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Design for Carbon Conversion Product Pathways with Nuclear Power Plant Integration (PCC)

September 2022

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Design for Carbon Conversion Product Pathways with Nuclear Power Plant Integration

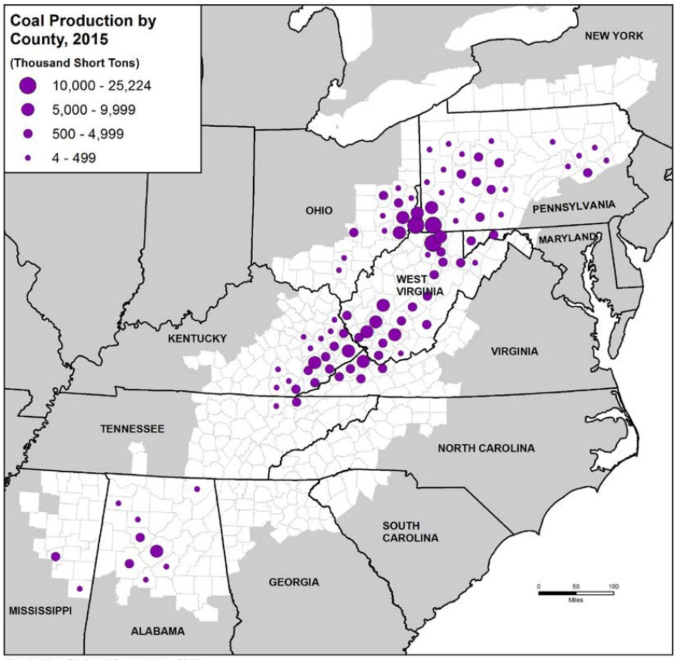
Abstract

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 will be used to determine each component's sensitivities, costs, inputs, and outputs. 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.

1. Introduction

The expansion in the renewable energy capacity across the United States has created new jobs and supported global goals of a carbon dioxide reduction in the energy sector. However, the volatile nature of these renewable technologies are 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 United States, which is concentrated in 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 but more simplified process design and goals. The result will be a robust process design to convert coal to valuable products using nuclear power and steam.

The current research will further the development of integrated energy systems through five main objectives:

- Computationally demonstrate an application for nuclear technology integration with heat, electricity, and steam to generate a material product
- Computationally demonstrate an application for coal as a valuable feedstock for products other than heat or electricity generation, with zero emissions and toxic solid waste discharge
- 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
- 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 United States, before expanding to other coal states in the United States
- Evaluate the feasibility of nuclear for coal and carbon conversion using the Framework for the Optimization of Resources and Economics 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. 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 and to utilize the resulting CO_2 from the refinery processes. This case is also intended to update the models from this study and provide a flexible modeling framework for future coal conversion scenarios.

Figure 2 shows the final flowsheet for modeling the carbon refinery. This is presented here to assist readers with following along with the decision-making process. The processes and markets that will be described in this paper are: coal conversion to syngas (pyrolysis), conversion of coal liquids to gaseous products (hydrothermal gasification), syngas conversion to carbon products (polymers), char conversion to carbon products (activated carbon), and carbon utilization (formic acid [FA] synthesis).

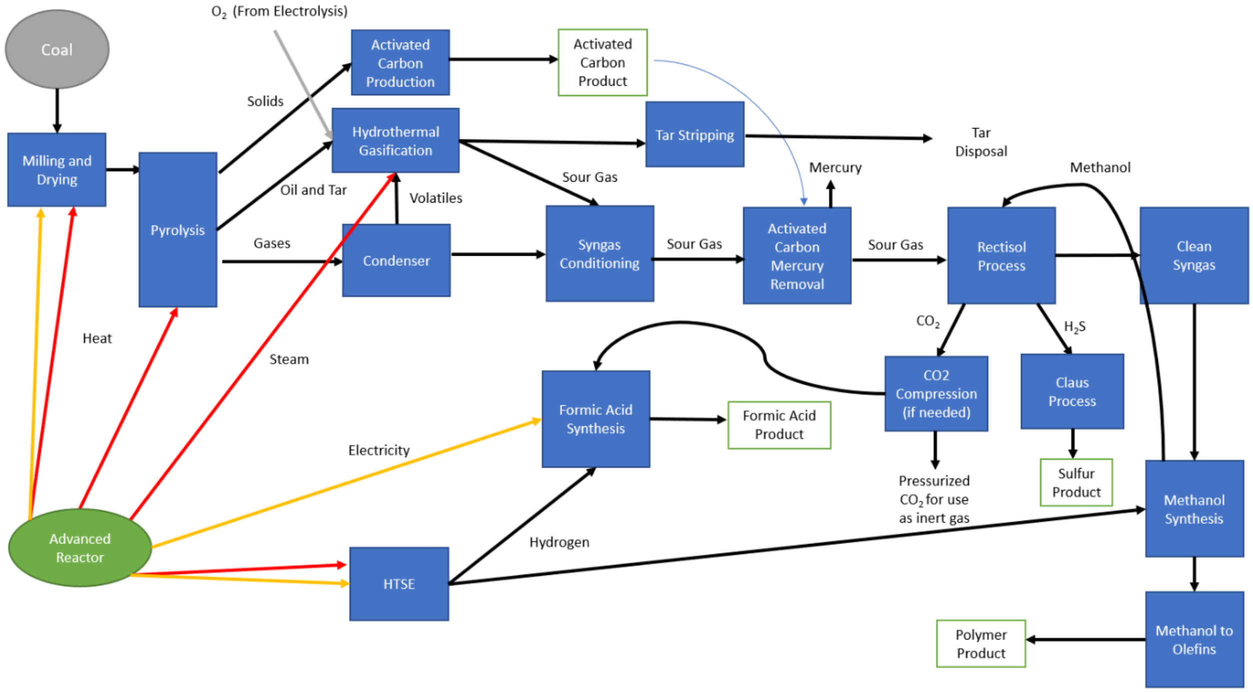


Figure 2. Schematic of the "Carbon Conversion Refinery."

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; when combusted to produce electricity from a steam cycle, however, it can also be broken down into gaseous and liquid products. Converting coal into these alternative forms can help reduce or control pollutants (National Energy Technology Laboratory, n.d.).

2.1 Technical Considerations

Gasification and pyrolysis are the essential steps to the thermal conversion of solid carbonaceous materials to liquid or gaseous products (Hauserman 2018). These processes are essential for the future development of coal applications.

