputs used in the model will be useful for creating a model of the FA synthesis process in the Holistic Energy Resource Optimization Network analysis tool. The consumed and produced materials are listed in Table 12.

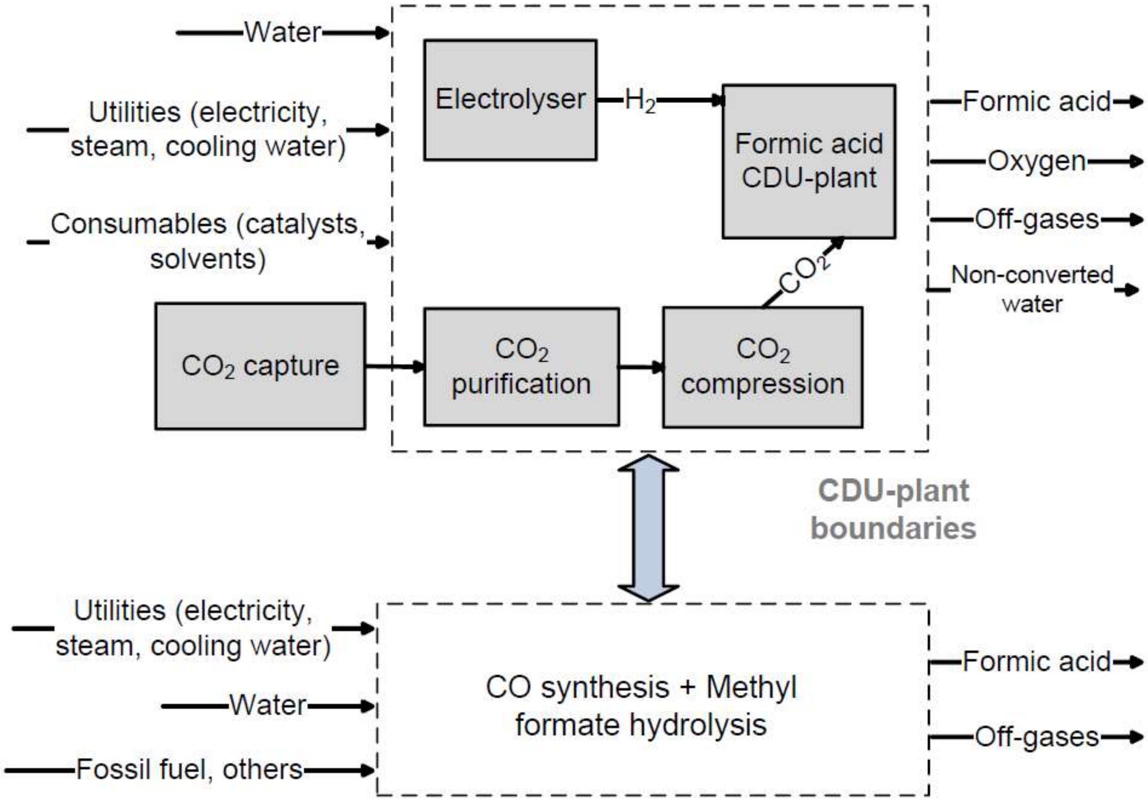


Figure 32. Block diagram of FA synthesis from carbon monoxide and carbon utilization (Pérez-Fortes et al. 2016).

Table 12. Material inputs and outputs for a proposed FA model.

Material	**Inlet**	**Outlet**
CO_2	0.834	0.166
H_2	0.060	0
H_2O	0 (electrolyzer not considered)	0.60
Make-ups (catalyst, solvent, amines)	0.266	0
FA	0	1
Electricity consumption (without electrolyzer) (MWH/tFA)	0.296	
Heating needs	2.783	
Cooling needs	2.962	

The main barrier to CO_2 utilization for FA production is the high cost of production compared to the low price of FA. Figure 33 details the installed costs and operational costs of an FA process using electrolysis. However, coupling FA production with the carbon refinery will reduce the burden of some of these costs on the FA process alone and distribute them among other components. The largest portion of the capital costs is dedicated to the electrolyzer, about 43% according to the study. Since the electrolyzer will also be used for methanol production at the refinery, the capital costs can be distributed between those products. In terms of operating costs, the consumables (including the cost of CO_2 purchase) and utilities (steam and electricity) are the major contributors. CO_2, steam, and electricity will all be supplied to the process by other parts of the refinery, rather than being purchased at market price. This should bring down the cost of production significantly and include the cost savings by utilizing CO_2 as opposed to carbon sequestration.

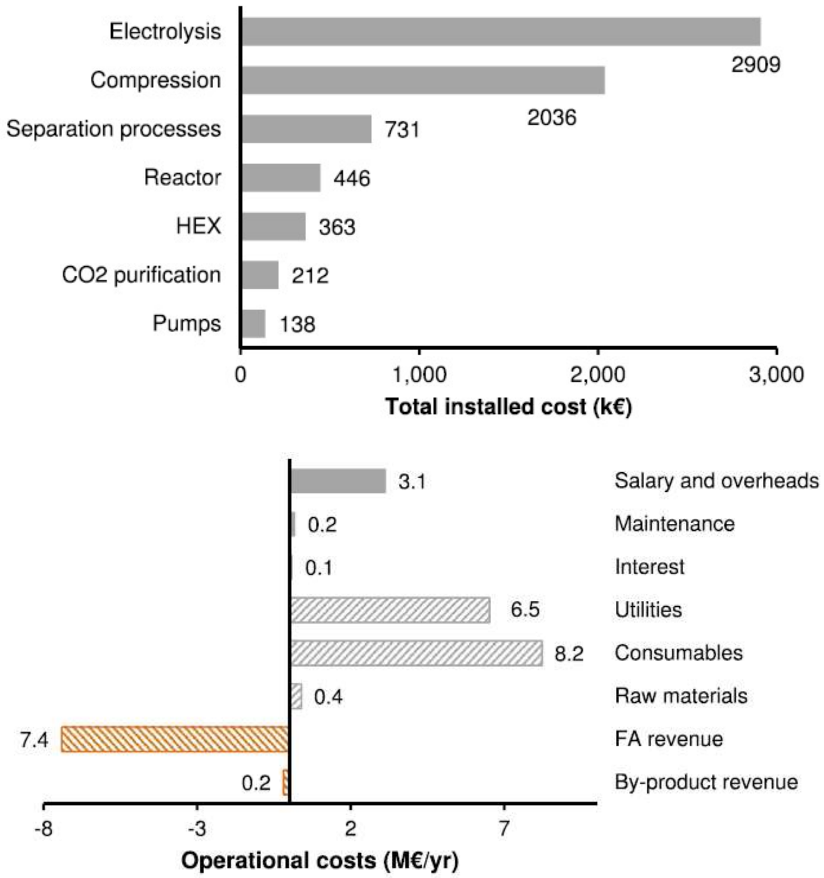


Figure 33. Capital and operating costs for FA production with hydrogen production from electrolysis with fixed costs of production in gray bars, variable cost of production in gray striped bars, and FA and oxygen revenues in orange striped bars (heat exchanger [HEX]) (Pérez-Fortes et al. 2016).

Carbon Savings

Compared to the conventional FA process shown in Figure 32, Pérez-Fortes et al. (2016) estimate that the CO_2 emission reduction from the carbon utilization is 92%, or 2 tCO_2/tFA not emitted. They also estimate that about 0.42 tons of heavy fuel oil are saved per ton of FA produced by the carbon utilization process. Of all the products considered in Table 10, FA has the third highest CO_2 utilization rate.

Market Analysis

The global market size for FA is $878.7 million annually with a CAGR of 4.94% (Market Research Future 2021). FA market opportunities exist in meat production, animal products, leather products, textiles, and rubber. This product is often used in preservation and as an antibacterial agent in livestock feed. FA's connection with agriculture and food production creates a stable market both domestically and internationally. When applied to silage and fresh hay, FA helps reduce the loss of nutritional value. This becomes especially important for the winter preservation of cattle feed. Roughly 30% of global consumption was from cattle feed preservation. From Figure 34, the U.S. Department of Agriculture reports more than 28 billion pounds of beef was processed domestically in 2021—the highest level of production on record dating back to 1970 (United States Department of Agriculture 2022a). Beef production increased 18% in 2021 from the recent low of 23.8 billion pounds in 2015.

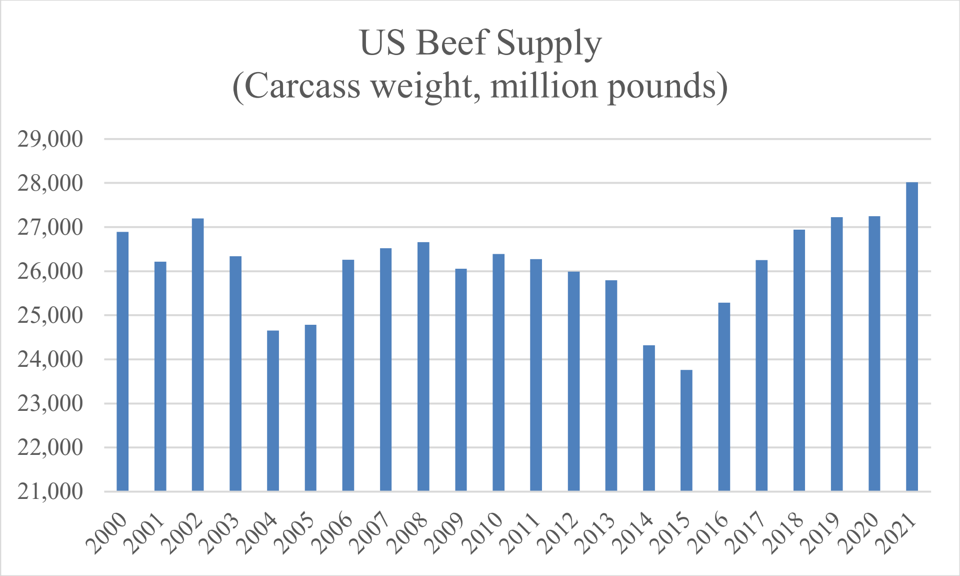


Figure 34. U.S. beef supply in millions of pounds (2000–2021) (United States Department of Agriculture 2022a).