2.1.1 Option 1: Pyrolysis

Pyrolysis is an oxygen-free decomposition process operated between 300 and 1300°C, depending on the feedstock and application, and near atmospheric pressure or 50–200 bar in a hydrogen-rich environment in the case of hydropyrolysis (Sludge Processing 2020c). A graphical depiction of the process is shown in Figure 3. 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, about 300°C over 5–10 minutes. Intermediate pyrolysis targets oil and liquid production at a heating rate of 30–300°C/minute at 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 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.

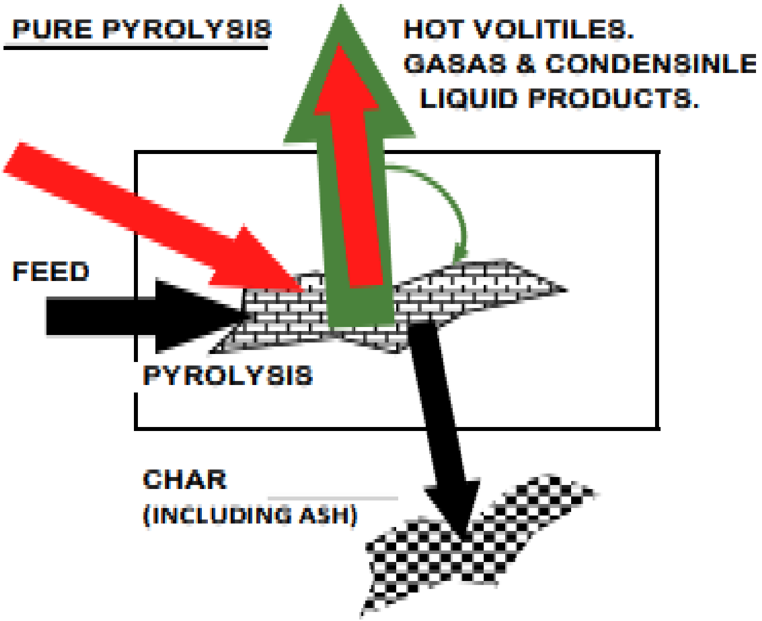


Figure 3. Schematic of the pyrolysis process (Hauserman 2018).

2.1.2 Option 2: Gasification

Gasification can be an additional step added onto the pyrolysis process, but both take place within the same reactor (Sludge Processing 2020a). A graphical depiction of this process is shown in Figure 4 and 5. 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, where the feed is broken down into char and oil fractions. In the final stage, the remaining carbonaceous material is gasified, with 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.

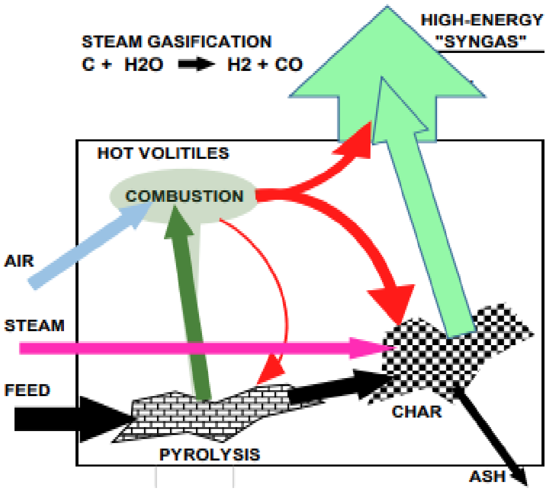


Figure 4. Schematic of the steam gasification process (Hauserman 2018).

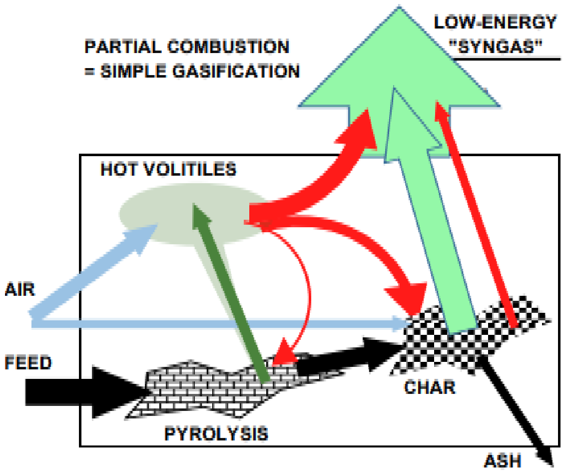


Figure 5. Schematic of the simple gasification process (Hauserman 2018).

2.2 Final Decision: Pyrolysis

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. 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.

3. Conversion of Coal Liquids to Syngas

Coal tar (also known as crude tar) is a highly viscous brown and black liquid byproduct of coal pyrolysis (R R, Goyal, and Kaur 2015). Tars of varying compositions are produced at different pyrolysis temperatures. The exact chemical composition of the tar produced from coal pyrolysis will not be determined in this modeling effort. Due to limitations in predicting heavy end chemical composition in pyrolysis, that determination would require experimental methods with specific coal samples.

3.1 Technical Considerations

Tar is water insoluble and fuel resistant, with a boiling point of 200–250°C. Coal tar is used primarily to produce refined chemicals and coal tar products, such as creosote oil and coal tar pitch, through fractional distillation. Tar can also be decomposed into syngas through supercritical water gasification.

3.1.1 Option 1: 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, and 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, and 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 6 shows the temperature and pressure operating condition regimes for the three different hydrothermal conversion processes: hydrothermal carbonization, hydrothermal liquefaction, and HTG or SCWG. The figure shows the critical point for water of 374°C and 221 bar, beyond which the process needs to run.

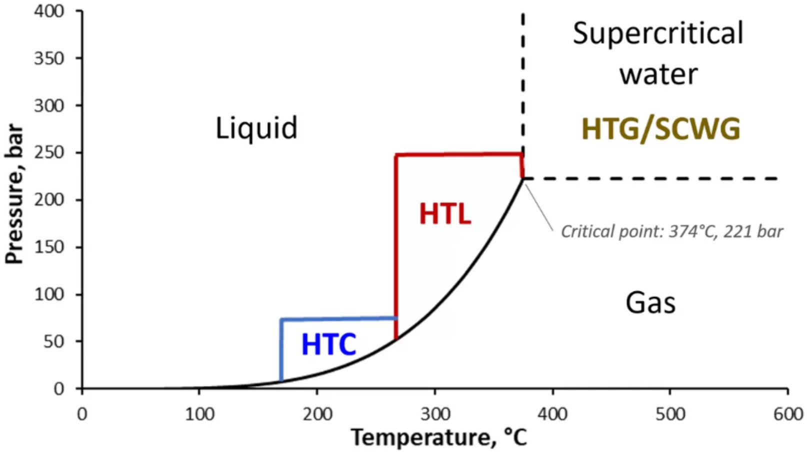


Figure 6. Temperature and pressure operating condition regimes for the three different hydrothermal conversion processes: hydrothermal carbonization, hydrothermal liquefaction, and HTG or SCWG (Sludge Processing 2020b).

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 HTG include the high capital and operating costs involved with the high pressure and corrosion prevention and mitigation requirements of the process.

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 300ºC and 46% at 350°C. Over 97% of the extraction product was gasified through catalytic hydrothermal gasification at 350°C.

Miri et al. (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 7 provides a schematic of the Aspen model used for the study.

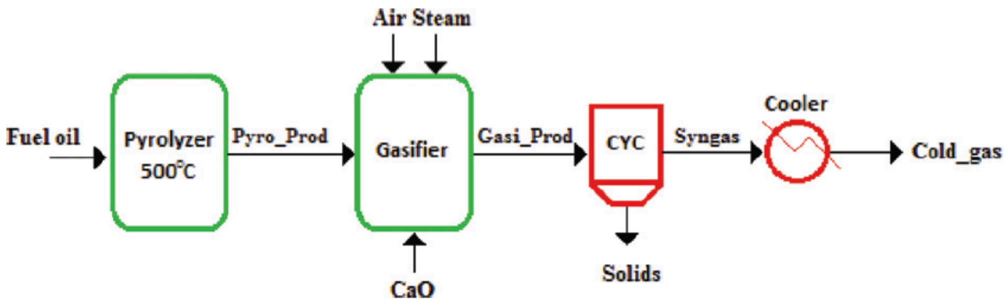


Figure 7. A schematic diagram of the Aspen Plus model (Miri, Shahraki, and Motahari-Nezhad 2019).

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.

3.1.2 Option 2: 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 is 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 8).

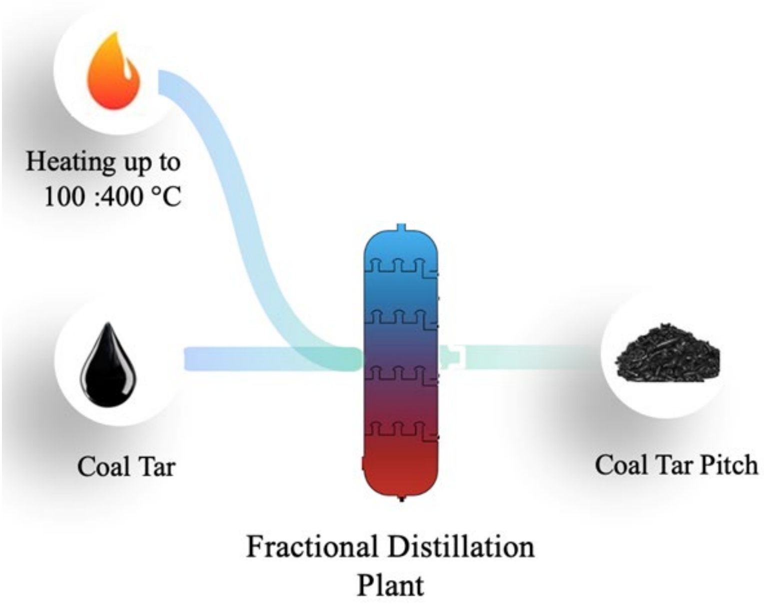


Figure 8. A simple representation of producing the coal tar pitch via fractional distillation.

3.2 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 (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. Producing 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 ability 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 United States (U.S.). Koopers Inc. recently shut down plants in the U.S., UK, and China due to oversupply in the market. 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 (Wikipedia 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 (2009); Austin, Texas; Dane County, Wisconsin; Washington; and several municipalities in Minnesota and other states (Coal Tar Free USA).

Table 1. 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, yearend:					
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, we can either decide to not process the coal tar or consider producing carbon black from the thermal decomposition of 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. is worth $148.4 billion. 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.

3.3 Final Decision: Hydrothermal Gasification

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 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. It is a wiser financial decision to invest in gasification equipment to obtain more syngas, which is more versatile. With an efficient hydrothermal gasification process, there should be very little tar product remaining. Syngas is a much more desirable product to maximize in the refinery.

4. Syngas Conversion to Carbon Products

Syngas, on its own, is an extremely versatile product. It can be burned on its own as fuel, converted to liquid fuels or pure hydrogen, and synthesized into chemicals. Because syngas on its own is mostly used as fuel, it was not suitable as a product for the refinery.

4.1 Technical Considerations

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 9. 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. Because this study focuses on non-fuel product pathways, the methanol-to-olefins process, with polymers created downstream, will be the goal of the methanol pathway. 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. The market analysis in the following subsections narrow down options for product pathways.

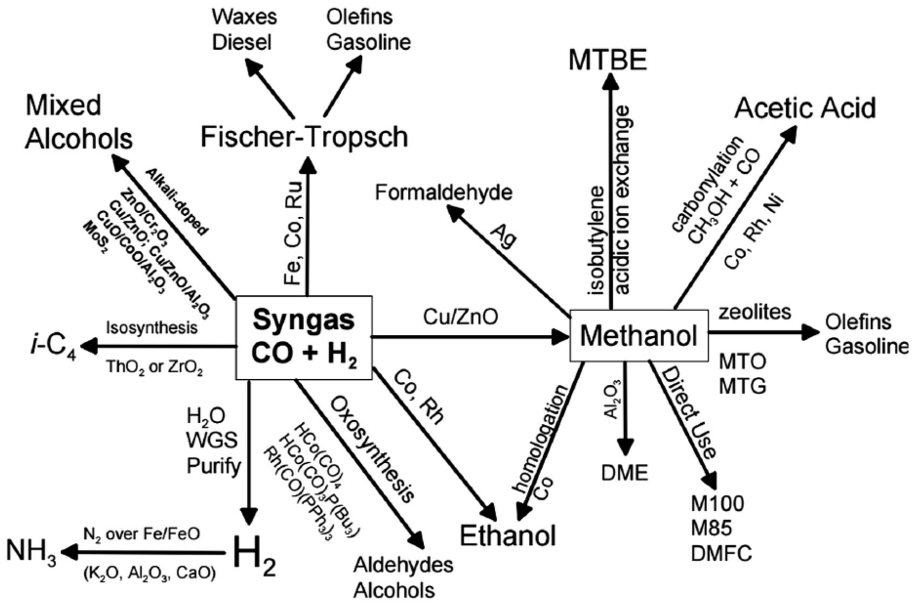


Figure 9. Some established fuels and chemical products pathways using synthesis gas (Spath and Dayton 2003).