In late 2015, BASF opened a plant in Geismar, Louisiana to produce FA (BASF Corporation 2015). The company claims the product benefits multiple industries, including oil, gas, deicing, industrial cleaners and descalers, animal nutrition, leather, and textiles. BASF also lists FA as a suitable substitute for sulfamic, phosphoric, and acetic acid (BASF Chemical Intermediates Division). In cooler climates, the product can also be used for deicing runways and roadways with a lower chemical oxygen demand than comparable acetates. One BASF syngas supplier, Air Products and Chemicals, closed its doors in 2020 due to reduced customer demand, according to a news article (Mosbrucker 2020). Air Products and Chemicals produced carbon monoxide for fuel operations at the BASF FA plant. The company recently lost a property tax abatement for their facility that was made available through an Industrial Tax Exemption Program.

Summary

In terms of technical integration, FA synthesis appears to be the best choice for carbon utilization. The process only requires feedstocks already produced at the refinery (hydrogen, carbon dioxide, steam, and electricity), and FA has many markets and uses. It is, however, a low-cost product and may not be as profitable as other options. Also, according to Table 10, it has the third highest carbon utilization rate of any of the products considered.

3.7.2 Acetic Acid

Acetic acid is typically synthesized from methanol carbonylation via the Monsanto or Cavita process. Carbonylation is the most frequently employed route for acetic acid, in which methanol and carbon monoxide react in a liquid phase in the presence of a rhodium-based catalyst. This process produces about 95% acetic acid, with side products such as FA and formaldehyde.

Based on literature, acetic acid synthesis that involves carbon utilization typically does so by CO_2 and H_2 hydrolysis to form methanol, before continuing with methanol carbonylation to create acetic acid (Somiari and Manousiouthakis 2017). While this process would utilize CO_2, it would require a separate process to generate methanol than the syngas conversion already implemented in the refinery. The process would also require CO feedstock to convert the methanol to acetic acid and would result in more carbon dioxide as a byproduct. Another proposed process synthesizes acetic acid using methane and CO_2; although, there is not a current methane feedstock stream at the refinery (Wang et al. 2019). There is, however, ongoing research into a process that synthesizes acetic acid using methanol, CO_2, and H_2, which are all current feedstocks at the refinery. This process, proposed and studied by Qian et al. (2016), would utilize CO_2 and result in the direct production of acetic acid and water. Although this is a promising option for the refinery, this process has not been studied beyond the lab scale, and based on the literature, there is no cost information for equipment or production, and it is not commercialized. This process would be an option for a future iteration of the carbon refinery design if it is developed further.

Market Analysis

The global market size for acetic acid is $8.92 billion annually (Grand View Research 2020). China accounts for 55% of the world capacity, and the U.S. produces 17%. China has a large coal-derived methanol production capability, and nearly 75% is consumed in China and other Asian countries (IHS Markit 2021a). Grand View Research reported a 5.2% CAGR acetic acid industry growth (Grand View Research 2020). Some market growth is tied to complement goods, including the vinyl acetate monomer used in paint and other coatings and as a food condiment and acidity regulator. The largest producers include BP Chemicals, Celanese Corporation, Eastman Chemical Company, and Dow.

Summary

Because the CO_2 conversion to acetic acid process has only been developed at the lab scale, it is unsuitable for modeling with the carbon refinery. This may be considered in the future if the conversion process continues to be developed.

3.7.3 Urea

The largest consumer of CO_2 is the fertilizer industry, where about 130 $MtCO_2$ per year is to manufacture urea (International Energy Agency 2019). Urea is typically synthesized from ammonium carbamate (via ammonia) and CO_2. Urea is a long-release-type fertilizer that maintains a presence longer in the soil. It is usually combined with ammonium nitrate and nitric acid in a solution of liquid fertilizer termed UAN. The NO_3 from the ammonium nitrate and nitric acid can be readily used by plants. As a liquid, it can be easily mixed with pesticides and other macro- and micronutrients and applied more evenly than solid fertilizers. Because of the nitric acid solution, corrosion inhibitors need to be added to prevent the corrosion of handling systems. The NH_4^+ can be readily absorbed by some plants or converted in the soil to nitrate. Urea takes time in the soil to be converted to NH_4^+ and nitrate, which slowly releases nutrients over time to the soil and plants. UAN comes in different nitrogen percentages, UAN-28 (28 wt% nitrogen), UAN-30, and UAN-32.

Urea is generated by synthesizing CO_2 with ammonia. The typical process for ammonia production involves the reaction of nitrogen with hydrogen from syngas; although, the hydrogen can also come from electrolysis. Both the Haber-Bosch process for ammonia production and the synthesis of urea have well-established commercialized processes. The electrochemical synthesis of ammonia from H_2O and N_2 is also possible; although, it is a much newer technology than Haber-Bosch.

Although the production of urea would require an additional ammonia synthesis process, the entire process will still use feedstocks already present at the refinery and would consume CO_2. The CO_2 used to produce urea is typically obtained from the steam methane reforming process used to generate hydrogen for ammonia synthesis. A CarbonNext report (2017) notes that, if the hydrogen used to produce ammonia is generated from carbon-free electricity sources, the CO_2 source for urea will have to come from elsewhere, giving the carbon refinery an advantage because it already has a stream of waste CO_2. Urea production is also preferrable to ammonia because it is in a crystalline form, making it easier to transport and store. There have been recent studies on the direct synthesis of urea using CO_2, N_2, and H_2O (Chen et al. 2020) and CO_2 and nitric oxide (Huang et al. 2021); however, there do not appear to be any commercial processes in the development for the near or medium term.

Process Requirements

The international group thyssenkrupp introduced a design for a small-scale ammonia plant using hydrogen. The design includes an alkaline electrolyzer and an Uhde dual-pressure ammonia process. As shown in Figure 35, the electric power and treated water consumption of the plant are fairly stable as the process is scaled up. The cooling water consumption benefits significantly from scaling. These values could be used to interpolate or extrapolate the power and water demands of ammonia production for the refinery.

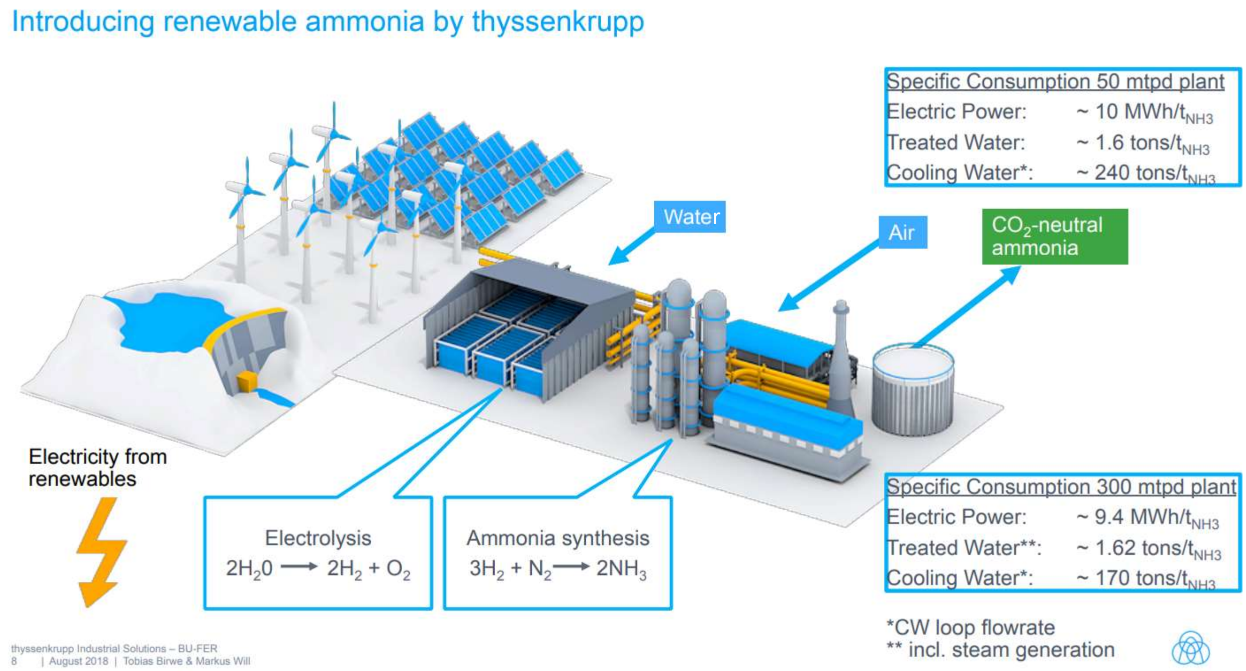


Figure 35. Electricity and water demands for renewable ammonia (Will 2018).

The production of urea from CO_2 and ammonia has been well documented and commercialized over the last several decades. Because the production of urea requires only steam, ammonia, and CO_2, a standard urea production process could be incorporated into the refinery without changes to eliminate CO_2 production.

Market Analysis

The global market size for ammonia is $48.65 billion annually. Ammonia and urea market growth is expected to stay at 5.2% CAGR (Grand View Research 2018a). Liquid ammonia dominated the market with a 45% share and has a market growth rate of 5.7% CAGR. Ammonia can be used in agricultural fertilizer and is tracked by the USGS as a mineral commodity, which reduces the risk associated with not being able to obtain market trends. Ammonia can be used as an environmentally friendly refrigerant as it has no ozone depletion potential or global warming potential. It also has a smaller heat transfer area in compressors. China produces ammonia using a coal gasification process, which differs from most other locations that use natural gas. It was reported by Grand View Research that 50% of production in the U.S. was through the use of natural gas.