4.1.1 Methanol-to-Olefins Processes

There are several pathways to obtain ethylene and propylene from methanol. The first is the methanol-to-olefins (MTO) process. The advanced MTO process yields greater than an 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 liquid natural gas are advantageous because the profit margin for olefins is higher (DuBose 2015). Another process is the dimethyl ether/methanol-to-olefins (DMTO) process, which produces about a 1-to-1 ethylene-to-propylene ratio (Ye, Tian, and Liu 2021). An alternative to these processes is the methanol-to-propylene process (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 n.d.).

The polymerization process 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 component compositions and reactor conditions determine the amount of branching and chain lengths (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.

4.2 Market Considerations

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 handle as much of the downstream processes as possible using nuclear heat and electricity.

4.2.1 Methanol Market

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 have a 4.5% global CAGR between 2017 and 2022. 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, as depicted in Figure 10. 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. According to MMSA, 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 toward using the product in fuel cells and olefin production. The methanol global market demand is less than 67% of total nameplate capacity for supply.

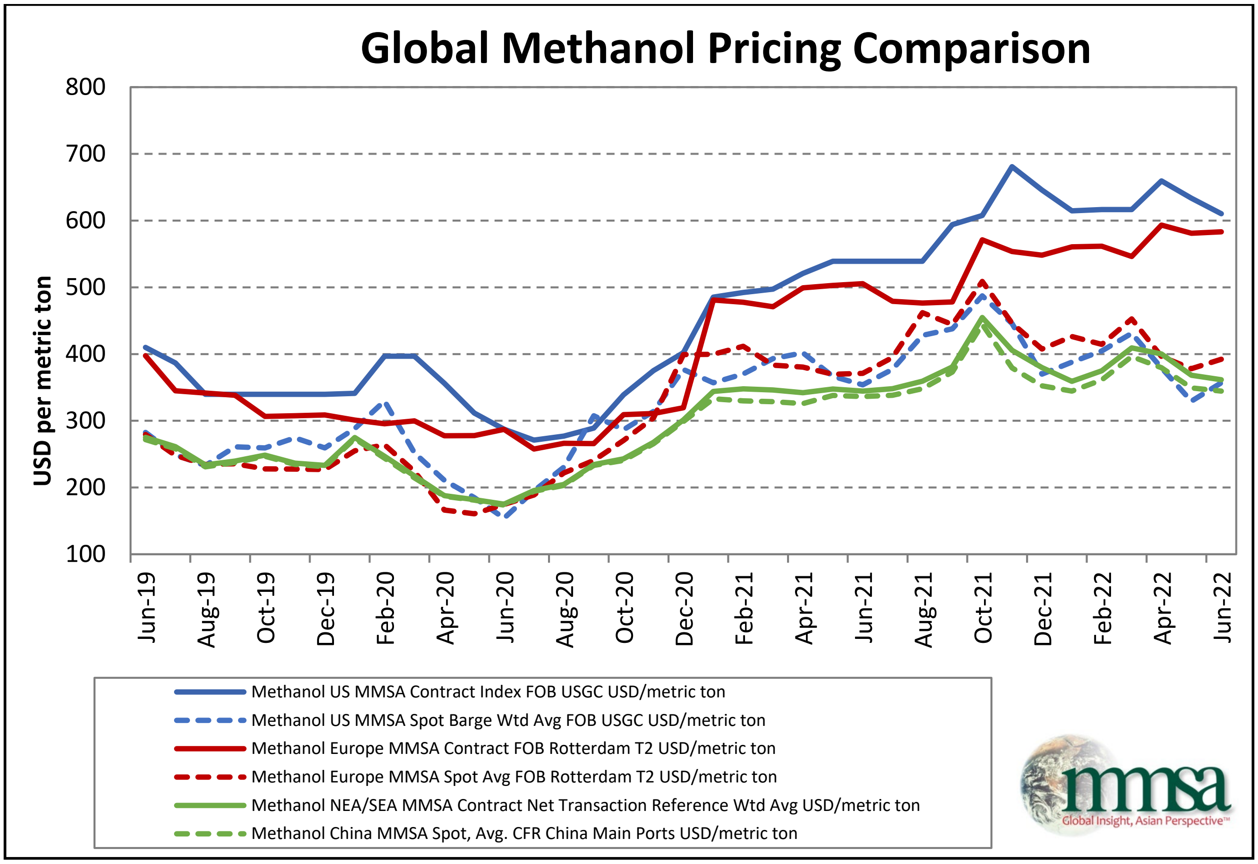


Figure 10. Global methanol price comparison (Methanol Market Services Asia 2022).

Data obtained through the Methanol Institute and MMSA shows 34% of the demand for methanol was used for methanol-to-olefin production, as depicted in Figure 11. 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 demand.

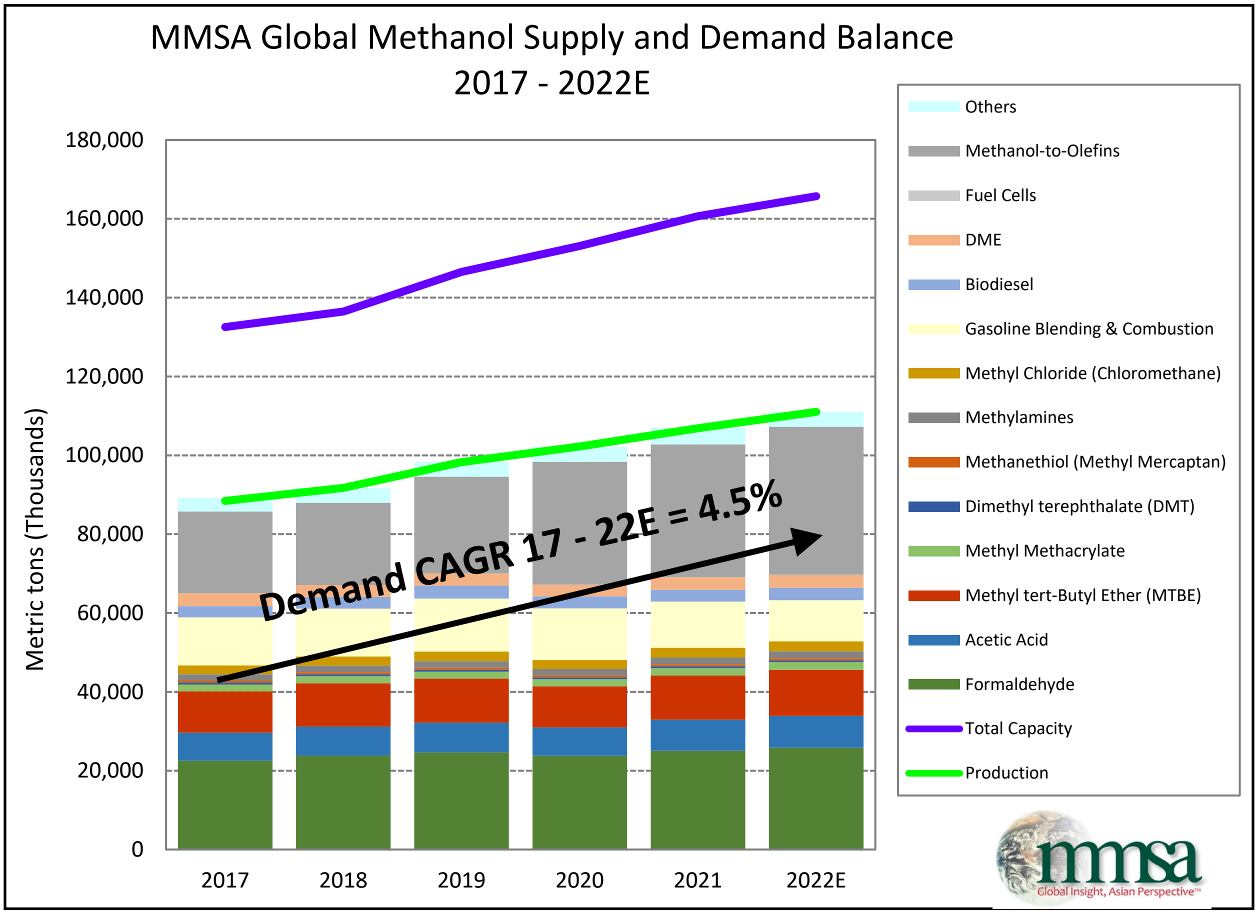


Figure 11. Global methanol supply and demand balance (Methanol Market Services Asia 2022).

4.2.2 Polyethylene

According to Grand View Research (2019), increased environmental protection and health warnings are dampening demand. Bio-based polyethylene is showing up on the market. Along with bio-based 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.

4.2.3 Polypropylene

Polypropylene market growth is expected to increase following the production of lightweight vehicles. Grand View Research (2021c) expects the market to increase by 3.0% 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. The Grand View Research report (2021c) indicated the market is comprised of small- to medium-sized companies but also includes large companies, like SABIC, Exxon Mobil, China Petrochemical Corp, BASF, Eastman Chemical, and LG Chem.

4.2.4 Polyisobutylene

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 automotive and electronics producers. Lubricant applications made up more than half of industry revenues.

4.2.5 Butyl Rubber

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 12, annual motor vehicle production in the U.S. fell by 28% between 2016 and 2020 according to the Bureau of Transportation Statistics. 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 (United States Department of Transporation 2022).

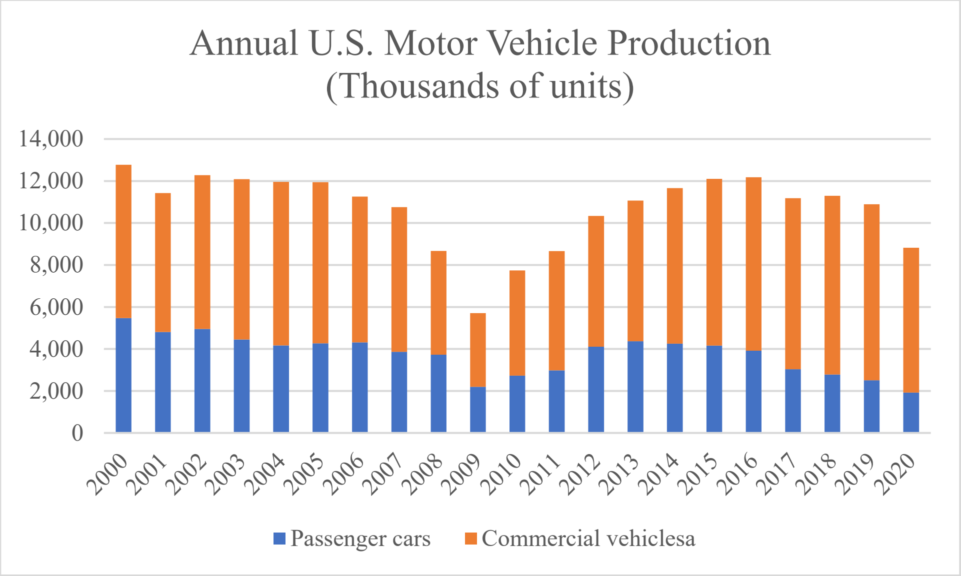


Figure 12. Annual U.S. motor vehicle production from 2000 to 2020 (United States Department of Transporation 2022).

4.2.6 Final Decision: Methanol to Olefins for Polymer Production

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.

5. Char Conversion to Carbon Products

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.

5.1 Technical Considerations

Char, or coke, is a vital material for industrial, medical, and construction applications. It can also be used directly at the refinery to absorb mercury and other harmful material from flue gas. This would further the goals of the refinery to decrease hazardous waste output, however, other applications for char are considered as well.

5.1.1 Option 1: Activated Carbon Production

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 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).

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 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× 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.