Because of the large market for ammonia, there are several major producers, including Yara International, BASF SE, CF Industries, Potash Corp, and others. Roughly 60% of ammonia production capacity was in Louisiana, Oklahoma, and Texas because of large natural gas reserves (U.S. Geological Survey 2021). U.S. production increased by 37% between 2016 and 2020 according to USGS statistics. New plants were not expected to be online before 2022. During the COVID-19 pandemic, plants remained operational as they were considered part of a critical industry.

Net import reliance has decreased steadily since 2016, as shown in Table 13 and Figure 36. The economic viability of ammonia production in the U.S. was made possible through low natural gas prices. These savings made it possible for U.S.-based producers to reinvest funds into existing plants and reduce imports.

As a derivate of ammonia, urea has similar consumers and is typically used in fertilizer, urea formaldehyde, melamine, animal feed, and diesel exhaust fluid. The Asia-Pacific region reportedly makes up 60% of the global market. A Reuters article from September 2021 outlined multiple reasons for sudden price increases for urea in China. According to the article, urea prices doubled because of coal costs and government regulations on high energy consuming projects (Reuters Staff 2021).

The U.S. government is implementing incentives to boost production. The U.S. Department of Agriculture announced plans for a $250 million grant program to support innovative U.S. fertilizer production (United States Department of Agriculture 2022b) to help small- to medium-sized businesses. According to Nutrien, the U.S. was the 2nd largest importer of urea in the world in 2019.

Table 13. U.S. ammonia market statistics from 2016–2020 (U.S. Geological Survey 2021).

	2016	**2017**	**2018**	**2019**	**2020**	**2021**	**2016–2020**
Production	10,200	11,600	13,100	13,500	14,000	14,000	37%
Imports for consumption	3,840	3,090	2,530	2,020	1,980	2,200	-43%
Exports	183	612	224	338	369	260	42%
Consumption	13,800	14,100	15,300	15,200	15,700	16,000	16%
Stocks, producer, year-end	400	320	490	420	310	360	-10%
Price, average, free on board gulf coast, dollars per short ton	$267	$247	$281	$232	$223	$510	91%
Employment, plant, number	1,300	1,500	1,600	1,600	1,600	1,600	23%
Net import reliance as a percentage of apparent consumption	27	18	14	11	11	12	-56%

1,000s of metric tons unless otherwise noted

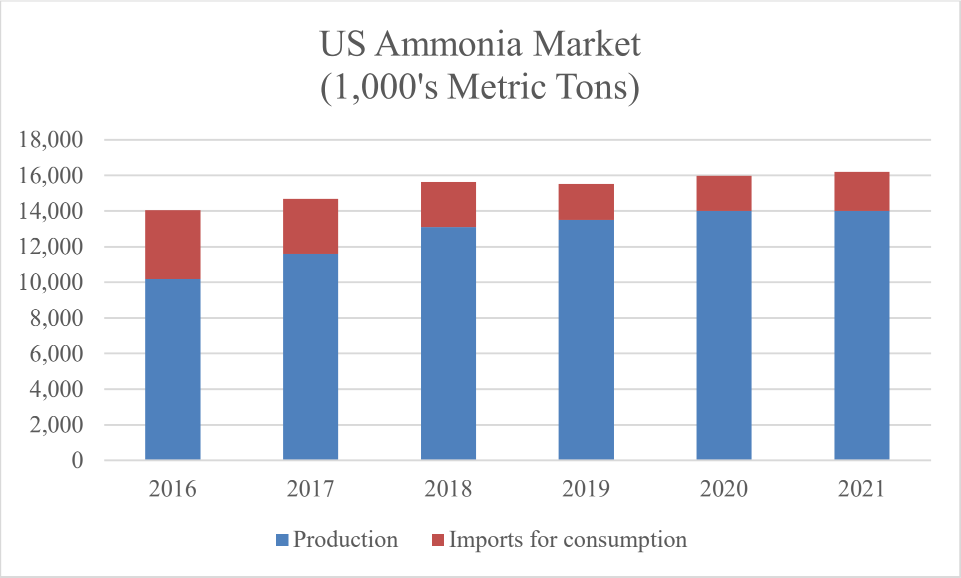


Figure 36. U.S. ammonia market production and imports (U.S. Geological Survey 2021).

Summary

Urea is a high-demand product with a well-established process for CO_2 utilization. The only drawback to producing urea at the carbon refinery is that it will require ammonia as a feedstock, which is not currently produced as a product pathway at the refinery. Because of the very positive outlook for the market and technical readiness, urea will remain in consideration for integration with the carbon refinery.

3.7.4 Formaldehyde

Formaldehyde is typically synthesized through methanol oxidation. Formaldehyde is an excellent candidate for carbon utilization because it is primarily used in resins, plastics, and paints, which would sequester large quantities of CO_2 into long-lived products.

There are two potential routes to produce formaldehyde that utilize CO_2. The first is a direct synthesis of CO_2 by hydrogenation, producing FA as an intermediate before reducing it to formaldehyde. Depending on the market analysis results, it may be beneficial for the refinery to produce formaldehyde as a final product rather than FA. No commercialized processes to reduce FA to formaldehyde were found in the literature. The second route is the reduction of CO_2 using borane; although, this has only been achieved at the laboratory scale (Heim, Konnerth, and Prechtl 2017).

Chan et al. (2018) also suggest converting CO_2 to formaldehyde using the reverse water-gas shift reaction to produce carbon monoxide as an intermediate. The authors were able to convert CO_2 to formaldehyde via this route without detecting FA as an intermediate. They postulate that this route might be more favorable for CO_2 hydrogenation into formaldehyde; however, this process has only been explored at the lab scale.

Market Analysis

The global market size for formaldehyde is $7.81 billion annually (Grand View Research 2021a). A report by IHS Markit estimated that North and South America make up roughly 10% of the global consumption of formaldehyde (IHS Markit 2021b). Complement industries for formaldehyde include construction (adhesives and glues), automotive, furniture, textile, healthcare, oil gas, agriculture, water treatment, and cleaning products. End users of this product are usually located close to the point of production due to the cost of transportation. As a result, there is very little global trade due to transportation and stability concerns. Formaldehyde's hazardous product characteristic limits market growth.

Grand View Research (2021a) estimated a 5.7% CAGR between 2021 and 2028. Major producers include Foremark Performance Chemicals, Georgia Pacific, Celanese Corp., BASF SE, and Dupont.

Summary

Because converting CO_2 to formaldehyde has only been developed at the lab scale, it is unsuitable for modeling with the carbon refinery. This may be considered in the future if the conversion process continues to be developed.

3.7.5 Methanol

One popular suggestion for carbon usage is converting CO_2 to methanol. Methanol is already produced in this way and is a significant target because of its high demand across the world—100 million tons annually (Guil-Lopez et al. 2019). However, Figure 37 shows that the CO_2 hydrogenation process to form methanol using commercialized $Cu/ZnO/Al_2O_3$ catalysts results in the in-between synthesis of two other marketable products: formate and formaldehyde. Copper-based catalysts are mostly used for CO_2 hydrogenation to methanol due to its low cost and higher catalyst activity. Although other catalysts have been studied for the hydrogenation of CO_2 to methanol, they are often in addition to copper catalysts (Borisut and Nuchitprasittichai 2019). Choosing formate and formaldehyde as the final product over methanol would bring down capital and operating costs, while diversifying the potential markets for the refinery. It is possible that, after a market analysis, it will be more beneficial to increase methanol production using this method.

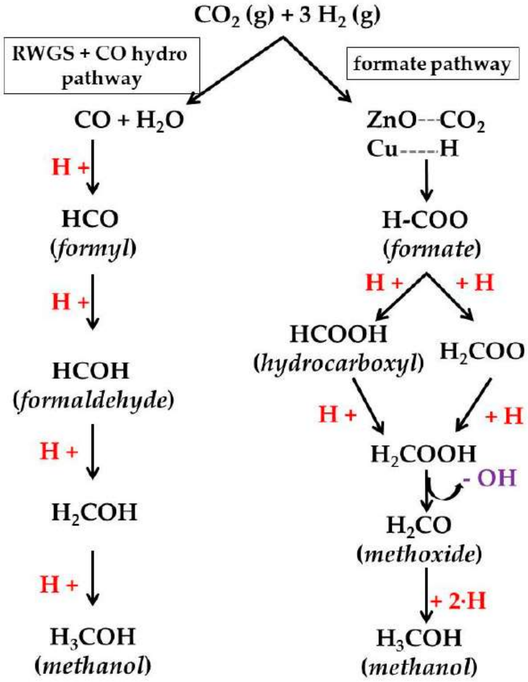


Figure 37. Pathways of methanol synthesis from CO_2 hydrogenation over Cu-based catalysts (Guil-Lopez et al. 2019).

Market Analysis

Data Bridge Market Research (2022) estimated methanol to have a global market size of $29.2 billion in 2021. According to Methanol Market Services Asia (MMSA) (2022), the methanol market and all its derivatives has a 4.5% global CAGR between 2017 and 2022, as shown in Figure 38. The total supply capacity for methanol products is expected to reach more than 165.7 million metric tons in 2022, up from 132.5 in 2017. The average U.S. contract price for methanol was $613 per metric ton for the 12 months ending in June 2022. Prices for methanol have increased by more than 46% in 2022 (using a 12-month average ending in June), compared to the same period in 2021. From Figure 39, North America makes up only 5% of global market demand, China and the rest of Asia make up 40 and 46%, respectively. Additional commercialization of methanol is moving the direction of using the product in fuel cells and olefin production. Methanol global market demand is less than 67% of total nameplate capacity for supply.

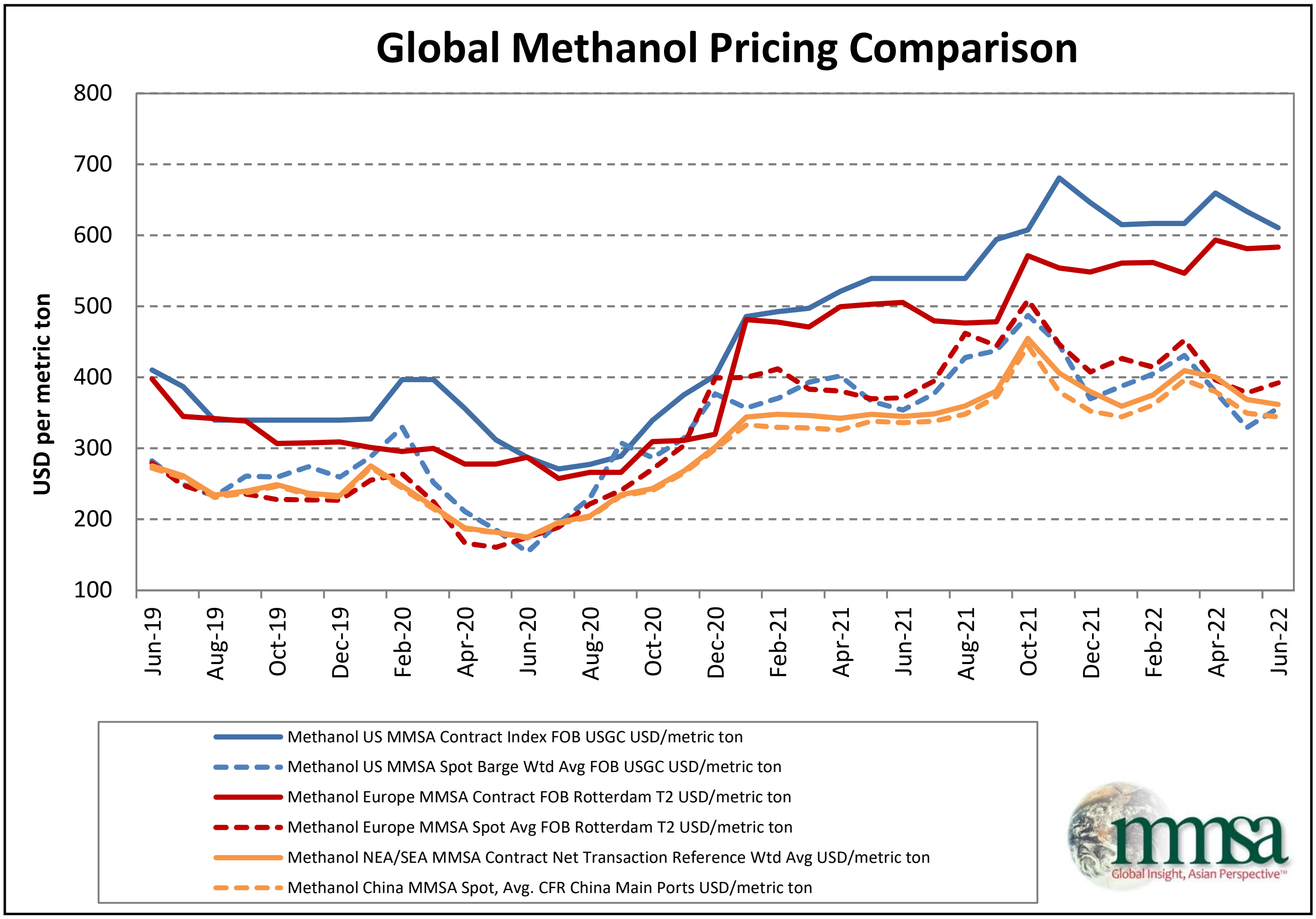


Figure 38. Global price comparison for methanol (Methanol Market Services Asia 2022).

Data obtained through the Methanol Institute and MMSA shows 34% of the demand for methanol was used for methanol-to-olefin production. Approximately 23% of demand for methanol was for formaldehyde production and 11% for methyl tert-butyl ether. Combined, alternative fuels made up 15.2% of the demand.

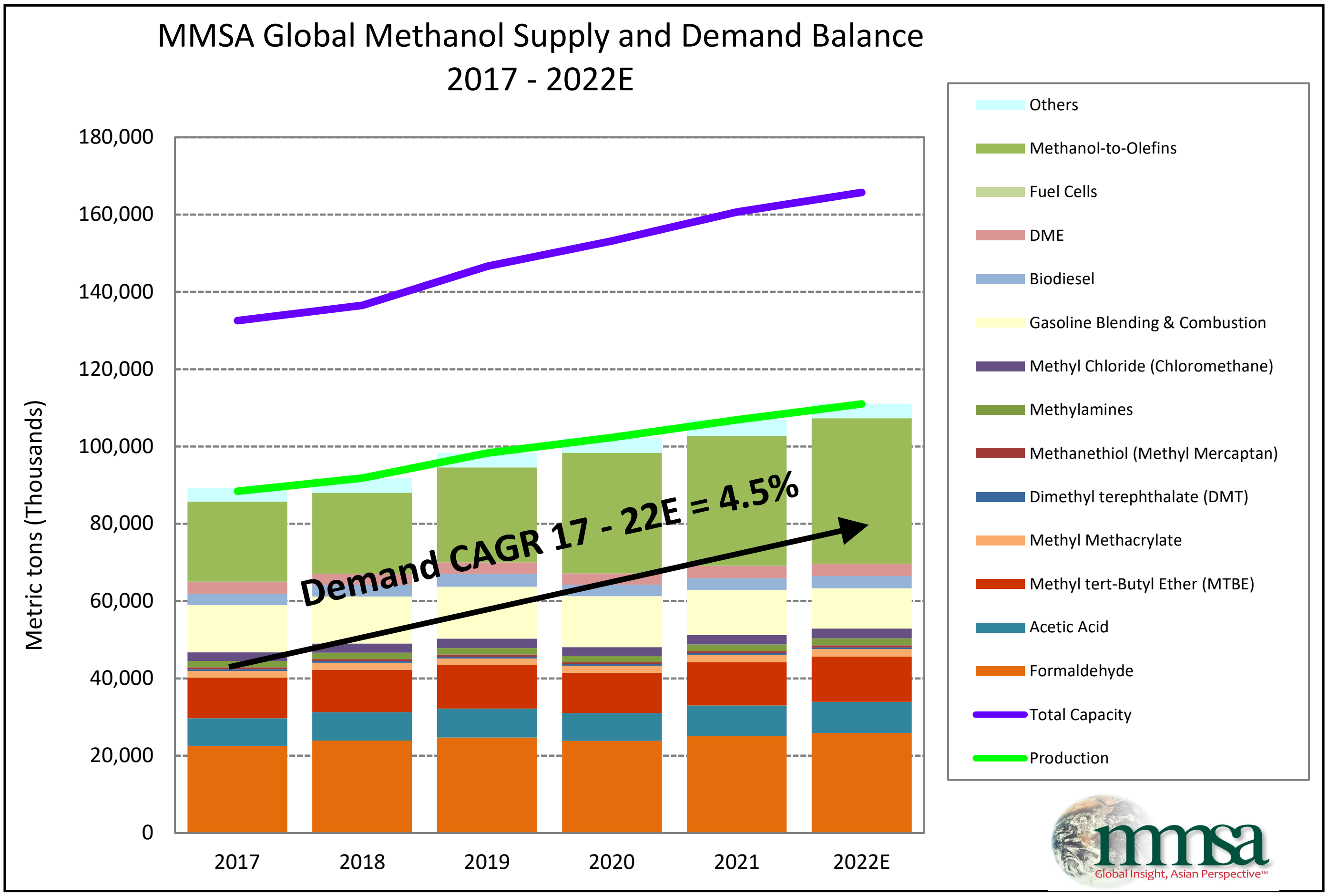


Figure 39. Global methanol supply and demand (Methanol Market Services Asia 2022).

3.7.6 CO_2 Utilization Feasible Markets

Because of the simplicity of integration with the refinery, FA is the first choice for a carbon utilization stream. In the refinery model, a carbon utilization stream for FA will be included, which will require optimizing the electrolysis unit to provide hydrogen for the synthesis process. Urea is not included in the model but is still considered as a potential product. The costs and revenues associated with urea production (through ammonia production or purchase) are estimated based on the resulting CO_2 outputs of the refinery.

3.8 Char Conversion to Activated Carbon

Char is the solid product of coal pyrolysis. Its percentage yield changes with the pyrolysis temperature, pyrolysis pressure, and heating rate (Ladner 1988). It is a carbonaceous substance that can be chemically or physically treated to develop an interconnected series of “holes” or pores inside the carbon (General Carbon Corporation 2022). This internal pore network results in a vast surface area for adsorption. It can attract and hold organic chemicals from vapor and liquid streams, cleaning them of unwanted chemicals. This processed, porous version of carbon is a fine, odorless, black powder called the activated (or active) carbon, coal, or coke.

Activated carbon is a valuable feedstock for the refinery because it can be used to remove mercury from syngas. The market analysis indicates that the market is growing, but there are some concerns that the market may be reduced regionally because of the shrinking demand for coal power. Moving forward, the research team will begin by assessing the viability of producing activated carbon based on the amount produced versus consumed for the syngas cleaning process and the cost of production versus the purchase price of activated carbon.

Activated carbon is used in the industrial, medical, and pharmaceutical sectors. One application is water purification, treatment of wastewaters, extraction of solvents, and removal of harmful substances (Tian et al. 2021). Medical applications include the emergency treatment of poisoning, reducing cholesterol levels, treating cholestasis during pregnancy, assisting kidney function by filtering out undigested toxins, treating diarrhea, and teeth whitening (Medical News Today 2021).