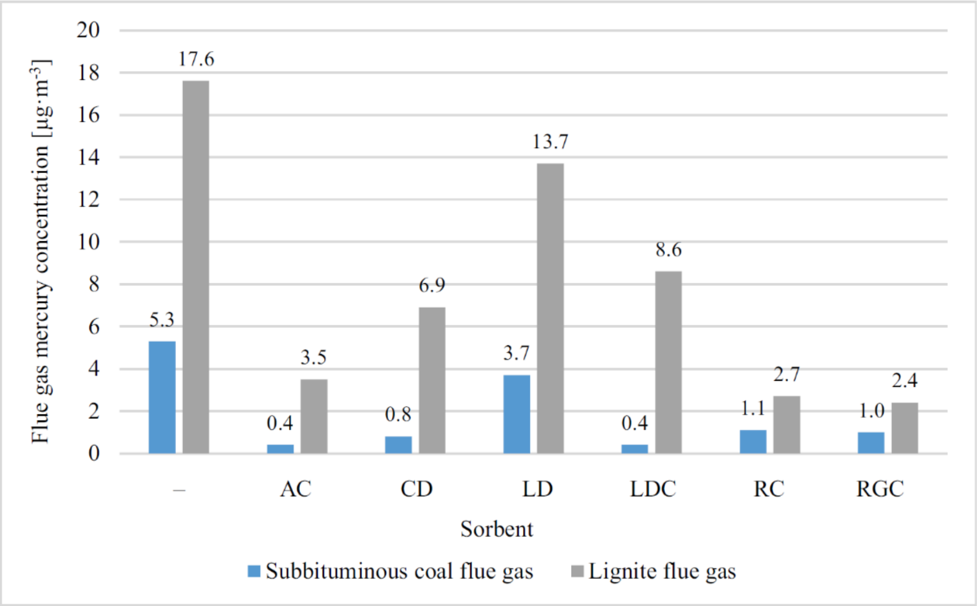


Figure 13. Concentration of mercury in raw flue gas compared to cleaned flue gas emitted to the atmosphere (Marczak 2019) using activated carbon (AC), coke dust (CD), lignite dust (LD), lignite dust char (LDC), rubber char (RC), and granulated rubber char (GRC).

Char activation can be done 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 AC 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, AC can be processed for many uses. The physical activation process is represented in Figure 14.

The AC can also be produced by chemical activation (replacing the 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.

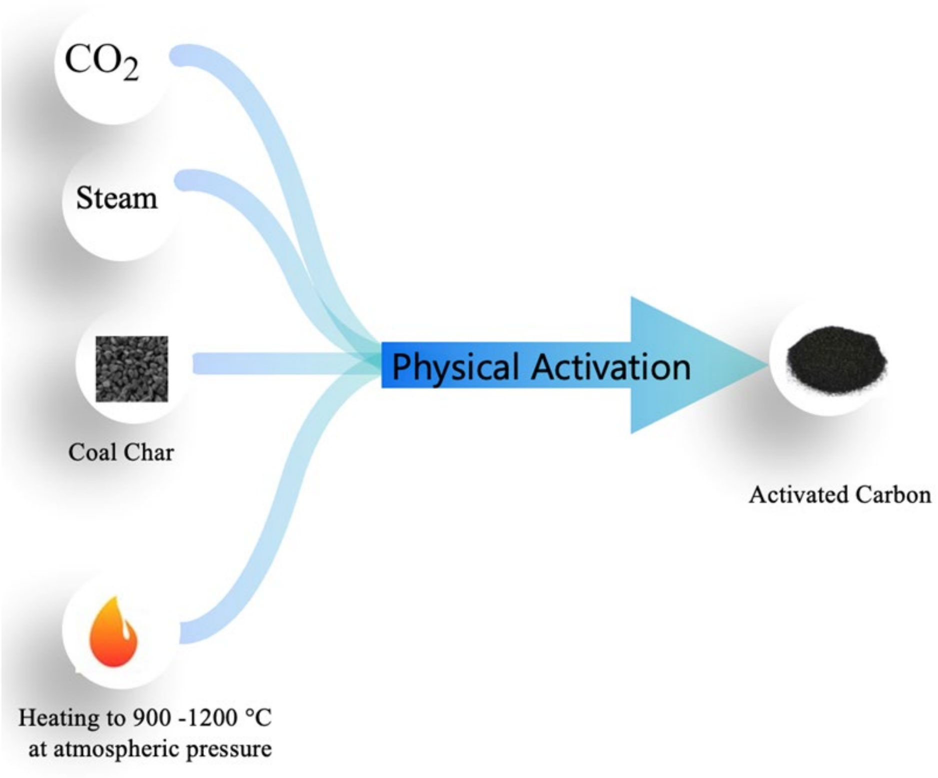


Figure 14. A representation of producing AC through physical activation.

5.1.2 Option 2: Other Char Applications

The 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 pollution through releasing airborne particles, it still releases greenhouse gases (Laukkonen 2022). Another major application for coke is steel production.

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

Carbon-based reducing agents are also useful in extracting metals. For example, coal is a reducing agent that turns iron into pig iron, which is the basic ingredient in steel. This process also produces carbon monoxide as a waste product. In the future, coke might be replaced by other greener reducing agents (Kelk, n.d.).

5.2 Market Considerations

Char or AC 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 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 AC also has applications for wastewater treatment, which may become increasingly important when mitigating environmental concerns and water shortages. There is an industry association forming based in Beckley, WV that hosts the CoalChar.com website. The market is highly competitive and trending toward vertical integration, putting strains on mid-chain suppliers, to reduce volatility in sourcing and maintaining quality standards.

5.3 Interim Decision: Activated Carbon

AC 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. The research team will begin by assessing the viability of producing AC, based on the amount produced versus consumed for the syngas cleaning process, and the cost of production versus the purchase price of AC.

6. Carbon 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 15 describes some of the processes in which CO_2 can be transformed. Table 5 shows some of the applications for CO_2 utilization and their production rates.