Activated carbon is the first choice for the char market, but coal char (coke) can have many other applications (Osokina et al. 2017). The compounds that result in smoke are removed from coal during pyrolysis so the char is high in carbon and can be burned without releasing smoke. Therefore, coke is used as a fuel substitute for coal in domestic heating. Even though the smokeless fuel does not contribute to the pollution through releasing airborne particles, it still releases greenhouse gases (Laukkonen 2022).

The coal coke is rich in carbon so it can be used as an adsorbent (Simate et al. 2016) for the treatment of drinking water and removal of pollutants. This is the same application as for activated carbon production.

Another application for coke is steel production as the coke is used as a reducing agent and fed into a furnace along with raw iron ore to produce pig iron which is a basic ingredient in steel production. This process also produces carbon monoxide as a waste product. In the future, coke might be replaced by other greener reducing agents (Kelk 2022).

3.8.1 Activation Process Description

Char activation can be accomplished directly (physical activation) through heating in a chamber while gas is pumped in. This exposes it to oxygen for oxidization purposes. When oxidized, the active carbon is susceptible to adsorption, the process of surface bonding for chemicals—the very thing that makes activated carbon so suitable for filtering waste and toxic chemicals out of liquids and gases. Char is oxidized (via steam, carbon dioxide, or both) and heated between 900 and 1200°C, causing the oxygen to bond to the carbon's surface. Following oxidization, activated carbon can be processed for many uses. The physical activation process is represented in Figure 40.

The activated carbon can also be produced by chemical activation (which replaces pyrolysis and physical activation) (Gombojav, Jambal, and Byambajav 2020). Still, the physical activation method is more environmentally friendly since the active agents in the activation process are less polluting for the environment.

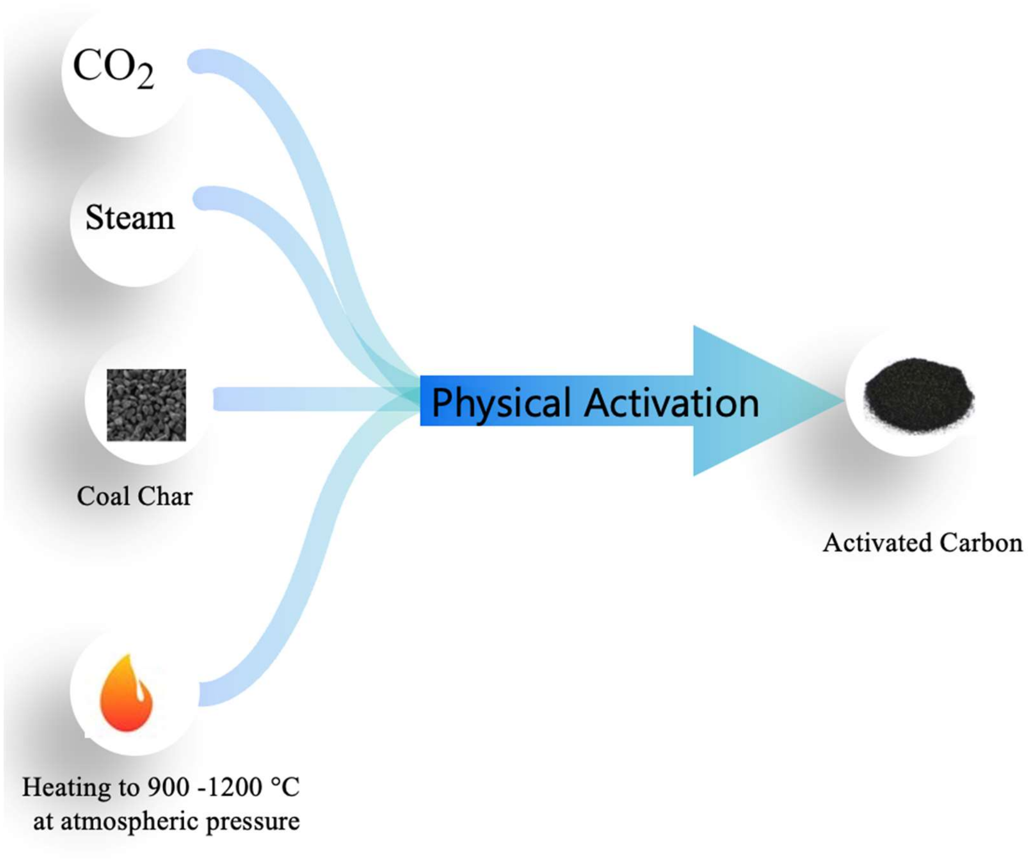


Figure 40. A representation of producing activated carbon through physical activation.

One of the fundamental factors that affect the cost of activated carbon production is the production yield (Ko et al. 2004). The production yield (tons of activated carbon produced per ton of raw material) is 24% for coal. Thus, 100 Tons of coal will yield 24 Tons of activated carbon (after pyrolysis and physical activation). This yield is lower than some of the other raw materials (63% for petroleum coke, 47.5% for carbon black, 45% for charcoal) (Stavropoulos and Zabaniotou 2009). Therefore, producing activated carbon from coal char may not be an attractive investment. Even producing activated carbon from low-yield raw materials such as waste (yield =15%) might be less expensive compared to coal (total operating costs are 15% lower).

3.8.2 Market Analysis

Char has a global market size of $3.44 billion annually. Char or activated carbon can be manufactured from a variety of sources, which weakens market power among coal-based producers. According to Grand View Research (2022), the market will have a growth rate of 2.9% CAGR between 2022 and 2030. Uses of char stem from robust industries like agriculture where it is used for soil amendment and acidification. Char as activated carbon also has applications for wastewater treatment, which may become increasingly important when mitigating environmental concerns and water shortages. The market is highly competitive and is trending toward vertical integration, putting strains on mid-chain suppliers to reduce volatility in sourcing and maintaining quality standards.

4. ASSESSMENT OF ADVANCED NUCLEAR REACTORS FOR COAL CONVERSION PROCESSES

This section aims to evaluate various types of advanced nuclear reactors as sources of heat and steam for the coal conversion processes demonstrated in Figure 3. The reactors' evaluation criteria are determined based on the needs of the coal conversion processes (namely, pyrolysis, hydrothermal gasification, electrolysis, activated carbon production, FA synthesis, methanol synthesis and Rectisol® process). Pyrolysis is given special attention as the initial step for the other coal conversion processes.

Table 14 summarizes the significant criteria that affect the rate and products of the coal conversion processes. Among these criteria, temperature is the primary factor. For example, the concentration of the pyrolysis products may change by varying the process temperature. Pressure is another significant criterion, but its effect may change for different coal types and pressurizing gas. In principle, all nuclear reactors can produce heat for coal processing, but some criteria can be decisive in identifying the most appropriate reactor type.

Table 14. Requirements of the coal conversion processes.

Process	Temperature	Pressure	Needed Energy Form
Pyrolysis	The quantity and type of products depend on the temperature range. - Lower-temperature pyrolysis (400–750°C) yields more tar and oils. - Higher-temperature pyrolysis (900–1100°C) yields more char (needed for the iron and steel industry), and gases. - The pyrolysis temperature is assumed to be 800°C in the pyrolysis model.	The effect of the pressure depends on the pressurizing gas. - With an inert pressurizing gas, a decrease in the tar and total volatile yields is observed with increasing pressure (Rađenović 2006). - With nitrogen as a pressurizing gas, coal pyrolysis was shifted to a lower temperature (50°C) with pressure increasing from ambient to 5 MPa. The devolatilization rate of coal pyrolysis was decreased, and the coal char yield was increased slightly (Yang, Chen et al. 2007).	Heat transferred via heat exchanger
Hydrothermal gasification	400–700°C (Boukis and Stoll 2021). The higher the temperature, the higher the reaction rate.	25–30 MPa (Boukis and Stoll 2021)	Steam
High-temperature steam electrolysis (2019)	750–1000 °C	5 bar for maximizing system efficiency (Wendt and Knighton 2022b)	Steam + electricity
Activated carbon production	900–1200°C	Ambient pressure	Heat transferred via heat exchanger
FA synthesis	180°C	250 mbar	Steam + electricity
Methanol synthesis	217 °C	75 bars	Electricity
Rectisol® process	-40 °C	28–70 bar	Electricity

4.1 Coolant Maximum Temperature and Temperature Range

The required temperature level determines the applicability of an advanced reactor to a specific purpose.

Table 14, Table 15, and Figure 41 show the correspondence between the temperatures provided by U.S. advanced nuclear reactors (at different stages of design and construction) and the temperatures required by the coal conversion processes.

Considering the low-temperature pyrolysis (instead of high-temperature pyrolysis) and the steam electrolysis as basic initial steps that precede the other processes, the reactor should provide heating temperatures greater than 750°C (note, however, that a lower temperature reactor could be coupled to heat augmentation techniques to also achieve these high temperatures). Based on this criterion, the most suitable candidate reactor designs include gas-cooled reactors such as:

- The Steam Cycle High-Temperature Gas-Cooled Reactor (SC-HTGR) by Framatome.
- The X-energy reactor (Xe-100) by X-energy.
- The Micro Modular Reactor (MMR) by Ultra Safe Nuclear.
- Prismatic modular high-temperature gas-cooled reactor (HTR) by General Atomics.
- The Energy Multiplier Module (EM2) gas fast reactor by General Atomics.

However, none of the reactor designs in Table 15 provides sufficient high-temperature heating for fast (high-temperature) pyrolysis or activated carbon production without heat augmentation. Still, the SC-HTGR outlet temperature can be increased up to 950°C (Stewart, Velez-Lopez et al. 2021). The EM2, Xe-100, SC-HTGR, and Prismatic HTR designs have a high coolant outlet temperature and wide temperature range, which enable supplying heat to various processes and generating various products.