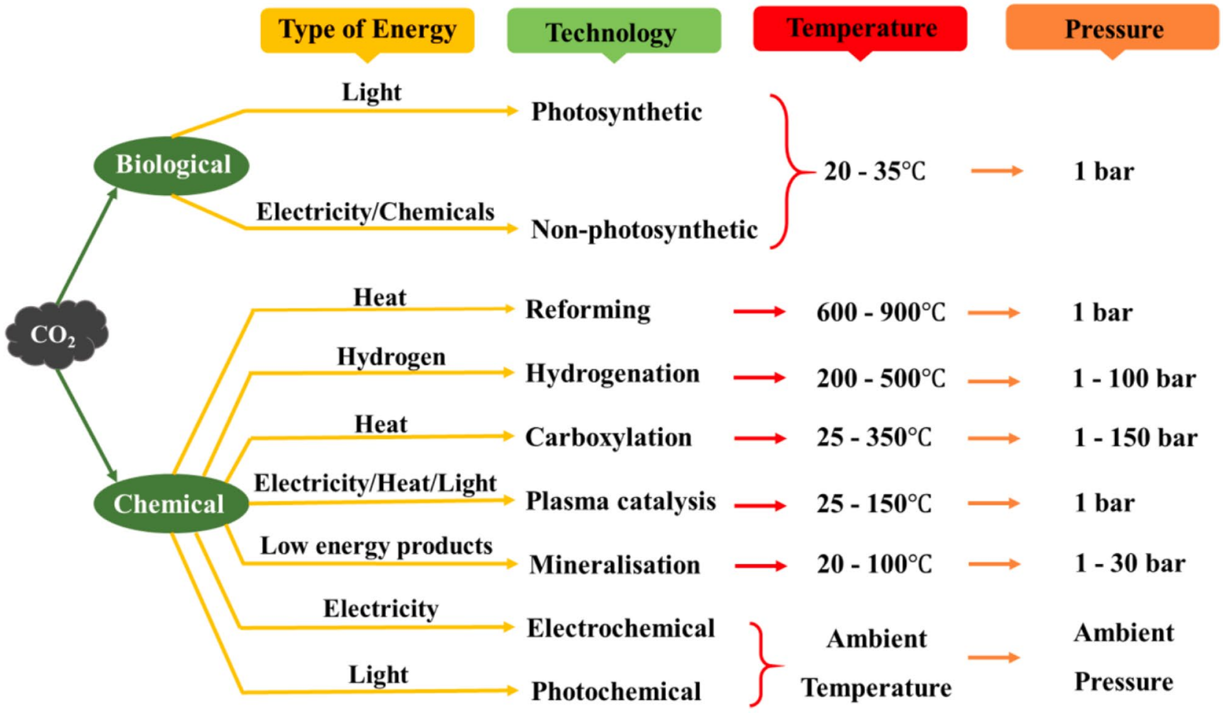


Figure 15. Pathways for CO_2 conversion (Kamkeng et al. 2021).

Table 2. Products and applications for carbon dioxide utilization (Kamkeng et al. 2021).

Utilization Mode	Application or 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
	FA	0.9	1.0
	Organic carbonates	0.5	5.0
	Total	232.4	—

The four options selected to explore for carbon utilization are FA, acetic acid, urea, and formaldehyde for their recent interest or commercialization, large market opportunities, or INL mission interest. Each of these products are 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 6 shows the carbon utilization rates for six products along with other material inputs.

Table 3. 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	1.467	0.067	N/A
FA	0.96	0.043	N/A
Urea	0.73	0	Ammonia
Acetic Acid	0.47	0	Methane

6.1 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 CO_2 and H_2 synthesis. Both of these processes could be easily integrated into the carbon refinery with readily available sources of steam, electricity, hydrogen, and carbon dioxide.

6.1.1 Technical Considerations

Rumayor, Ramos, and Irabien (Rumayor, Dominguez-Ramos, and Irabien 2018) compared a model of a CO_2 electrolyzer to a synthesis process modeled by Pérez-Fortes and coworkers. The comparison considered the production of 1 kg FA at a commercial concentration of 85 wt%. From Table 7, 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 for 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 formic acid synthesis and hydrogen electrolysis processes combined to produce 1 kg FA.

Table 4. 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, the CO_2 and H_2 synthesis process for FA production will be considered. 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.

6.1.2 Market Considerations

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 domestic and international market. 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 16, 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 by 18% in 2021 from the recent low of 23.8 billion pounds in 2015.

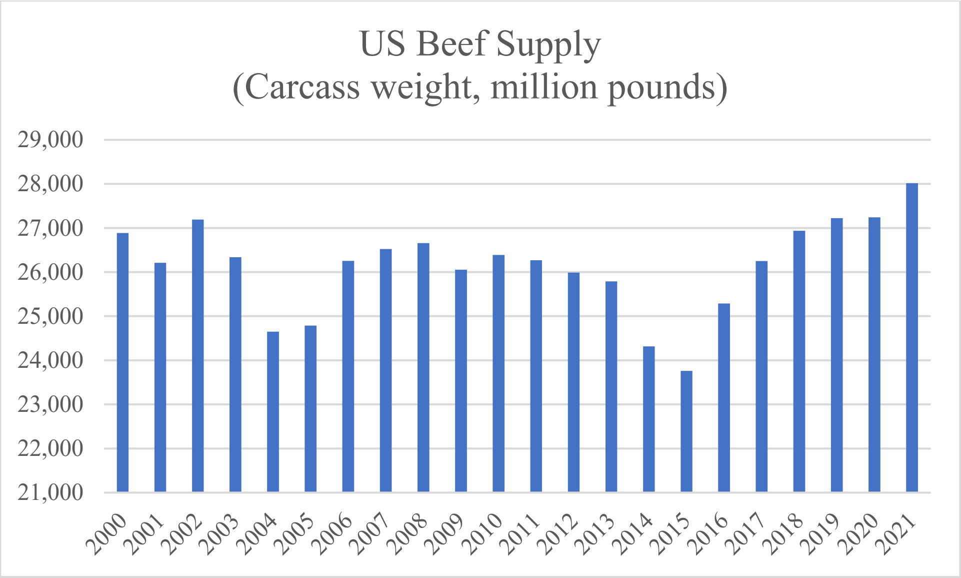


Figure 16. U.S. beef supply in millions of pounds (2000–2021) (United States Department of Agriculture 2022a).

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.

6.1.3 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 3, it has the second highest carbon utilization rate of any of the products considered.

6.2 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.

6.2.1 Technical Considerations

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 and coworkers, would utilize CO_2 and result in the direct production of acetic acid and water (Qian et al. 2016). 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.

6.2.2 Market Considerations

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 (2020) reported a 5.2% CAGR acetic acid industry growth. 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.

6.2.3 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.