Conversely, LWRs cannot supply process heat above 350°C and thus will not meet the needs of the carbon conversion processes without significant heat augmentation. On the other side, the HTGRs have high-temperature supply capacity and very high electric efficiency (>50%) enabled by the high coolant temperatures. Therefore, the HTGRs (as heat sources) do not lose much of their electricity cogeneration capacity compared to the LWRs. For example, a typical LWR (steam temperature = 290 °C) loses 72% of its electrical output due to cogeneration while an SC-HTGR (steam temperature = 696°C) loses only 47% (Framatome 2019).

For low-temperature LWRs to provide heat at higher temperatures, some electricity production must be sacrificed. Therefore, to determine if the LWR provision of heat at higher temperatures is economical, more specifics about the demand for coal processing products and their profitability versus the profitability of electricity are needed. More details on heat augmentation and the capability to deliver high-temperature process heat with a nuclear reactor that has a lower outlet temperature is discussed in the next section.

Table 15. An overview of U.S. advanced reactors (International Atomic Energy Agency n.d.).

Reactor				Design Status	Output (MW^{th})	Coolant Temp (°C)		Steam	
Reactor Name			Vendor			Inlet	Outlet	Temperature (°C)	Pressure (MPa)
BWR	ABWR-II	Advanced Boiling Water Reactor II	GE-Hitachi	Under Design	4,960	277	288	288	7
	BWRX-300	Boiling Water Reactor X-300	GE-Hitachi & Hitachi GE	Conceptual Design	870	270	287	287	7

Reactor				Design Status	Output (MW^{th})	Coolant Temp (°C)		Steam	
Reactor Name			Vendor			Inlet	Outlet	Temperature (°C)	Pressure (MPa)
			Nuclear Energy						
	ESBWR	Economic Simplified Boiling Water Reactor	GE-Hitachi	Licensed	4,500	276	288	288	7
PWR	AP 1000	Advanced Passive PWR	Westinghouse	Construction	3,400	279	325	273	6
	AP-600	Advanced Passive Pressurized Water Reactor		On Hold	1,940	280	316	272	6
iPWR	NuScale/ VOYGR	NuScale SMR	NuScale Power	Under Regulatory Review	200	265	321	—	4
GCR	Prismatic HTR	Prismatic Modular High-Temperature GCR	General Atomics	Under Design	350	322	750	541	17
	MMR (Ultra Safe Nuclear Corporation 2021)	Micro Modular Reactor	Ultra Safe Nuclear	Under Regulatory Review	15	300	630	—	—
	SC-HTGR	Steam Cycle High-Temperature Gas-Cooled Reactor	Framatome	Conceptual Design	625	325	750	560	16
	Xe-100 (Mulder 2021)	X-energy	X-energy	Under Regulatory Review	200	260	750	565	17
	Holos Quad (Margulis, Stauff et al. 2021)		HolosGen	Conceptual Design	22	—	650: 760	—	—
GFR	EM2	Energy Multiplier Module	General Atomics	Conceptual Design	500	550	850	—	—
LFR	G4M	Gen4 Module	Gen4 Energy	Under Design	70	—	500	—	—
	W-LFR	Westinghouse Lead-Cooled Fast Reactor	Westinghouse	Conceptual Design	950	390	650	—	—

Reactor				Design Status	Output (MWth)	Coolant Temp (°C)		Steam	
Reactor Name			Vendor			Inlet	Outlet	Temperature (°C)	Pressure (MPa)
MSR	LFTR	Liquid Fluoride Thorium Reactor	Flibe Energy		600	500	650	—	—
	Mk1 PB-FHR	Mark 1 Pebble-Bed Fluoride-Salt-Cooled High-Temperature Reactor	University of California, Berkeley	Under Design Under Regulatory Review	236	600	700	—	—
	FHR (Kairos Power n.d.)	Fluoride Salt-Cooled High-Temperature Reactor	Kairos Power		311	585	650	—	19
	SmAHTR	Small Modular Advanced High Temperature Reactor	Oak Ridge National Laboratory		125	670	700	—	—
	ThorCon	Hybrid Thorium Uranium Liquid Fuel Molten Salt Small Modular Reactor	ThorCon U.S.	Detailed Design	557	565	704	547	26
SFR	PRISM	Power Reactor Innovative Small Reactor	GE-Hitachi	Under Design	840	—	485	—	—
	TWR-P	Travelling Wave Reactor-Prototype	TerraPower		1,475	360	500	—	—
	ARC-100 (Energy) (Association 2021)	Integral Fast Reactor	ARC with GE-Hitachi, USA	Under Regulatory Review	286	355	510	—	—

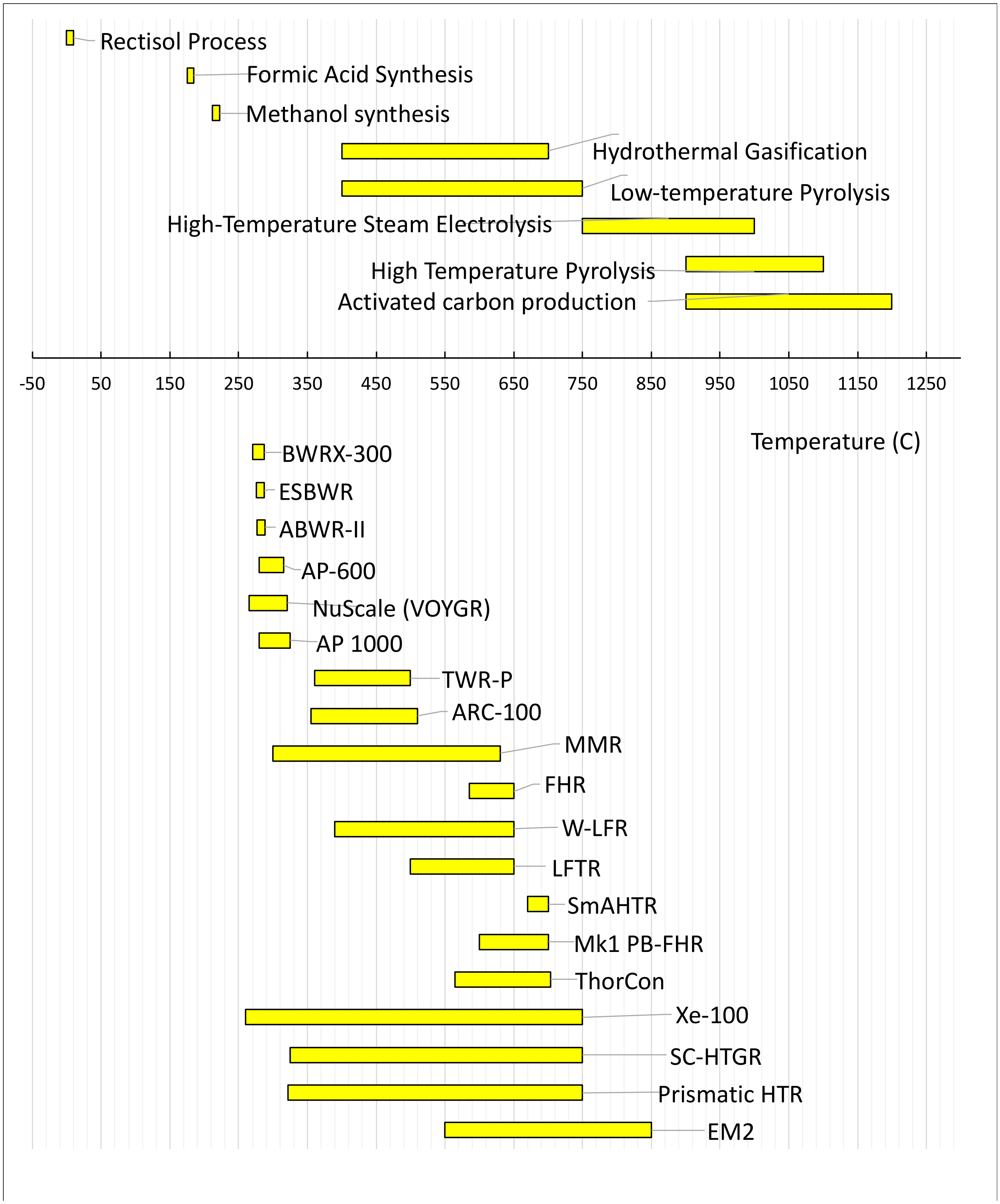


Figure 41. The temperature range of the U.S. advanced reactors coolants (lower plot) and high-temperature coal conversion processes (upper plot).

4.2 Heat Augmentation

Heat augmentation or boosting methods might enable separating the requirement for high-temperature process heat production from the nuclear part of the plant, so the reactor would run at a relatively low temperature while the high-temperature heat production would be limited to an external circuit, thus avoiding nuclear constraints (e.g., materials constraints or regulatory constraints) (Marmier and Futterer 2008). Heat augmentation methods include electric superheating and resistive heating to the desired temperature level and using heat pump technology via compression to the desired temperature level. The generated heat is delivered to a heat exchanger and some of the compression work can be recovered in a turbine. Thus, heat pumps are more efficient than electric superheating. The next subsections present two types of heat pumps.

4.2.1 Mechanical Heat Pumps

Mechanical heat pumps are devices that increase the temperature with the help of external mechanical energy source. Mechanical drivers include electric motors or steam turbines. The resulting temperature upgrade is up to 200°C. It is worth noting that using mechanical heat pumps to deliver high-temperature heat impacts the energy efficiency. For instance, replacing the very-high-temperature reactor (having an outlet temperature of 850°C) with an advanced gas-cooled reactor having an outlet temperature of 640°C plus a mechanical heat pump reduces the overall energy efficiency by 17% (Marmier and Futterer 2008). The overall efficiency was estimated assuming the cogeneration of high-temperature process heat and electricity. A reduced energy efficiency is expected to impact the nuclear power economics. Using the mechanical heat pump with LWRs with much lower outlet temperatures (~300°C), as demonstrated in Figure 41, will be more challenging. An alternative technology for heat augmentation is the chemical heat pumps.

4.2.2 Chemical Heat Pumps

Chemical heat pumps (CHPs) are systems that use reversible chemical reactions to change the output temperature of the primary energy source. CHP technology is preferable, compared to other heat boosting methods, for achieving higher temperatures as they avoid the efficiency penalty associated with the thermal-to-electrical energy conversion. CHPs have the potential to operate at temperatures higher than 1000°C and provide a temperature boost of several hundred degrees with an efficiency above 70%, but the coefficient of performance and energy efficiency declines as the pump outlet temperature increases (Armatis 2021). While the CHP potential is accepted by researchers, there are no experiments demonstrating temperature boosting greater than 100°C, and the CHP technology readiness level is still low.

The high-temperature reactor heat still requires more boosting for some of the coal conversion processes (in Figure 41 and

Table 14), especially very-high-temperature processes, such as fast pyrolysis and activated carbon production. Even though CHPs can be used to augment the LWR's heat, higher energy efficiency and improved performance and economics are expected when using a CHP with high-temperature reactors (Armatis 2021). Besides, gas-cooled reactor developers predict costs that are expected to be lower than large-scale LWRs (Bragg-Sitton 2020).

4.3 Steam Pressure and Temperature

Relatively high-pressure, high-temperature steam is required for pyrolysis, hydrothermal gasification, and electrolysis processes. Therefore, the reactor types that have primary coolants other than water have the advantage of producing steam with a higher pressure. For example, according to Table 15, the gas-cooled high-temperature reactors, such as the Xe-100, SC-HTGR, and Prismatic HTR, produce high steam pressure (16–17.3 MPa) at high temperatures (541–565°C).

4.4 Other Factors

Other consideration includes the design status of different reactor and the economic factors. As demonstrated in Table 15, some reactor designs are "conceptual" or "under design," and are thus far from being commercially ready, so the deployment of these designs may take a decade or more.

Economic criteria, such as the overnight costs, construction times, and discount rates, also should be considered too. For economic competitiveness, the nuclear reactor should be used in cogeneration mode (as a process heat supply and electricity source). More data about the reactor designs listed in Table 15 are needed to evaluate their economic competitiveness.

5. Path Forward

Now that decisions have been made for the design of the refinery and the target markets, modeling can proceed. The components and processes in the refinery will be modeled in Aspen Plus and Aspen HYSYS to determine the required equipment, heat and electricity demands, and material transfer functions. The Aspen Process Economic Analyzer (APEA) can estimate the cost of a system based on the size of the components. Several APEA estimates would generate a cost function, or a continuous curve to estimate of the cost of a component based on its size.

Material transfer functions and cost functions will be used to create a dispatch model in HERON. The HERON model will be used to optimize the size of the system based on the cost of components and the revenue from the products. The optimized cases will provide insight to the value of the markets and processes involved in the carbon refinery and will help finding focus areas for future cases.

To evaluate the benefits of refining coal feedstock into products, this section defines three baseline cases and three use cases. Figures of merit for comparison include capital and operating costs, revenue, and carbon emissions.

5.1 Baseline Cases

Three baseline cases have been defined the carbon refinery, all of which are based on incumbent processes and applications. Because these processes are well-established in industry, they will not be modeled in detail. Industry averages and estimates will help determine the costs, revenues, and carbon outputs for each case. Each of these cases will be modeled in the next stage of this research.

5.1.1 Baseline Case 1: Advanced Reactor Coupled to Electric Grid

For decades, nuclear power plants have been constructed solely to generate electricity to be sold to the grid. More recently, nuclear power has been considered for cogeneration applications, notably hydrogen production via electrolysis and desalination. The carbon refinery is another application of nuclear cogeneration. The purpose of this comparison case is to determine the cost and revenue difference for nuclear generation at the carbon refinery versus the incumbent process of nuclear power for electricity only. The nuclear plant capacity in this case will be the same as the capacity needed for the carbon refinery.

5.1.2 Baseline Case 2: Incumbent Methanol Production Process

Methanol is typically produced by steam methane reforming to generate syngas, followed by the conversion to methanol. The details of this process and other applicable processes for comparison will be detailed as this work progresses. The amount of methanol output from steam methane reforming will be the same as the optimized methanol output designed for the carbon refinery.

5.1.3 Baseline Case 3: Oil to Olefins Via Steam Cracking

Olefins are typically produced by steam cracking to break down the heavy compounds in oils. The details of this process and other applicable processes for comparison will be detailed as this work progresses. The olefins output from steam cracking will be the same as the optimized olefins output designed for the carbon refinery.

5.2 Experimental Cases

The experimental cases are intended to evaluate the processes discussed in the body of this report. Several iterations of the refinery design will lead up to the design in Figure 3. The cases leading up to the full refinery design are intended explore how the optimized design changes as processes are added, and to isolate some of the processes by evaluating the differential NPV and cost of carbon avoided between cases.

5.2.1 Experimental Case 1: Coal to Methanol via Pyrolysis with Carbon Sequestration or Sale

The schematic for Experimental Case 1 is shown in Figure 42. The processes used in this case will be the same as outlined earlier in this report (see Section 3). The main difference between this case and Case 2 is that the CO_2 will not be converted into a product; instead, it will determine the cost of sequestering or selling the CO_2 as a raw material to determine the value of carbon utilization versus carbon sequestration.

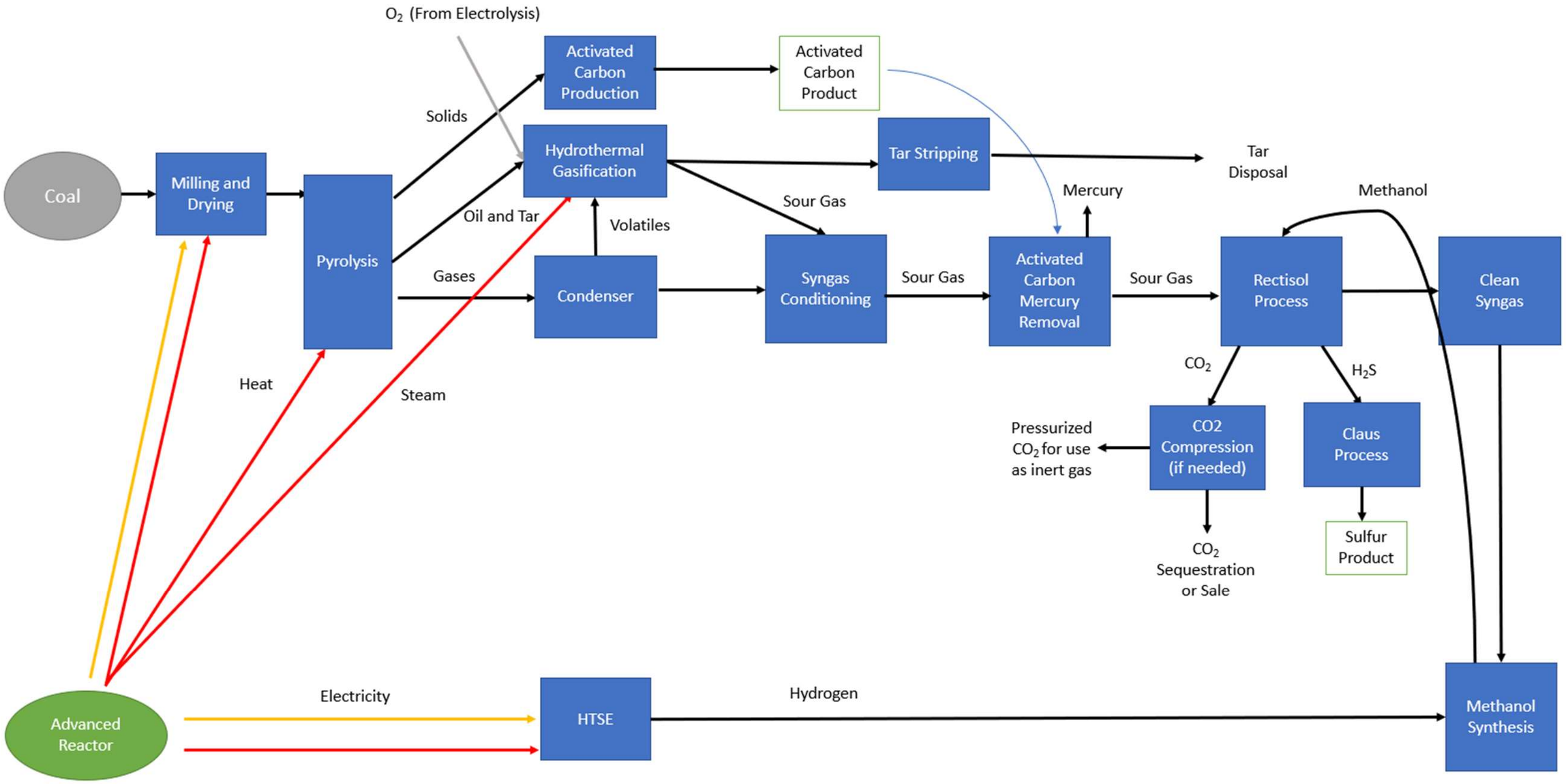


Figure 42. Flowsheet for Experimental Case 1.

5.2.2 Experimental Case 2: Coal to Methanol via Pyrolysis with Carbon Utilization

The schematic for Experimental Case 2 is shown in Figure 43. The processes used in this case will be the same as outlined earlier in this report. The main difference between this case and Case 1 is that the CO_2 will be converted into a product. The model will include FA synthesis from CO_2, but the cost of urea production will also be estimated based on the total CO_2 output from this case.