6.3 Urea

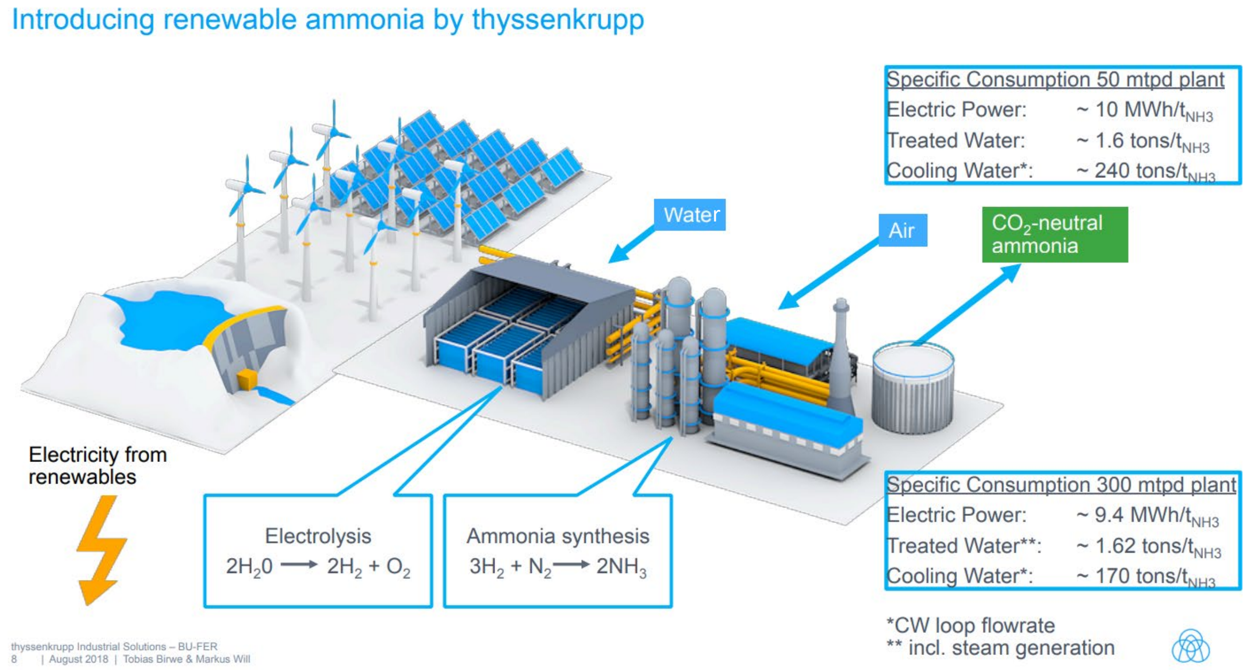
The largest consumer of CO_2 is the fertilizer industry, where about 130 $MtCO_2$ per year is used to manufacture urea (International Energy Agency 2019). Urea is typically synthesized from ammonium carbamate (via ammonia) and CO_2. Urea is a long-release-type fertilizer that maintains a presence longer in the soil. It is usually combined with ammonium nitrate and nitric acid in a solution of liquid fertilizer called 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.

6.3.1 Technical Considerations

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 producing 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 (2017) report 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 2020) and CO_2 and nitric oxide (Huang 2021); however, there do not appear to be any commercial processes in the development for the near or medium term.

The international group thyssenkrup 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 17, 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.



Introducing renewable ammonia by thyssenkrupp

Specific Consumption 50 mtpd plant
Electric Power: ~ 10 MWh/t_{NH3}
Treated Water: ~ 1.6 tons/t_{NH3}
Cooling Water*: ~ 240 tons/t_{NH3}

Water

Air

CO_2-neutral ammonia

Electricity from renewables

Electrolysis
$2H_20 \longrightarrow 2H_2 + O_2$

Ammonia synthesis
$3H_2 + N_2 \longrightarrow 2NH_3$

Specific Consumption 300 mtpd plant
Electric Power: ~ 9.4 MWh/t_{NH3}
Treated Water**: ~ 1.62 tons/t_{NH3}
Cooling Water*: ~ 170 tons/t_{NH3}

*CW loop flowrate
** incl. steam generation

thyssenkrupp Industrial Solutions – BU-FER
8 | August 2018 | Tobias Birwe & Markus Will

Figure 17. Electricity and water demands for renewable ammonia (Will 2018).

Producing urea from CO_2 and ammonia is 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.

6.3.2 Market Considerations

Ammonia and urea market growth is expected to stay at 5.2% CAGR (Grand View Research 2018). Liquid ammonia dominated the market with a 45% share and has a 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 Figure 18. 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 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 second largest importer of urea in the world in 2019.

Table 5. 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

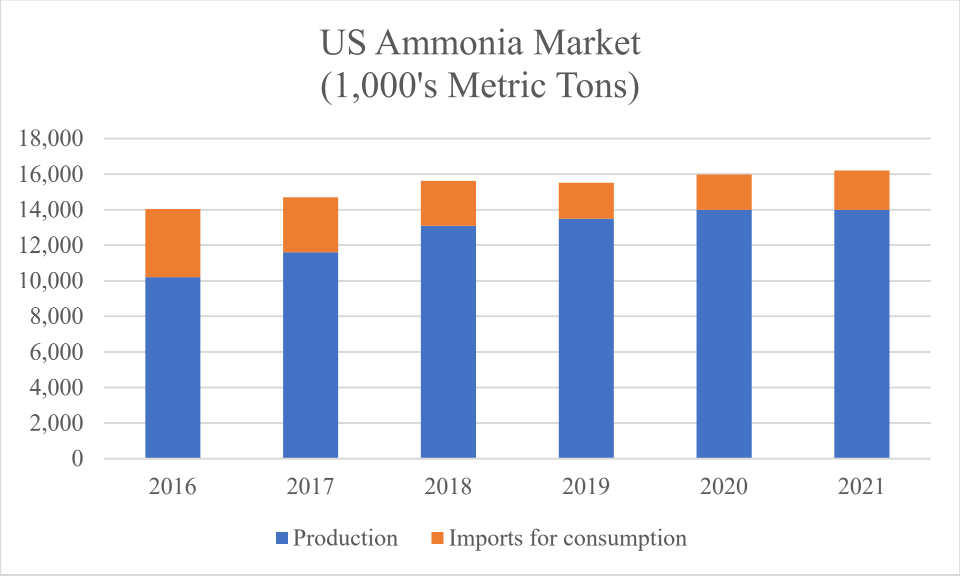


Figure 18. U.S. ammonia market production and imports (U.S. Geological Survey 2021).

6.3.3 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.

6.4 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.

6.4.1 Technical Considerations

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 a pathway of 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 laboratory scale.

6.4.2 Market Considerations

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. The products 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.

6.4.3 Summary

Because converting CO_2 to formaldehyde has only been developed at the laboratory 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.

6.5 Interim Decision: Formic Acid

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 high-temperature steam electrolysis unit to provide hydrogen for the synthesis process. 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.

7. 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 blue hydrogen 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 AC 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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