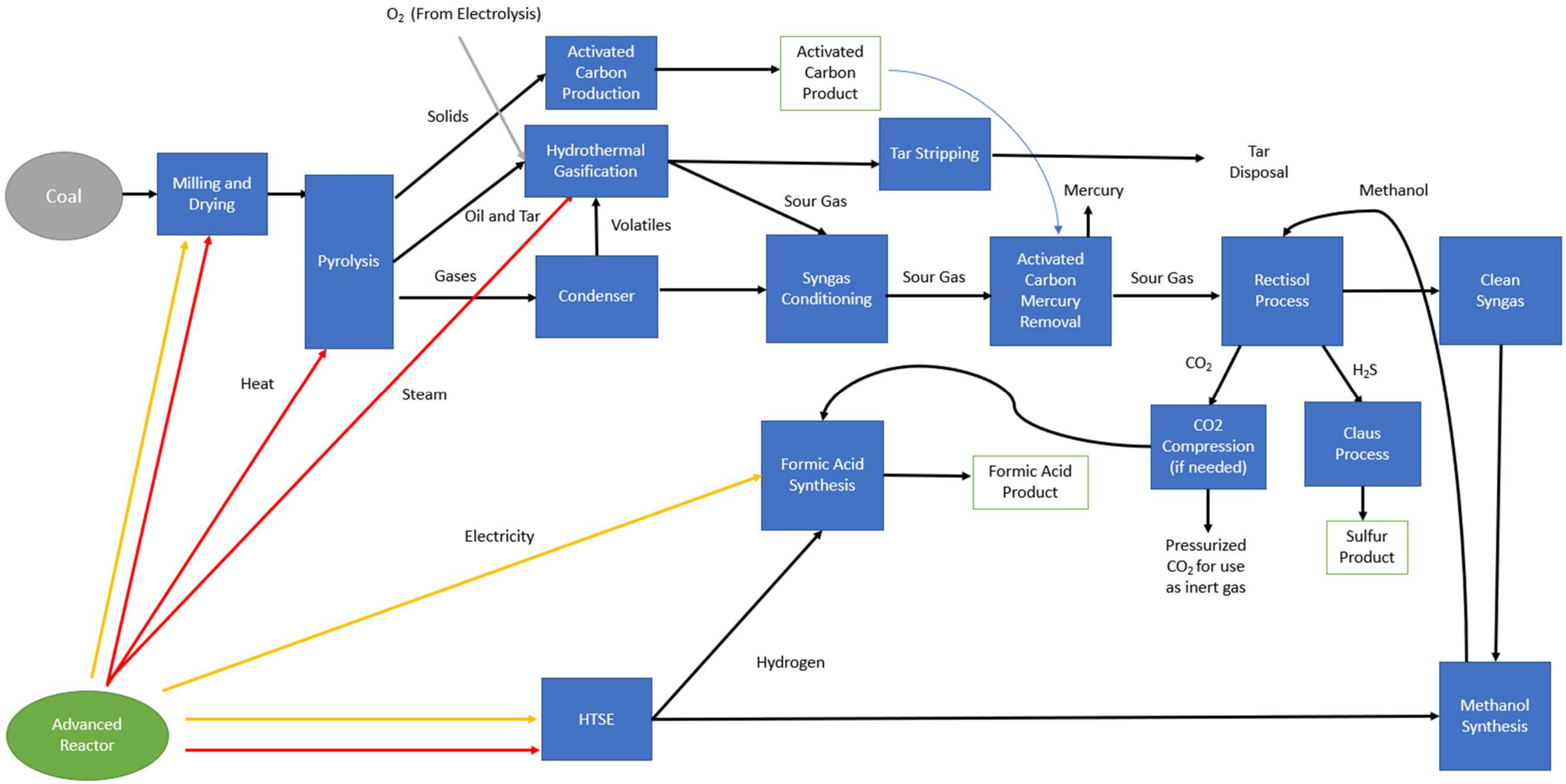


Figure 43. Flowsheet for Experimental Case 2.

5.2.3 Experimental Case 3: Coal to Methanol to Olefins with Carbon Utilization

The schematic for Experimental Case 2 is shown in Figure 44. The processes used in this case will be the same as outlined earlier in this report. The main difference between this case and Case 2 is that the methanol production will continue to olefins production and represents the full proposed carbon refinery.

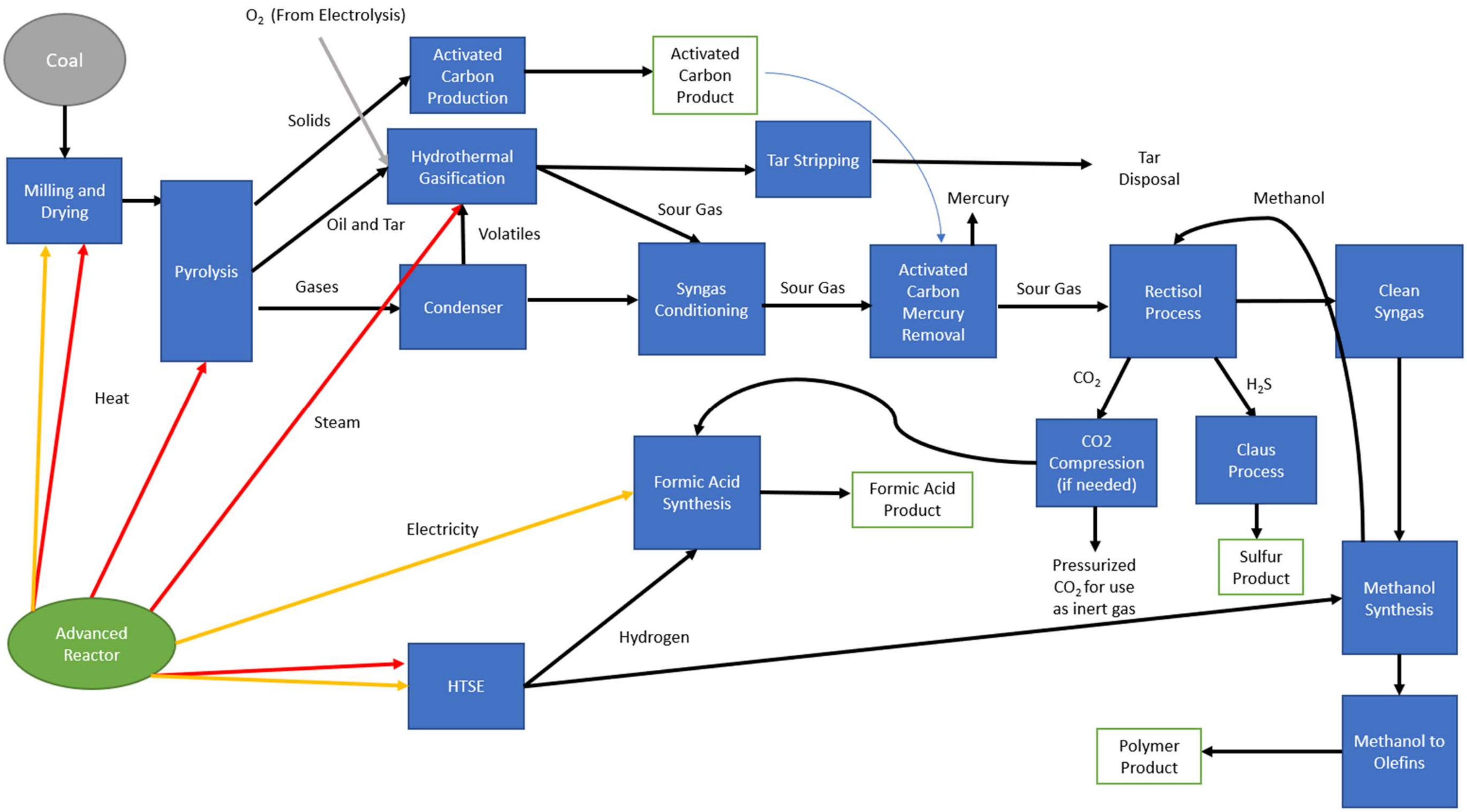


Figure 44. Flowsheet for Experimental Case 3.

5.3 Future Cases

As discussed in Section X, fertilizer (e.g. ammonia and urea) is a target industry for CO2 utilization. The fertilizer industry already consumes the most CO2 feedstock of any other insdustries, and often use large amounts of nitrogen and hydrogen in the synthesis process. The fertilizer market is constantly growing due to a growing population and higher expected standards of living globally. Eliminating the typical CO2 output from fertilizer processes while increasing the CO2 consumption overall could allow the industry to transition to carbon-negative. Future iterations of the carbon refinery will use nuclear electricity and heat to design and optimize a fertilizer plant.

6. Conclusion

The carbon refinery design has two major requirements: it must produce products that will be profitable and only the minimum feasible amount of CO_2 and pollutants can be released into the atmosphere. This required a thorough review of both the technical and market aspects of producing products from coal feedstock. Ultimately, the goal is to convert a majority of the pyrolysis products into syngas, which will be synthesized into methanol and further into polymers. The supply of nuclear heat and electricity to the refinery, as well as the generation of hydrogen via electrolysis will result in a near-zero carbon emitting process to generate these products. CO_2 produced by the refinery will be utilized in FA synthesis to avoid emitting CO_2 to the atmosphere. Solid products of pyrolysis will be used to generate activated carbon to clean flue gases in the refinery. Once these processes are appropriately modeled, they will be transferred to the Framework for the Optimization of Resources and Economics toolset for dynamic modeling and economic analysis. Results from the carbon refinery will be compared to the cost and carbon dioxide output of the incumbent processes for creating methanol and polymers.

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